Lab-scale Biological Wastewater Treatment Reactors to Assess the Combined Effects of Cold Temperatures and Ozonation on Waste Biosolids Reduction

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Abstract

The treatment and disposal of waste biosolids from activated sludge wastewater treatment plants can contribute a large portion of the total operation costs. Many technologies are being explored to address this issue, and ozonation of return activated sludge (RAS) has been shown to economically reduce waste biosolids production in Europe. However, as European winter temperatures rarely fall below 12 °C, little research has been done on biosolids reduction by ozonation at cold temperatures like during Canadian winters. A previously performed global sensitivity of a model describing ozone transformations suggested that, below 12 °C, the nitrification and other processes in a treatment plant could be less stable in the plant with RAS ozonation than without. Thus, the objective of this research was to experimentally determine the behaviour at cold temperatures of RAS ozonation for the reduction of biosolids production, and the effects of the process on treatment performances. Four 2-L sequencing batch reactors (SBRs) were designed and built, and the operation was optimized. The SBRs were fed a synthetic municipal wastewater, and operated at 0.5-day hydraulic retention times (HRTs) and 15-day solids retention times (SRTs). One SBR pair was maintained at 8 °C while the other pair was kept at room temperature (~20 °C). Within each pair, one reactor was operated as a non-ozonated control, while a portion of the suspended solids of the other was periodically ozonated such as to reach a biosolids reduction target of 40%. Analyses of chemical oxygen demand (COD), suspended solids, and ammonium concentrations were performed and tracked over a 6-month period. It was found that after an initial adaptation phase, biosolids inventory in the ozonated reactor remained similar to the control and maintained an acceptable COD conversion at both temperatures. The ammonium removal in the cold ozonated reactor did not recover once ozonation began, as it did in the warm reactor, and full nitrification was lost in both cold reactors when the nitrogen concentration was increased. A preliminary computer model of the cold SBRs was developed. The calibrated model satisfactorily predicted the solids inventory and effluent soluble COD. Therefore, while biosolids and COD conversion with ozonation can be maintained at a temperature of

8 °C, reactor nitrification performance was found to be unstable so far at that temperature, but further research is needed to fully understand this unexpected result.

Résumé

Le traitement et l'élimination des biosolides produits aux usines d'épuration par boues activées peuvent contribuer à une grande partie des frais de fonctionnement. À travers le monde, de nombreuses technologies sont examinées pour résoudre ce problème. En Europe, l'ozonation des boues activées recirculées (return activated sludge [RAS] en anglais) peut réduire économiquement la production de biosolides. Cependant, les températures hivernales d'Europe tombent rarement en dessous de 12 °C, donc peu de recherches ont exploré la réduction des biosolides par ozonation à des températures froides, comme celles des hivers canadiens. Une analyse de sensibilité globale réalisée précédemment sur un modèle décrivant les transformations de l'ozone a suggéré qu'en dessous de 12 °C la nitrification et d'autres processus d'une usine d'épuration pourraient être moins stable si un système d'ozonation des RAS est installé. Ainsi, l'objectif de cette recherche était de déterminer expérimentalement le comportement à des températures froides de l'ozonation des RAS sur la réduction de production de biosolides, ainsi que l'effet de ce processus sur les performances du traitement biologique. Quatre réacteurs biologiques séquentiels (RBS) de 2 L ont été conçus et construits, et l'opération a été optimisée. Les RBS ont été alimenté par de l'eau usée municipale synthétique. Ils étaient opérés avec un temps de rétention hydraulique de 0,5 jour et un temps de rétention des solides de 15 jours. Une des paires de RBS fut maintenue à 8 °C tandis que l'autre paire fut opérée à température ambiante (~20 °C). Dans chaque paire, un des réacteurs était le réacteur contrôle (c'est-à-dire non traité à l'ozone), tandis qu'une partie des matières en suspension (MES) de l'autre réacteur était périodiquement exposée à l'ozone pour atteindre un objectif de réduction de la production de biosolides de 40%. Les analyses de la demande chimique en oxygène (DCO), des matières en suspension et des concentrations d'ammonium ont été effectuées et suivies sur une période de 6 mois. Après la phase initiale d'adaptation, l'inventaire des biosolides dans le réacteur ozoné était comparable à celui du réacteur contrôle. De plus, l'enlèvement de la DCO fut maintenue à des niveaux acceptables aux deux températures d'opération pour tous les réacteurs. Une fois que l'ozonation a commencé, l'enlèvement de

l'ammonium dans le réacteur ozoné à température froide ne s’est pas rétabli à un niveau similaire à celui avant l’ozonation malgré que le réacteur à température ambiante ait bien réussi le rétablissement. Cependant, la nitrification complète a été perdue dans les deux réacteurs à température froide lorsque la concentration d'azote a augmenté. Un modèle informatique préliminaire des RBS à température froide a été calibré. Le modèle calibré a pu prédire la quantité de matières solides et la concentration de DCO soluble dans l’effluent, avec une marge d’erreur acceptable. Par conséquent, tandis que l’inventaire des biosolides et la conversion de DCO avec l’ozonation peuvent être maintenus à une température de 8 °C, les performances de nitrification du réacteur étaient instables à cette température. Des recherches supplémentaires sont nécessaires pour comprendre pleinement ce résultat inattendu.

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Table of Contents

List of Tables

List of Figures

Abbreviations and Symbols

WWTP	Wastewater treatment plant
GHG	Greenhouse gas
SBR	Sequencing batch reactor
PFR	Plug flow reactor

Measured Constituents		Unit
BOD	Biological oxygen demand	[g.m^{-3}]
COD	Chemical oxygen demand	[g.m^{-3}]
sCOD	Soluble chemical oxygen demand	[g.m^{-3}]
DO	Dissolved oxygen	[g.m^{-3}]
TSS	Total suspended solids	[g.m^{-3}]
VSS	Volatile suspended solids	[g.m^{-3}]
MLSS	Mixed liquor suspended solids	[g.m^{-3}]
MLVSS	Mixed liquor volatile suspended solids	[g.m^{-3}]
RAS	Return activated sludge	[g.m^{-3}]
WAS	Waste activated sludge	[g.m^{-3}][d]
SRT	Solid retention time	[g-N.m^{-3}]
TKN	Total Kjeldahl Nitrogen	

COD pools of ASM3		
S_B	Soluble biodegradable COD	[g-COD.m^{-3}]
S_U	Soluble undegradable COD	[g-COD.m^{-3}]
X_{ANO}	Autotrophic nitrifying organism biomass COD	[g-COD.m^{-3}]
X_{OHO}	Ordinary heterotrophic organism biomass COD	[g-COD.m^{-3}]
$X_{OHO,Stor}$	Storage compound COD in ordinary heterotrophs	[g-COD.m^{-3}]
X_U	Particulate undegradable COD from the influent	[g-COD.m^{-3}]
$X_{U\_bio,lys}$	Biomass debris	[g-COD.m^{-3}]
XC_B	Particulate/colloidal biodegradable COD	[g-COD.m^{-3}]
S_{O2}	Dissolved Oxygen	-[g-COD.m^{-3}]
S_{NHx}	Ammonium and ammonia nitrogen	[g-N m^{-3}]
S_{NOx}	Nitrate and nitrite	[g-N m^{-3}]

Model parameters describing ozone transformation of solids		
Stoichiometric solids transformation and inactivation fractions		
f_{Bio}	Fraction of biomass in particulate COD excluding storage	[NU]*
$f_{Bio,storage}$	Fraction of biomass in particulate COD including storage	[NU]
$f_{mnr,O3}$	Fraction of transformed COD that is mineralized	[NU]
$f_{SB\_O3,inact}$	Soluble biodegradable COD fraction of inactivated biomass	[NU]
$f_{SU\_O3,inact}$	Soluble undegradableCOD fraction of inactivated biomass	[NU]
$f_{SB\_O3,trans}$	Soluble biodegradable COD fraction of transformed non-biomass	[NU]
$f_{SU\_O3,trans}$	Soluble undegradableCOD fraction of transformed non-biomass	[NU]

*no unit

Transformation and inactivation rates and constants

$b_{\text{ANO,O3,inact}}$	Inactivation rate of autotrophic nitrifiers due to ozone	[d^{-1}]
$b_{\text{OHO,O3,inact}}$	Inactivation rate of ordinary heterotrophs due to ozone	[d^{-1}]
$q_{\text{Xtot,O3,sol}}$	Overall relative solids COD solubilization by ozone rate constant normalized to the aerated solids COD inventory	[d^{-1}]
$q_{\text{XU\_XCB,O3,trans}}$	Non-biomass solids transformation rate due to ozone	[d^{-1}]

Chapter 1
Introduction and Problem Statement

The treatment of wastewater is an issue that every modern municipality must address. While small rural communities may only require the most basic of treatment, large urban centers usually require large, complex facilities in order to achieve government effluent discharge levels. With city populations growing, there is a need for new and innovative technologies to upgrade plants and improve treatment levels and efficiency. Biological wastewater treatment plants (WWTP) are one of the most common types of treatment plants for municipal wastewater because they treat a relatively high flow containing medium concentrations of dissolved and colloidal organic matter and low levels of toxic compounds (Metcalf et al. 2010). As the biological wastewater treatment process is a living continuously growing process, a portion of the biosolids accumulated during treatment must be constantly wasted in order to achieve a steady-state system. This waste biosolid is usually disposed of by applying it to agricultural land, in landfills or by incineration (Hébert 2011).

There has recently been an increased interest in biosolids handling and disposal for biological wastewater treatment plants. There are a number of factors that have contributed to this increase in attention. One of them is the overall increase in the mass of solids produced by plants due to an increase in wastewater treated (LeBlanc et al. 2009). The increase in wastewater can be attributed to both a population increase in urban areas as well as stricter regulations on discharging untreated wastewater into receiving water bodies. In 1983, approximately only 70% of the Canadian population had their wastewater treated, but by 2006 that percent has risen to 87.1% (Environment-Canada 2011). The Canadian government estimates that around 6 trillion (6×10^{12}) litres of wastewater is treated per year across Canada, and new regulations require that any system that has the capacity to deposit a daily effluent volume of 10 m^3 or more must meet national quality effluent standards (Environment-Canada 2011).

Another factor recently contributing to the renewed interest in increasing biosolids handling efficiency is the increase in costs of landfilling, which represents 35% of all solid disposals in Québec. Recently, the cost has risen from $30/ton to approximately $100/ton, which can lead to biosolids disposal being the greatest single cost to a treatment plant. The estimated percent of total wastewater treatment costs attributed to biosolids treatment and disposal in Montreal, Quebec is 45% (LeBlanc et al. 2009).

Although the increase in costs of disposal have had an immediate effect on treatment plants in Quebec, new regulations put in place to curb greenhouse gas (GHG) emissions will make biosolids management even more difficult. "In 2011, in addition to the Plan d'action sur les changements climatiques, Québec set other GHG reduction objectives in its new policy on residual material (Politique québécoise sur la gestion des matières résiduelles) which entails: the complete ban of organic matter (including municipal sludge) from landfills or incineration by the year 2020" (Villeneuve and Dessureault 2011). As of 2011, landfilling and incineration accounted for 80% of the biosolids disposal in Quebec. The driving force behind this legislation is to reduce carbon emissions from the incineration process and uncontained fermentation of landfilled sludge, and promote the recycling of organic materials by land application or anaerobic digestion (Hébert 2011).

Methods of biosolids disposal are becoming more restricted and expensive, while the quantity of waste produced continues to rise. It is for these reasons that research into waste biosolids minimization technologies is being pursued. Instead of having to treat the waste once it is produced, biosolids reduction technologies decrease the total amount of biosolids that needs to be disposed of onsite, reducing transportation and treatment costs.

1.1 Problem Statement

There are a number of innovative technologies currently being researched and used for biosolids reduction at wastewater treatment plants. One stream of research involves reducing the yield coefficient of the bacteria by promoting cell lysis, which can be

achieved using a number of oxidizers or other physical-chemical methods, in which a portion of the carbon released by the lysed cell is liberated during cell respiration, achieving biomass reduction (Pérez-Elvira et al. 2006). Of these methods, the ozonation of activated sludge suspended solids has achieved the highest degree of biosolids disintegration. This is because ozone does much more than only lyse the cells, but it also transforms non-degradable volatile suspended solids into degradable chemical oxygen demand (COD) (Frigon and Isazadeh 2011).

Biosolids reduction by ozonation has successfully been applied to full-size treatment plants in Europe and Asia and has reduced waste biosolids by 40 to 90% in some cases (Pérez-Elvira et al. 2006). While there are a number of set up configurations for this technology, most commonly the ozone is bubbled through a portion of the returned activated sludge (RAS) where it solubilizes COD and inactivates microorganisms. The ozone treated RAS is then fed back to the aerated mixed liquor tank.

Although this technology is commercially used, the exact mechanisms occurring during RAS-ozonation are not fully understood, and a pilot-scale study is usually needed before the full-scale installation in order to determine the potential biosolids reduction, verify the possibility of adverse effects to treatment levels, and ascertain the cost associated with biosolids reduction. These types of studies are time and space consuming and expensive. A much more effective method for this pre-installation study is the use of a mathematical model. Typical activated sludge wastewater treatment plants have successfully been modeled for many years now (Gujer et al. 1999), but the addition of the ozonation process into the model has only been recently developed (Frigon and Isazadeh 2011). There are promising results from this extension to the model predicting accurate biomass and other concentrations, but the predictability of effluent quality becomes uncertain at extreme conditions, such as low temperatures that can occur during Canadian winters. A previously conducted global sensitivity test of a model describing ozone transformations demonstrated that, below 12 °C, the nitrification and other processes in a treatment plant could be less stable in the plant with RAS ozonation than without (Isazadeh et al. in prep).

As there are no full-scale treatment plants that use biosolids reduction by ozonation in North America, and temperatures in treatment plants Europe and Asia rarely fall below 15 °C, there is little operational data on the effects of cold temperature on this process. Therefore, experimental results at these conditions are needed to investigate the effects and validate the model predictions. This report presents the results of a study in which the effects of biosolids reduction and cold temperatures on effluent quality are measured and compared to low temperature treatment without ozonation, and to treatment with and without ozonation at room temperature.

1.2 Objectives

In order to maximize the level of control and the validity of the results, this study is done at a laboratory-scale level using four sequencing batch reactors (SBRs), where two are held at room temperature and two at low temperature. Ozone is then applied to one of each of the paired reactors for biosolid reduction. The scope and objectives of this project are as follows:

- Design and build four temperature controlled SBRs and accompany setup that can maintain a steady biomass concentration
- Develop a laboratory-scale batch reaction ozonation protocol for biosolids reduction
- Apply developed protocol to reactors and determine effects on heterotrophic and nitrifying biomass, and on effluent COD and ammonium levels at both cold and warm temperatures
- Develop a preliminary model of the reactors with results obtained from study using an extension model to the International Water Association (IWA) Activated Sludge Model 3 (ASM3) to describe the ozone reactions with the biosolids (Frigon and Isazadeh 2011, Isazadeh et al. *submitted* 2013)

1.3 Thesis Organization

A classical format was chosen for this thesis. After the current initial chapter, a literature review (Chapter 2) and a materials and methods (Chapter 3) follow. Then, the results and discussion section is divided into four chapters that illustrate the different stages of project development. The reactors were operated for more than 430 days (Figure 1). During this time period, a large amount of data was generated; and the chapter division facilitates the presentation of data in a coherent and understandable manner. The chapters build upon each other, and results presented in one chapter are the basis of decisions and other results in further chapters. Each chapter presents an objective for that stage of experimental development, and the relevant data and results that support the accomplishment of the objective. In order to maintain clarity, the timeline of the project presented in Figure 1 is centered around the beginning of biosolids ozonation on Day 0. All other dates are related back to this event. The negative dates document building of the reactor and the development of their operation (Chapters 4 and 5), and the positive dates document the ozone treatment experiment (Chapters 6 and 7).

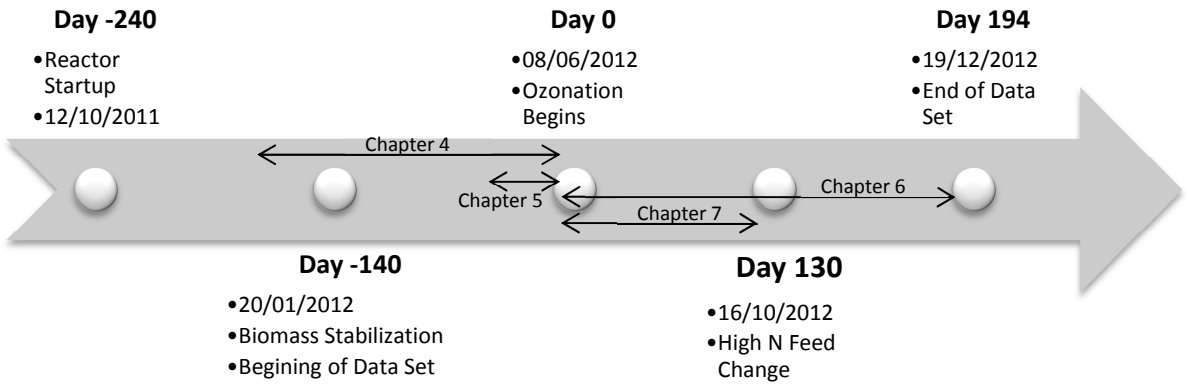


Figure 1. Overall project timeline and general time period of each chapter. All figures and references to time in following chapters use the presented notation, with pre-ozonation phase being from Day -140 to Day 0, when ozonation begins. Ozonation phase can be divided into two stages: low nitrogen feed and high nitrogen feed starting on Day 130. Data sets end on Day 194.

Chapter 2
Literature Review

Activated sludge wastewater treatment systems remove biochemical oxygen demand (BOD), COD, certain nutrients, and total suspended solids (TSS). The system is mainly comprised of an aeration tank and a clarifier (Figure 2). Wastewater enters the plant and is mixed with a slurry of suspended solids called the return activated sludge (RAS) to form the mixed liquor. This liquor is aerated in a specific tank to promote microbial growth and provide contact between mixed liquor suspended solids (MLSS) and the influent TSS. The mixed liquor then flows to the clarifier where MLSS are settled out and separated from the treated water. This effluent can go for further treatment or be discharged. The settled solids are pumped from the bottom of the clarifier and either wasted from the system as waste activated sludge (WAS) or returned to the aeration tank as RAS. It is this recycling of solids containing biomass that allows for a stable community of waste-consuming microorganisms to flourish and the system to be 'activated'. Because the solids contain non-degradable volatile solids and biomass, they are often referred to as biosolids, especially when the WAS is dewatered for final disposal.

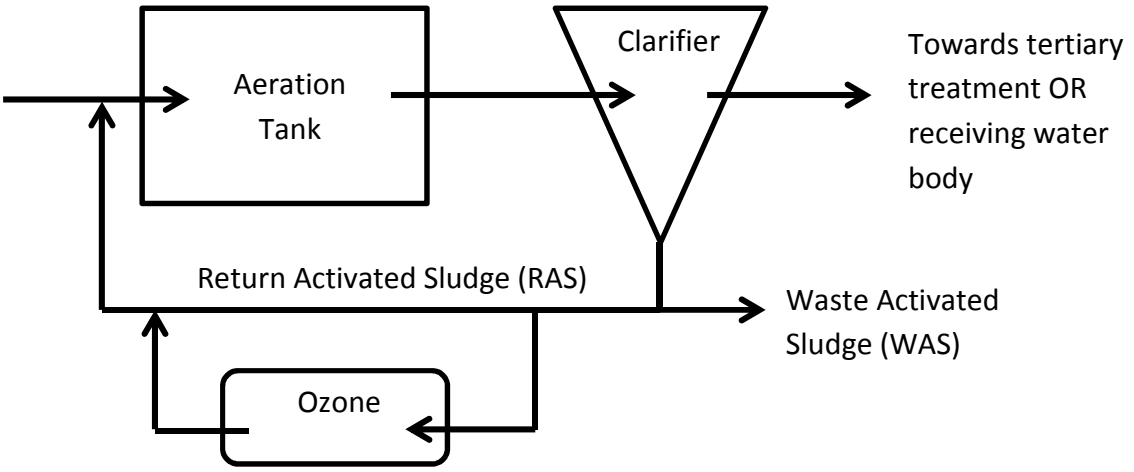


Figure 2. Schematic of a typical activated sludge wastewater treatment plant including a typical location for ozone application

2.1 Microbial Populations and Other Solids in MLSS

Biomass in wastewater treatment is a mixture of many different types of bacteria, protozoa and other living microorganisms, but the microorganisms involved in the treatment process are grouped together based on the substrate they utilize for engineering purposes. The majority of the biomass is grouped under heterotrophs as they mainly metabolize organic carbon, although they also consume a portion of nitrogen and other nutrients required for cell growth. Heterotrophs are very resilient to environmental stressors due to their fast growth rate. In literature, the typical maximum specific growth rate of heterotrophs is >10 d^{-1} at 20 °C, and the maximum specific rate of substrate utilization is >25 g BOD/g volatile suspended solids (VSS)-d (Rittmann and McCarty 2001). Both of these factors demonstrate how quickly heterotrophs can uptake substrate and multiply, leading to their environmental resilience.

Often in the literature, the term autotrophic microorganism is used to describe the other major part of the biomass. This general name is given to the class of microorganisms that use carbon dioxide (CO_2) as their main carbon source, and they do not use carbon compounds as electron-donor (Rittmann and McCarty 2001). However, this grouping is very broad and includes photosynthetic organisms, which are not important for the scope of this project. Instead of using the term autotrophic

microorganisms, in this report, we will more precisely refer to nitrifiers, the group of microorganisms that oxidize ammonia (NH_4^+) as first electron-donor converting it to nitrite (NO_2^-) and nitrate (NO_3^-). This group of bacteria are quite different from the heterotrophs, as they are much more sensitive to changes in environmental conditions. The typical maximum specific growth rate of nitrifiers is <1 d^{-1} at 20 °C, and the maximum specific rate of substrate utilization is <3 g BOD/g VSS-d (Rittmann and McCarty 2001). Comparing these values to that of heterotrophs, it is easy to see why if stressed, nitrifiers' recovery time is much longer than the one of heterotrophs. Some conditions known to inhibit or kill nitrifiers are high/low pH shifts, high concentrations of ammonium (3 g NH_4^+-N/L), low dissolved oxygen (DO) concentrations (<2 mg DO/L) and low temperatures (<12 °C) (Prinčič et al. 1998). Much research has gone into determining optimal conditions for this type of bacteria because nitrifiers transform the majority of ammonium in wastewater to nitrate. This is significant as many discharge regulations limit the amount of ammonium in the effluent stream.

A portion of solids in wastewater treatment is classified as non-degradable volatile suspended solids (VSS). This portion consists of inactive biomass from the influent or generated from biomass decay, and other refractory volatile suspended solid from the influent. In practise, it is difficult to differentiate between the two types. It is important to consider non-degradable VSS when working in wastewater treatment as it does contribute to the solids COD and VSS measurements, and hence of waste biosolids production. However, they do not contribute to the active biomass measurement from the MLSS (Rittmann and McCarty 2001).

2.2 Ozone for Biosolids Reduction

Ozone treatment for reduction of biosolids production can be applied in a number of configurations in activated sludge treatment plants. The most common method is to apply ozone to the RAS line (Figure 2). When the settled biosolids are pumped from the clarifier back towards the aeration tank, a portion of the biosolids is diverted to an ozone contactor, where the ozone is bubbled through the biosolids and returned to the

aeration tank. This configuration is the most common since it does not require large modification to traditional treatment plant set up and allows for a large amount of flexibility in the portion of RAS treated and amount of ozone used (Paul et al. 2012).

Ozone is an unstable gas and cannot be stored and shipped like many other gases. Therefore, ozone must be generated onsite with either air or oxygen. Ozone can be generated through photochemical, electrolytic or radiochemical methods. In wastewater treatment, the most common method is the corona discharge method in which an electrical field is generated by applying a high voltage across two electrodes and passing oxygen between them. When the O_2 molecules pass through this electrical field, they are broken apart into highly reactive atomic oxygens that then react with other O_2 molecules around to form O_3 molecules. The higher the concentration of O_2 present in the ozone generator gas stream, the higher the resulting ozone concentration that will be generated, which is why oxygen gas is more efficient than air for ozone generation (Crittenden et al. 2005).

Ozone has been used in water and wastewater treatment for many years. Its main uses have been disinfection, removal of pollutants through advanced oxidation and improvement of physical treatments. It is also used in activated sludge plants to limit the effects of foaming and bulking (Leeuwen 1988). The first mention of ozone as a biosolid reduction agent was by Gaudy Jr et al. (1971) who was researching total oxidation of biomass and cryptic growth for extended aeration wastewater treatment. In this study, ultrasonic methods were used to break the cell wall, but ozone was mentioned as another cell lyses method. The concept was greatly expanded on by Yasui and Shibata (1995) who developed the first full-scale prototype and achieved a 100% reduction of excess biomass using ozonation during a 6 week experimental period. Since then, the process has been described by numerous researchers using everything from laboratory-scale reactors to full-scale plant set ups (Cesbron et al. 2003, Lee et al. 2005, Salhi et al. 2003, Yan et al. 2009). Currently there are a number of treatment plants in Europe and Asia that employ this technology in their full sized plants (Sievers et al. 2004).

From the exposure of a portion of the RAS, the main observed effect is the reduction of waste biosolids production. Additionally, ozone exposure of RAS affects other processes that occur in a treatment plants. A slight increase in effluent VSS (around 15 mg VSS L^{-1}) had been observed at many plants, which has been attributed to the creation of microflocs during the ozonation process. However, this increase in solid loss amounts to less than 5% of the results from a conventional treatment plant and does not affect the reported sludge reduction (Foladori et al. 2010). Another effect observed in many ozonated plants is the increase in effluent soluble COD (sCOD). While the reported increase ranges from 15 to 40 mg COD L^{-1}, it is still well below regulatory limits. While the COD that is solubilized by the ozone is almost entirely biodegradable, the small increase in soluble COD in the effluent is the fraction of non-biodegradable produced during ozonation (Salhi et al. 2003).

2.3 COD Solubilization

The immediate effect of the exposure of RAS to ozone is the increase in the soluble COD concentration. The relationship between ozone dose and COD solubilized, or the solubilization efficiency, is extremely variable. Parameters that affect the efficiency are sludge floc size, concentration of soluble organic compounds, and the efficiency of the ozone transfer by the ozonation reactor (Foladori et al. 2010). Figure 3 shows this variability in the range of percent COD solubilization in function of the ozone dose for a number of studies as reported by Foladori et al. (2010). Although the data varies greatly between experiments, the overall shape or behavior of the reactions are similar. Initially there is a linear relationship between the ozone dose and COD solubilized, which then plateaus out at a certain level. The slope of the linear section is the sludge solubilization efficiency (Chu et al. 2009b).

Paraphrasing Naso et al. (2008), at lower dosages, ozone solubilizes particulate matter by oxidizing organics, whereas at higher dosages solubilized matter probably rapidly reacts with ozone forcing mineralization of the soluble COD and preventing further oxidation of particulate matter. So as the ozone dose increases, more soluble material is

released from the VSS, which eventually protects the remaining VSS from ozone attacks. Thus, the plateau likely represents the point at which mineralization is the dominant reaction (Cesbron et al. 2003).

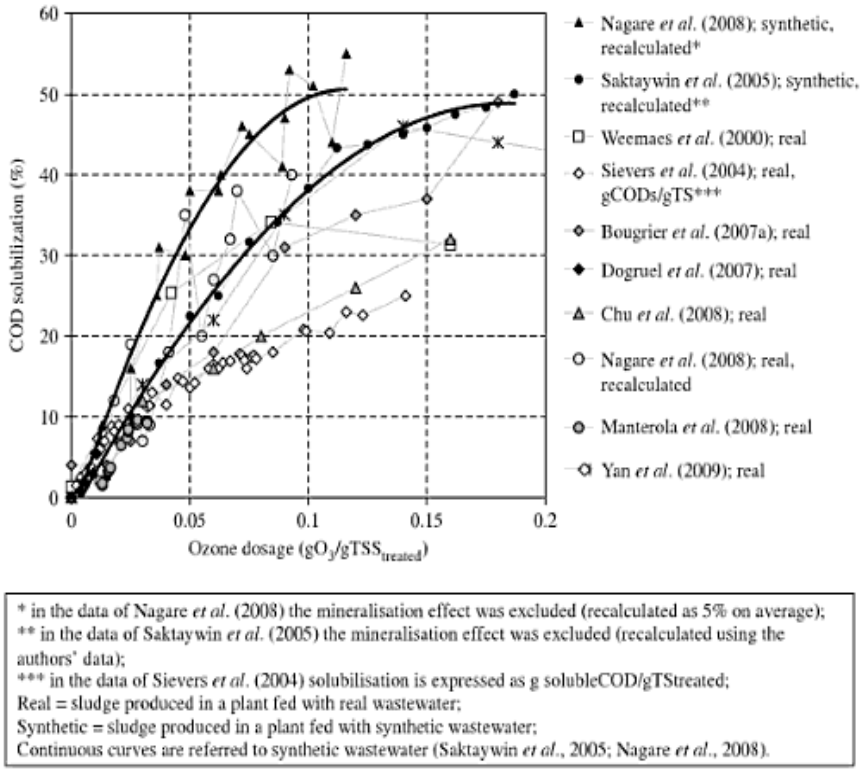


Figure 3. COD solubilization percentage as a function of ozone dose over total solids complied from multiple studies. Although all use different types of biomass and have slightly different slopes, the general shape of the curve is similar in all. (Foladori et al. 2010)

The units used in Figure 3 are commonly found in literature, yet are somewhat redundant. The ozone dose is presented as g O_3/g TSS and COD solubilization is presented as % solubilized COD (i.e., change in soluble COD/total COD). Noting that the main contributor to the COD in the RAS is the VSS part of the TSS, the denominators of the *x*- and *y*-axes are equivalent. This suggests that similar relationships would be observed if simply the solubilized COD concentration (mg COD/L) would be plotted against the volumetric ozone dose (mg O_3/L). In agreement with this interpretation are the observations of Manterola et al. (2008): when "higher ozone dosages are applied, and consequently the maximum solubilisation is reached, no more dependency [*on initial TSS concentration*] [*sic*] apparently exist showing, in both cases [*high and low*

initial TSS concentrations], similar COD solubilisation absolute values and therefore lower percentage values of solubilisation in the case of high TSS concentration". Similarly, research on increases in COD solubilization verses ozone dose on different types of sludges show an equivalent linear relationship indicating that ozone availability limits solubilization and not solids concentration. Therefore, normalizing by TSS and total COD appears unnecessary (Paul et al. 2012). For this reason, results presented in this report are in terms of mg of soluble chemical oxygen demand (sCOD) produced in function of mg O_3 dosed.

2.4 Ozone Mechanisms

The reaction of biosolids with ozone is a complex process that is still an active area of research. Generally, it has been theorized as "the sequential decomposition reaction of floc disintegration, solubilization, and the subsequent oxidization of the released organics into carbon dioxide (mineralization)" (Chu et al. 2009b). Once exposed to ozone, the sludge floc is broken down to micro-particles, allowing ozone to reach cells in the interior of the floc. Ozone can then attack the cells, damaging them and eventually causing their lysis (Figure 4). Some authors suggest that a certain ozone dose threshold (~0.015 g O_3/g VSS) needs to be reached before cell rupture can occur (Albuquerque et al. 2008). Cell lysis releases the intra-cellular components into the water, increasing the sCOD substrate (Foladori et al. 2010). This mechanism is known as the cryptic growth mechanisms of biosolids reduction.

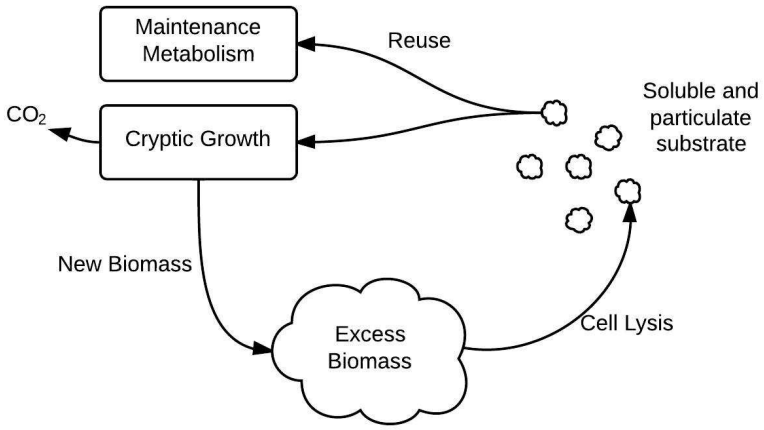


Figure 4. Schematic diagram of cryptic growth, one of the proposed mechanisms that contribute to excess biomass reduction. Non-biodegradable biomass is solubilized by the ozone and fed back to the reactor. A portion of the carbon is released as CO_2

Current modeling research suggests that cryptic growth alone is insufficient to accurately predict sludge reduction by ozonation. Another theory suggests that ozonation does more than just inactivating or killing biomass, but it also converts non-biomass (mainly non-degradable) particulate matter into degradable fractions, some of these being soluble and some remaining particulate. The cryptic growth theory and the combined inactivation and non-biomass transformation theory were compared by a model best fit analysis for data from an ozonated pilot-scale plant (Frigon and Isazadeh 2011). While the cryptic growth model was not able to fit the data adequately, the combined model provided an adequate fit. Despite the need to assume some level of non-biomass transformations, this analysis found that biomass inactivation likely occurs at a specific rate higher than the rate of non-biomass transformation.

There is much data in support of inactivation caused by ozonation. The change in the whole microbial activity is evaluated using respirometry by measuring the oxygen uptake rate or by heterotrophic plate counts. There is a large expected drop in cellular activity after ozonation, which follows a first order reaction (Zhang et al. 2009). Different studies reported a range of ozone doses and corresponding decreasing in activity. At doses as low as 0.02 g O_3/g VSS a decrease of nearly 80% was observed in one study (Chu et al. 2009a), while in another study, a dose of 0.03-0.04 g O_3/g TSS led

to a 70% loss of activity (Saktaywin et al. 2005). Finally, another researcher reported a 97% loss of heterotrophic activity at ozone dose of 0.05 g O_3/g TSS (Lee et al. 2005). These data are contradictory to the ozone dose threshold necessary for inactivation suggested by others (Albuquerque et al. 2008). The controversy seems to be coming from the use of either respirometry or plate counts, with respirometry-based studies sometimes finding a threshold. Isazadeh et al. (*submitted* 2013) recently offered an explanation by finding that at very low ozone dose the oxygen uptake rate can increase, likely due to floc disintegration and a better penetration of the substrate stimulating the oxygen uptake rate. Despite these advances, a comprehensive and coherent description of the RAS ozonation mechanisms is still needed.

2.5 Sequencing Batch Reactor to Study RAS Ozonation and Nitrification

Sequencing batch reactors are commonly used in wastewater treatment studies as the compact nature of the setup is ideal for laboratory-scale experiments. While most SBR are designed and built for the specific experiment they are used for, common design layouts and operational strategies from previous setup can be used in the design for this project. The size of the SBR reviewed ranged from 1 L to 10 L depending on the goal of the experiment. Lee and Oleszkiewicz (2003) used 3 L SBRs to study the effects of grazing protozoa on nitrifiers, and used a temperature controlled room to maintain temperatures and magnetic stirbars to achieve mixing. Oleszkiewicz and Berquist (1988) previously used a temperature controlled room while operating 3.5 L SBR at 2-7 °C to study nitrification at low temperatures. While using temperature controlled rooms is an excellent option to maintain a single temperature, a different method must be used for this project since multiple temperatures are being investigated.

Naso et al. (2008) developed a 6 L SBR setup to investigate the effects on substrate fractioning with biomass ozonation using real wastewater and not controlling the temperature. To apply the ozonation in this batch system, biomass was collected three times per week, ozonated and returned to the reactor at the beginning of the next cycle. Dytczak et al. (2007) also used a similar protocol for batch ozonation with their 3 L SBR setup as they investigated denitrification and ozonation. In this study, 20% of the RAS

was withdrawn after each 24 hour cycle and ozonated before being returned to the system. As this was a short term study, ozonating each day was a suitable practice, but would not be for longer projects. In both of these studies, the cycle included an anoxic phase to promote denitrification, and while this shows the flexibility of treatment options for this type of reactor setup, it does not pertain to this project.

2.6 Effects of Low Temperatures on RAS Ozonation and Nitrification

Biosolids reduction by ozonation is a complex process that involves both chemical and biological systems. Therefore, changes in temperature can have a complex effect on the total efficiency of this process. In biological systems, low temperatures lead to lower activity, lower growth and decay rates, and slower substrate uptake rates. The normal operation temperatures of wastewater treatment ranges from 15-28 °C, and in this range the effects of temperature are insignificant, but temperatures as low as 5-8 °C have been reported for some treatment plants in winter. At these extreme temperatures, there is an expected drop in the treatment level. As well, although the growth rate is decreased, the decay rate is also significantly lowered, which usually leads to a higher MLSS concentration(Crittenden et al. 2005).

Studies on the effects of low temperature on the RAS ozonation process remain limited. Probably the most relevant data are from a pilot-scale experiment conducted during winter operation in Korea, which examined operation strategies for zero excess sludge (Lee et al. 2005). Over the course of 42 days, the temperature of influent entering the pilot plant dropped from 13.7 to 9.5 °C. The ozone dose was kept constant during this phase of operation. This resulted in an increase in MLSS from 3,200 to 5,300 mg/L and was thought to be due to insufficient acclimation period as well as low temperature. It has been observed that the biodegradation of particulates decreases significantly with temperature. During the second phase of the project, the ozone dose was adjusted frequently in order to lower the MLSS. There was no observed accumulation of inorganics in the reactors once the MLSS stabilized. The authors note that the ozone dose should be increased, even doubled, at temperatures below 10 °C to account for the

decrease in biodegradation rates and the increase in observed yields. The effluent quality was not affected by the introduction and changes in ozone dose (Lee et al. 2005), but only the COD and TSS results were reported.

Because of their sensitivity to changes in environmental conditions, understanding how nitrifying bacteria in municipal wastewater treatment plants respond is necessary for optimal plant operation. These types of bacteria already have a much slower growth rate compared to heterotrophic, so when exposed to any type of stressor, whether it is a decrease in temperature or a toxic shock, the recovery time is much longer than it is for heterotrophs. The most common stressor that is seen in wastewater treatment is the seasonal change in temperature, especially during the winter and spring snowmelt, which can bring the temperature of wastewater down to 5 °C and below. It has been observed that the efficiency of nitrification drops significantly at these low temperatures (Shammas 1986).

The nitrification rates at low temperatures were assessed in 4 parallel SBR with cycle lengths of either 8 or 12 hours by Oleszkiewicz and Berquist (1988). The operational temperature was set at 15 °C and slowly lowered incrementally, with the nitrogen removal rates measured once steady-state was achieved after each temperature drop. It was found that the 8 hour cycle reactors took much longer to acclimatize and showed much more sensitivity towards slight process changes. At temperatures down to 7 °C there were no pronounced changes in removal efficiencies, but at 5 °C, the total Kjeldahl nitrogen (TKN) removal efficiency dropped from 90 to 70%. This drop was not observed in the 12 hour cycle reactor, which maintained a removal rate of 90% at 5 °C. At 2 °C, the removal efficiencies deteriorated for both cycle reactors to around 50%. By adjusting the solids retention time (SRT) from 20-35 days to over 60 days, the 12 hour reactor recovered to achieve 90% TKN removal. So, nitrification is found to be feasible at 2 °C, although very specific conditions are necessary at achieve this (Oleszkiewicz and Berquist 1988).

More recently, temperature effects on nitrification have been studied in full-scale treatment plants. Because the SRT and temperature are the two main operational factors that can affect the activity of the nitrifying bacteria in activated sludge treatment systems, the study correlated nitrification effectiveness with SRT, temperature and COD loading over a 3 years period (Komorowska-Kaufman et al. 2006). It was found that when temperatures were lower than 15 °C and the SRT below 20 days, nitrification was somewhat unstable with its effectiveness varying between 61.7 to 99.3% of ammonia oxidized. Above SRT of 20 days, the effectiveness remained high regardless of temperature, with 88-99% of ammonia oxidized. When the COD/ammonia-N ratio was lower than 4, the nitrogen removal rate remained stable, with an effectiveness of above 95% ammonia oxidized. When the ratio was higher than 4, nitrification became unstable (Komorowska-Kaufman et al. 2006).

2.7 Modeling

Wastewater treatment plant models are actually a combination of a number of other models that describe all the processes in a plant such as activated sludge biochemical models, hydraulic models, oxygen transfer models and settling in sedimentation tank models. These models use a complex matrix of differential equations to simulate processes within a plant. They vary in mechanistic precision from black-box models describing simple conversion functions, to white-box models that are fully mechanistically based. Most of the models used would be considered grey-box models. The equations used in these models are based on general balance equations of mass and other conserved quantities. While many models have the capacity to predict many aspects of plant performance, the most common targets of model studies are cost reduction and effluent nutrient (nitrogen and phosphorus) reduction (Vanrolleghem et al. 2003).

The biological components of activated sludge wastewater treatment systems are usually modeled using consensus Activated Sludge Models (ASM1, ASM2-AMS2D, ASM3) proposed by the International Water Association (IWA). The main difference with

respect to the description of heterotrophs between ASM1/ASM2 (same description) and ASM3 is the description of decay processes. ASM1/ASM2 use the circular lysis-regrowth concept, while ASM3 uses the linear endogenous respiration with the addition of storage compounds (Gernaey et al. 2004). From an academic point of view, the ASM3 model is easier to calibrate than the ASM1/ASM2 models because in ASM1/ASM2 "all state variables are directly influenced by a change in a parameter value, [*while*] in ASM3 the direct influence is considerably lower thus ensuring a better parameter identifiability" (Gernaey et al. 2004). The flow diagram in Figure 5 illustrates the differences in the two models. Despite this, ASM1 remains the most used model by practitioners (Hauduc et al. 2009). Because determining all model components would be expensive and time consuming, it is suggested that default values from literature be used for less sensitive parameters (Vanrolleghem et al. 2003).

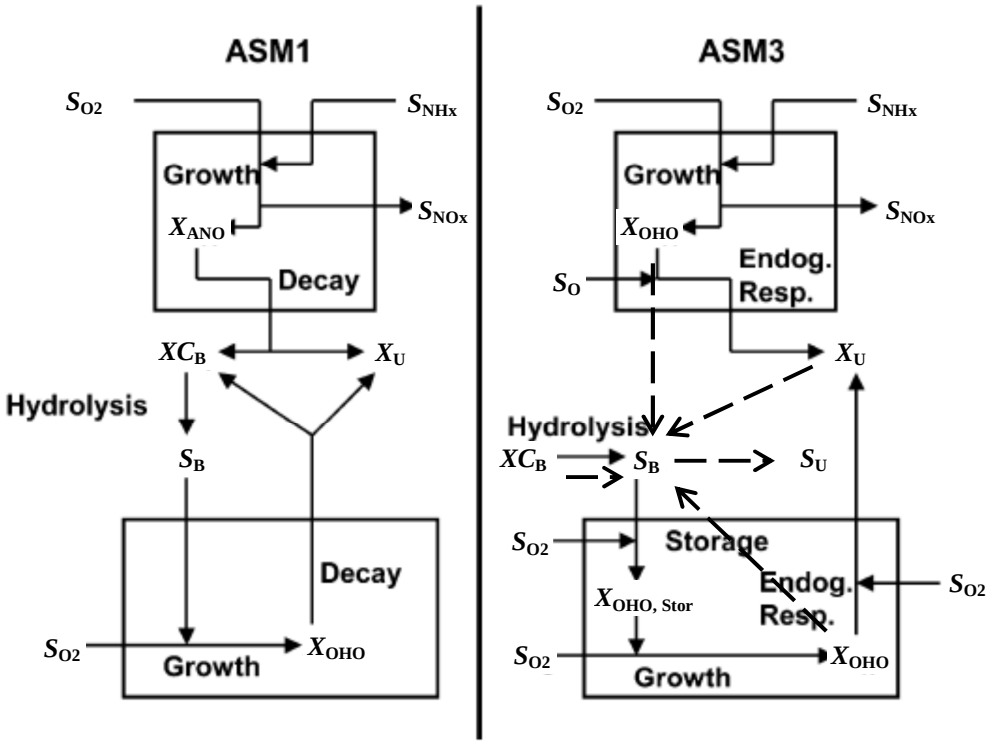


Figure 5. Substrate flow for nitrifiers and heterotrophs in the ASM1 and ASM 3 models. (Gernaey et al. 2004) Dashed lines indicate the transformation of COD by ozonation used in the extension proposed by Frigon and Isazadeh (2011). Definitions of symbols are found in Figure 6.

Often the calibration exercise assumes the default values for the biochemical parameters, and it splits the total influent COD into fractions with specific physical and reactive characteristics in the process. Influent COD is fractioned into readily biodegradable (typically soluble) COD (S_B), slowly biodegradable (typically particulate or colloidal) COD (XC_B), non-biodegradable soluble COD (S_U), and non-biodegradable particulate COD (X_U). The biomass is also considered part of the total COD fractioning as heterotrophic biomass (X_{OHO}), and nitrifiers (X_{ANO}); although the biomass fractions are typically assumed to be absent from the influent and only grow in the MLSS. The general uptake of carbon is described in ASM3 as XC_B is converted into S_B, and then the substrate is converted into storage $X_{OHO,Stor}$. The storage can then be used for growth resulting in more heterotrophic organisms X_{OHO} or in microbial metabolism resulting in the mineralization of carbon (Gujer et al. 1999). A breakdown of the COD fractioning and the symbols used are shown in Figure 6. The full Gujer stoichiometry matrix and process rates for the IWA-ASM3 model can be found in APPENDIX A.

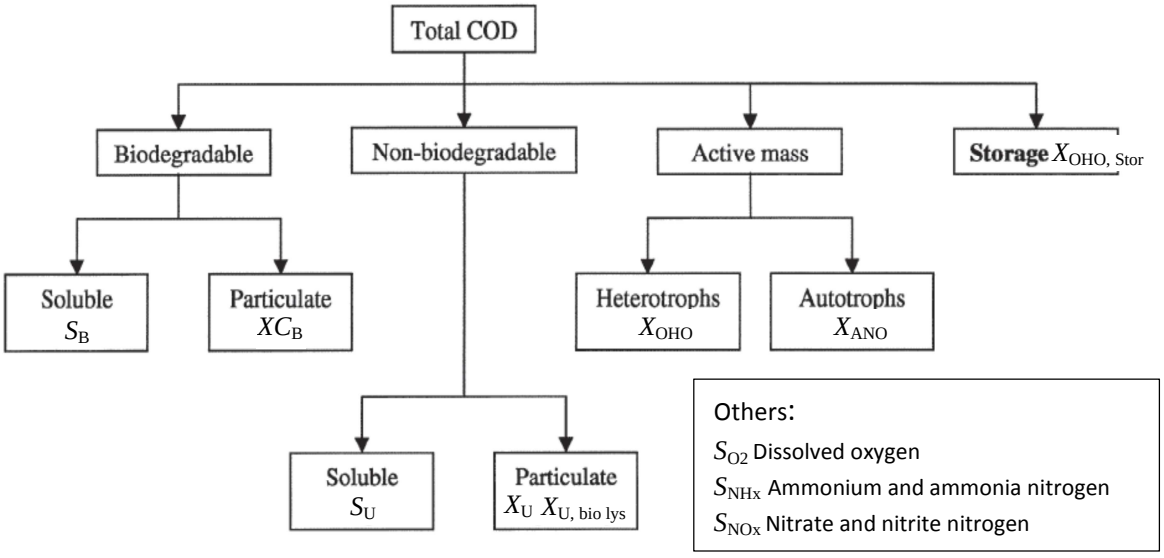


Figure 6. COD components used in ASM3 and their reference symbols. The fractions are grouped as biodegradable, no biodegradable, active biomass and storage COD (Petersen et al. 2003).

Frigon and Isazadeh (2011) first introduced an extension to the ASM3 model for the ozonation of excess sludge. The ASM3 model structure was adopted because of its simplicity and the increased identifiability of model parameters (Gernaey et al. 2004).

Two main reactions were added to ASM3 by the extension of describing RAS ozonation. First, a reaction was introduced that transforms/mineralizes non-biomass COD (X_U+XC_B) by ozone into S_B, XC_B or S_U COD at a first-order rate constant of $q_{XU_XCB,O3,trans.}$The dashed lines in Figure 5 illustrates this transformation from particulates to soluble products. Second, a reaction was also considered for the inactivation due to ozone of X_{OHO} and X_{ANO}, which occurred at a first order rate constant of $b_{Bio,O3,inact}$. While the predictability of the effluent COD and biomass levels was high (Frigon and Isazadeh 2011), some inaccuracies were found in the overall mass balances. In subsequent studies, the inaccuracies were corrected. The model was then studied to determine the possible effects of biosolids ozonation on nitrification (Isazadeh et al. *submitted* 2013).

Chapter 3
Materials and Methods

3.1 SBR Design and Setup

3.1.1 Reactor Design

The goal of the design and construction of the reactors was to build laboratory-scale reactors that simulate a biological wastewater treatment plant, and could work in parallel with minimal manual operation. Four reactors were to be used in this experiment: two to be held at a cold temperature (8 °C) and two held at room temperature (20 °C) with one within the pair receiving ozone treatment and one acting as a control. In addition, the supporting setup such as pumps, containers, controllers and probes were to be designed and assembled.

Because of the number of reactors to be built and the large setup space requirement, the reactors were designed with a working volume of 2 L. The reactors were double jacketed to allow for temperature control using water bath circulators (Model 250LC IsoTherm, Fisher Scientific, Waltham, MA). The reactors were constructed from two nestled cylinders, with the interior, 3.175mm (1/8”) thick and 127mm (5”) diameter cylinder containing the biological reaction, aeration, probes and influent/effluent pipes, and the outer, 6.35mm (1/4”) thick, 190.5mm (7.5”) diameter cylinder containing the circulation water. The cylinders, plates and lids of the reactors were built from non-reactive, clear Plexiglas. Even during the design and construction stage of the project, the system was constantly being optimized and improved which is demonstrated by the change in the initial and final reactor design schematics in Figure 7, and finished reactors in Figure 8.

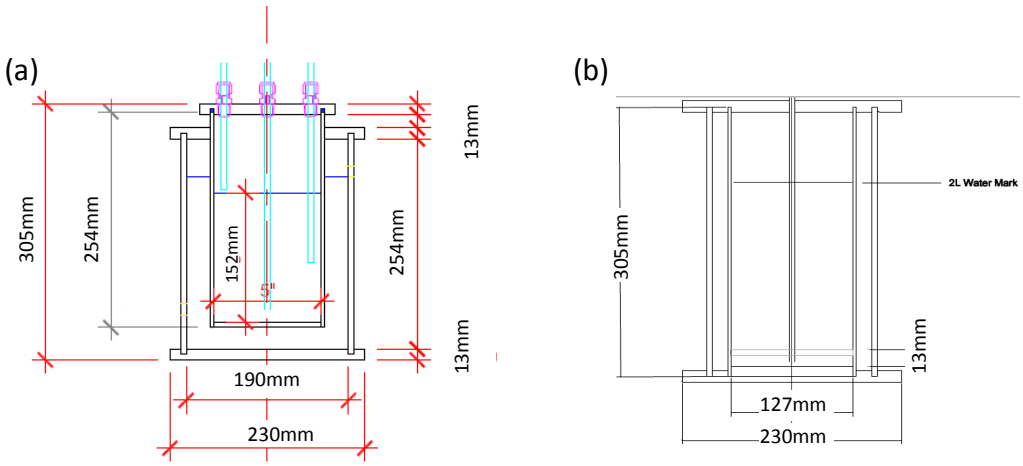


Figure 7. Initial (a) and final (b) reactor schematics. The main difference is the placement of the inner cylinder. In the final design, the inner cylinder is resting on the bottom rather than suspended. This simplifies the design allowing for a single layer lid.

Figure 8. Photograph of reactors in operation. Note the third reactor is in the settling phase while the others are in the aeration phase.

3.1.2 Setup Design

Influent, effluent, wasted and ozonated activated sludge suspended solids were pumped through the system by nine Masterflex peristaltic pumps (Model SI-77911-20, Cole Parmer, Montreal, QC). The schematic of the total layout of the setup shows the placement of the containers, pumps and reactors in relation to each other (Figure 9). The general flow of the set up goes from left to right, with the influent on one end and the effluent tanks on the other. The system was automated using a power on/off controller attached to the pumps and solenoid values. The Apex model AquaController from Neptune Systems (Model APEXLSYS, Neptune Systems, San Jose, CA) is a system of individually programmable outlets and probes that can be programmed to either turn on

or off based on timing or conditions with minimal external input. The full programming of each outlet can be found in the APPENDIX B.

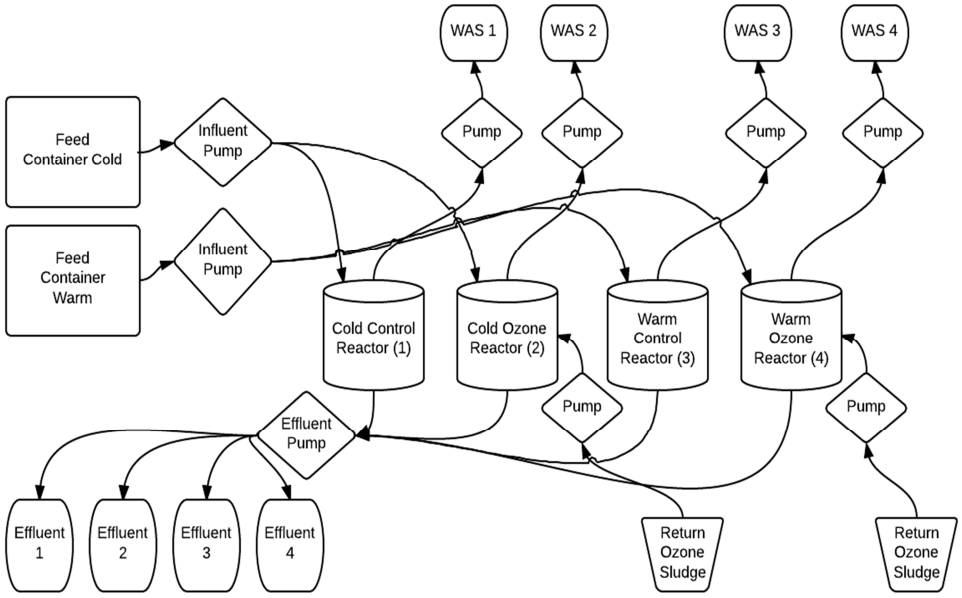


Figure 9. Full set-up schematic, showing the flow of the influent to the reactors, and the effluent from the reactors to individual containers. Also shown is the flow of mixed liquor from the reactors to the WAS containers, where a portion of it for the experimental reactors will be ozonated and returned to the reactors

3.1.3 Aeration

Aeration is provided by the in house compressed air line. Before being sent to the reactors, the air was passed through an oil and particle filter to remove any impurities. Because the experiment was not sensitive to airflow conditions, the air was not passed through a dehumidifier, and the air flow into the reactors was not monitored continuously. Air was introduced into the reactors through a diffusion plate which covers the entire bottom of the reactor and also provided the mixing. Initial design of the aeration plate required a high air flow to achieve full mixing due to the large 3.175 mm (1/8”) holes, but this caused undesirable foaming and splashing in the reactors. Therefore, the plates were redesigned with 0.8 mm (1/32”) holes drilled at an angle and spaced 25.4 mm (1”) apart to achieve mixing using much less air. The airflow was measured periodically and adjusted to ~2 L/min. At this flow rate, the dissolved oxygen level was sufficient throughout the cycle length as measured by a portable DO probe (Model HI 9828, Hanna Instruments, Smithfield, RI).

3.1.4 Mixed Liquor Seeding

Sludge from Régie d'Assinissement des Eaux de Bassin La Prairie (REABL) treatment plant was used to seed the reactors. The temperature of all reactors was initially kept at room temperature, 20 ± 1 °C. Solid concentrations inside the reactors were erratic as the population stabilized. The reactors were seeded with more sludge as needed during this acclimation period in order to keep the microbial population from collapsing.

Once the solid concentrations in the reactors began to stabilize, the temperature of two of the four reactors was slowly decreased. The rate of temperature decrease was 1 to 2 °C per week. This rate allowed the microbial population to adapt to the temperature change gradually and not shock the system, which could cause failure. Starting at 15 °C lowering the temperature to 8 °C took 2 months to accomplish without adverse effects on operation.

3.2 Influent Feed

For practical and control reasons, the reactors were fed a synthetic feed rather than actual municipal wastewater. Syntho is a synthetic municipal wastewater developed by Boeije et al. (1999) in order to study biological nutrient removal. This recipe was developed to mimic municipal wastewater as much as possible and is quite complex in its make-up. Unlike other basic recipes, Syntho has a wide range of both simple and complex compounds that provide the carbon, nitrogen and phosphorus to the system (Table 1). Linear alkylbenzene sulphonate (LAS) and alcohol ethoxylate (AE) are biodegradable surfactant agents that are included in the recipe to simulate gray water, or water used for washing. Because of this surfactant portion, the airflow needed to be carefully monitored to reduce foaming and bubbling. The diatomaceous earth is a non-reactive particle used to simulate inert particulate matter. The COD of this recipe is approximately 550 mg-COD/L and the TKN concentration is 35 mg-N/L. The Syntho feed was prepared in a stock solution at 250x normal concentration once a month and allocated into smaller containers and frozen until just before use.

Table 1. Modified Syntho Feed Recipe (Boeije et al. 1999).

C-source (mg L^{-1})		N-source (mg L^{-1})		P-source (mg L^{-1})		Sewage simulation (mg L^{-1})	
Peptone	22.5	Urea	75	$MgHPO_4 \cdot 3H_2O$	25	LAS	10
Na-acetate	180	NH_4Cl	11	$K_3PO_4 \cdot H_2O$	20	AE	10
Dry Meat Extract	22.5	Uric Acid	9			Diatomaceous Earth	10
Glycerol	60					Trace Element Solution	1
Potato starch	75						
Low fat milk powder	180						

A trace element solution was also included in the feed in order to include elements present at low concentrations in wastewater and necessary for microbial growth. The recipe seen in Table 2 includes many metals needed for electron transfer for cell growth (Bollmann et al. 2011).

Table 2. Trace Element Stock Recipe (Bollmann et al. 2011)

Ingredient	Stock Concentration (mg L^{-1})
Na_2EDTA	4292.0
$FeSO_4.7H_2O$	2780.0
$MnCl_2.4H_2O$	99.0
$NiCl_2.6H_2O$	24.0
$CoCl_2.6H_2O$	24.0
$CuCl_2$	13.4
$ZnSO_4.7H_2O$	143.0
$Na_2MoO_4.2H_2O$	24.0
WO_3	23.2.0
H_3BO_3	62.0

The influent feed for the reactors was prepared and stored in 24-L autoclavable carboys. Each paired set of reactors was pumped feed from the same container, which was either stored on the bench, for the warm reactors, or in a mini fridge for the cold reactors. Each carboy could hold enough feed for 12 cycles of two reactors (i.e., 3 days). In order

to maintain the stability of the COD in the carboys over these three days, the feed was autoclaved at 121 °C for 1 hour and allowed to cool before being fed to the reactors.

3.3 SBR Operation

Figure 10 describes the final design 6 hour cycle. After the effluent from the previous cycle was pumped out, there was 1 L of RAS remaining in the reactor. In the first step of the cycle, aeration was turned on for 8 min allowing the system to idle and the dissolved oxygen concentration to increase. After 8 min, the influent and ozonated sludge pumps were turned on to fill the reactors to 2 L. Aeration continued for approximately 5 hours; and near the end of that phase, the WAS pumps turned on and wasted directly from the aerated mixed liquor. Next, the aeration was turned off and the mixed liquor was allowed to settle for one hour. Lastly, the effluent pumps pumped out 1 L of effluent. The placement of the effluent pipe within the reactor guaranteed that no matter how long the pump was on, it would leave 1 L in the reactor. While 10 min of pumping was excessive, and only a few minutes were normally needed to remove the effluent, this time period was chosen as a safety backup. In the case that more influent was pumped into the reactor than normal, the effluent pump could remove the excess liquid, preventing the eventual overflow of the reactor. The cycle then started again with aeration turning back on.

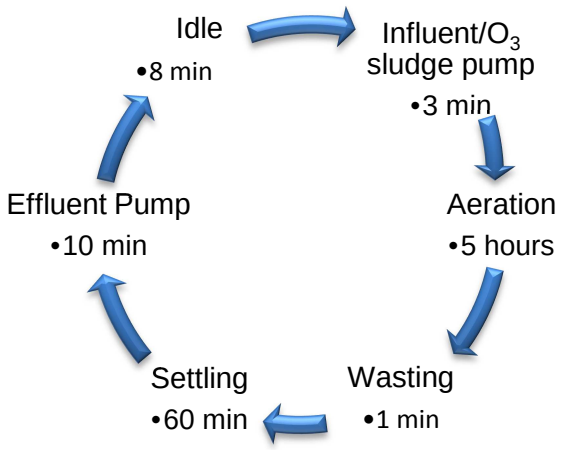


Figure 10. Six hour sequencing batch reactor cycle. All processes occur within the same container and only the operational conditions change between phases.

While the majority of operation was automated using the Apex controller (above), there was still a number of actions that needed to be done manually. This included preparing and hooking up the influent every three days. In order to reduce sludge build up on the sides of the reactors and prevent biofilm growth, the reactors were cleaned daily. This involved opening the lid and brushing down the sides of the interior cylinder. The WAS and effluent tanks were measured and emptied twice a week, and samples were obtained at the same time for analyses. Samples were also collected from inside the reactor. Analyses included suspended solids, COD, ammonium, nitrate, and nitrite concentrations (below).

3.4 Ozonation

The protocol presented here for ozonation is the final version after numerous optimizations and experimental results. The final amounts and volumes used in the ozonation protocol are from results discussed in Chapter 5. For each dose, 800 mL of WAS collected on sampling dates were placed in the biosolids-ozone contactor (Figure 11). Ozone was generated using Ultra High Purity 4.3 oxygen (Praxair, Mississauga, Ontario) by an Ozomax (Canton de Shefford, QC) model OZO 3VTTL ozone generator, and bubbled through diffusors into the sample. The oxygen pressure into the generator was 13 psi and the flow rate was 8 L/min. The residual ozone concentration was read and recorded by a gas ozone analyser (Mini-Hicon model, IN-USA, Norwood, MA). Any

foam that overflowed into the solids trap was returned to the rest of the sample after ozonation was complete. The dose was calculated from comparing the residual ozone concentration and the pre-measured ozone generation rate; the does was adjusted by varying the ozonation time. For the solubilisation experiments, the ozone dose was set to 225 mg O_3/L to reach a constant target waste biosolids reduction rate of ~40%. Because the maximum volume that could be ozonated at a time was 800 mL, the ozonation of the total volume of WAS to return to the reactors (1600 mL in 4 days) was done in two batches. The batches were mixed before being returned to the reactor setup. The ozonated biosolids were placed in a cooler at 4 °C and fed back into the reactors over the following 3-4 days.

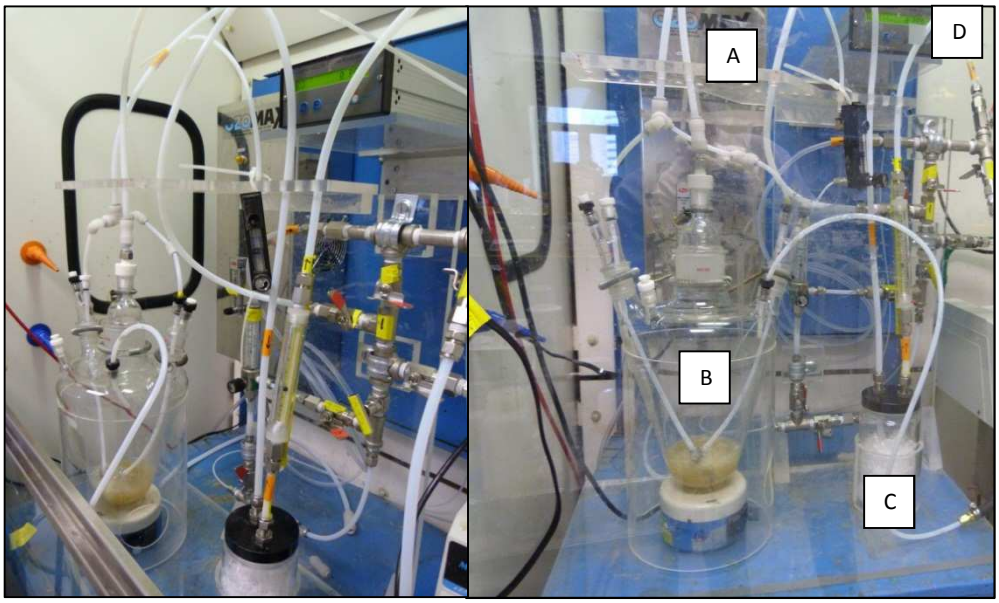


Figure 11: Lab batch ozonator showing (A) ozone generator, (B) biomass contactor, (C) solids trap, (D) residual ozone gas reader. Mixed liquor is placed in the contactor and ozonated for a predetermined time to achieve desired ozone

3.5 Analytical Methods

A number of parameters were measured continuously throughout the experiment to determine the performance of the reactors. The parameters chosen were similar to those tested in actual wastewater treatment plants. Effluent samples used in COD and nutrient analyses were collected once a day, combined into composite samples of 15 mL, and frozen at −20 °C to prevent any changes in composition before testing. WAS and effluent volumes were measured, recorded and sampled on the sampling days

(Tuesdays and Fridays). A 10 mL grab sample of the influent was taken on these dates. 15 mL samples were also collected after each batch ozonation. MLSS samples were grabbed directly from the reactors on the sampling dates before the wasting phase. The volumes used in the analysis of total and volatile suspended solids of the WAS, MLSS, and ozone samples was 5 mL, and the effluent sample volume was 50 mL. While the solids test was done on the sampling dates, 5 mL samples for COD and nutrients were frozen at -20 °C until analysis. The nutrient samples and soluble COD were centrifuged for 20 minutes at 4000 rpm before analysis. The analysis of total and volatile suspended solids (TSS,VSS; method 2540), total and soluble COD (method 5220D), ammonium (NH_4^+; method 4500-NH_3-F), nitrite (NO_2^-; method 4500-NO_2^--B), and nitrate (NO_3^-; method 4500-NO_3^--H) were performed following standard methods (APHA et al. 2005). Influent and ozone soluble COD samples were diluted 1 in 5 times; WAS, mixed liquor volatile suspended solids (MLVSS), and COD samples were diluted 1 in 10 times; and effluent COD was not diluted. Ammonium, nitrate and nitrite were measured colorimetrically in a microplate scale version in which 2 weeks of samples could be measured per plate. The exact protocols for these tests can be found in papers by Rhine et al. (1998) and Shand et al. (2008).

3.6 Model Setup and Calibration

The main objectives of the modeling exercise are (1) to develop the proper the physical layout description/abstraction and (2) to calibrate the model for the use of the synthetic wastewater Syntho. Using the developed ASM3 extension for ozonation from Frigon and Isazadeh (2011) and updated in Isazadeh et al. (*submitted* 2013), the physical layout of the reactors needed to be developed and sized correctly. The reactors were modeled in AquaSIM v 2.0 (Reichert 1998) as two separate advective only compartments (i.e., ideal plug flow reactors (PFR)), which is equivalent to sequencing batch reactors. This was done because, numerically, AquaSIM is better suited for constant operation rather than batch reactions. Also, modeling a SBR exactly is both difficult and time consuming, especially when simulating a long time period; and the ideal plug-flow simulation takes considerable less time and processing power. For these reasons, SBRs are commonly

modeled as ideal plug flow reactors (Wilderer et al. 2001). By translating the reaction phase in the SBR to the distance flow through time in the PFR, batch reactions can be modeled as a continuous flow reaction, simplifying programming and simulations.

Because of the large volume of waste mixed liquor removed from the ozonated reactor and stored between the batch ozonation, this processed was included in the model. As the containers were aerated and kept at low temperatures, this simplifies the programming. In order to capture the batch reaction nature of the wasting that occurred once a day over three days between ozonation and translate that into a continuous flow process, the wasting containers were separated into 3 mixed reactors, each with a hydraulic residence time (HRT) of one day (Figure 12). The appropriate volume of mixed liquor flows into each compartment from the end of the plug flow reactor, and as well the first compartment flows into the second, and the second into the third. This ensures the proper mix of biomass with different SRTs reach the beginning of the plug flow reactor.

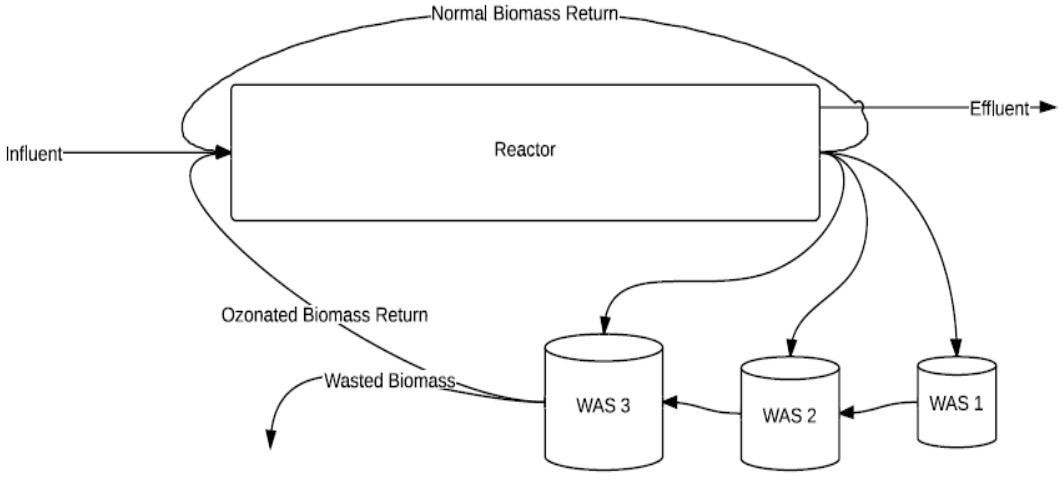


Figure 12. Simplified model diagram of ozonated reactor wasting layout. Three wasting containers with an HRT of 1 day were used to simulate the daily wasting and ozonated return of large volumes of mixed liquor.

This Gujer matrix of the extension to the ASM3 model used herein is presented in Table 3. The reaction rate of the ozone with the activated sludge VSS was measured as the rate of COD solubilized per day per system's solids COD inventory ($q_{Xtot,O3,sol}$); thus, the

measurement had the same unit as a first-order rate constant. The non-biomass solid transformation rate constant ($q_{XU\_XCB,O3,trans}$) and biomass inactivation rate constant ($b_{Bio,O3,inact}$) were calculated from $q_{Xtot,O3sol}$ through eq.1.

$$q_{Xtot,O3sol} = q_{XU\_XCB,O3,trans} \times (1 - f_{Bio,storage}) \times (f_{SU\_O3,trans} + f_{SB\_O3,trans}) + b_{Bio,O3,inact} \times f_{Bio} \times (1 - f_{XU\_Bio,lys}) \times (f_{SU\_O3,inact} + f_{SB\_O3,inact}) \quad \textbf{(eq. 1)}$$

where

$$f_{Bio,storage} = (X_{OHO}+X_{ANO}+X_{Stor})/(X_{OHO}+X_{ANO}+X_{STO}+XC_B+X_U) \quad \textbf{(eq 2)}$$

$$f_{Bio} = (X_{OHO}+X_{ANO})/(X_{OHO}+X_{ANO}+X_{STO}+XC_B+X_U) \quad \textbf{(eq. 3)}$$

$f_{SU\_O3,trans}$ and $f_{SU\_O3,inact}$ are the fractions of solubilized undegradable COD, $f_{SB\_O3,trans}$ and $f_{SB\_O3,inact}$ are the fractions of solubilized biodegradable COD, and $f_{XU\_Bio,lys}$ is the fraction of biomass debris ($X_{U\_Bio,lys}$) generated by decay (Isazadeh et al. *submitted* 2013).

The ASM3 model describing biological treatment is quite robust and accounts for the wide range of parameters that describe the biological processes. In fact, the models are over parameterized, with a number of overlapping or interconnecting variables. Because of this assumptions can be made in order to simplify calibration such as using common literature values and holding most biological parameters constant. This was the approach used in this model calibration. In order to compare laboratory results to model predictions, biosolids concentrations were converted to COD using 1.42 g-COD/g-VSS (Rittmann and McCarty 2001). The default biological values used in the model are the ones suggested in Hauduc et al. (2011) and can be found in APPENDIX A.

Once the physical layout was done, calibration was carried out by fitting the simulated results to the observed data. The COD fractions of the influent were calibrated using the control reactor data, and because the feed was autoclaved it was assumed the influent bacterial concentration was zero. Once the control results were satisfactory, the ozonated reactor was calibrated by adjusting the COD fractions generated from the ozonation process. The three main imputed measured parameters from the lab data are

influent COD, the SRT and the relative COD solubilisation rate ($q_{Xtot,O3,sol}$), the overall solids COD solubilization by ozone rate constant normalized to the solids COD inventory. The relative COD solubilisation rate is the main factor relating the ozone to waste biosolids reduction. While the solubilization curve presented in Chapter 5 was very important to reactor operation, only the outcome of the solubilization is important in modeling.

Table 3. Gujer stoichiometry matrix and process rates for the IWA-ASM3 model extension describing ozone conversions (Isazadeh et al. *submitted* 2013).

Process	COD or N pools									Rates
	S_B	S_U	S_{O3}	S_{NH4}	XC_B	X_{OHO}	$X_{OHO,Stor}$	X_{ANO}	X_U	
Transformation										
Undegradable	$f_{SB\_O3\ trans}$	$f_{SU\_O3\ trans}$	$f_{mnr,O3}$	i_{N_XU}	$1-(f_{SB\_O3,trans}+f_{SU\_O3,trans}+f_{mnr,O3})$				-1	$q_{XU\_XCB,O3,trans}\times X_U$
Biodegradable	$f_{SB\_O3\ trans}$	$f_{SU\_O3\ trans}$	$f_{mnr,O3}$		$-(f_{SB\_O3,trans}+f_{SU\_O3,trans}+f_{mnr,O3})$					$q_{XU\_XCB,O3,trans}\times XC_B$
Inactivation										
Heterotrophs	$f_{SB\_O3\ inact}\times(1-f_{XU\_Bio,lys})$	$f_{SU\_O3\ inact}\times(1-f_{XU\_Bio,lys})$		$i_{N\_XBio}-(f_{XU\_Bio,lys}\times i_{N\_XU})$	$(1-f_{SU\_O3\ inact}-f_{SB\_O3\ inact})\times(1-f_{XU\_Bio,lys})$	-1			$f_{XU\_Bio,lys}$	$b_{OHO,O3,inact}\times X_{OHO}$
Storage					$+1$		-1			$b_{OHO,O3,inact}\times X_{OHO,Stor}$
Autotrophs	$f_{SB\_O3\ inact}\times(1-f_{XU\_Bio,lys})$	$f_{SU\_O3\ inact}\times(1-f_{XU\_Bio,lys})$		$i_{N\_XBio}-(f_{XU\_Bio,lys}\times i_{N\_XU})$	$(1-f_{SU\_O3\ inact}-f_{SB\_O3\ inact})\times(1-f_{XU\_Bio,lys})$			-1	$f_{XU\_Bio,lys}$	$b_{ANO,O3,inact}\times X_{ANO}$

Results and Discussion

Chapter 4
Start Up and Biosolids Stabilization

4.1 Introduction:

Once the reactors were built and seeded, the next objective was to establish a stable microbial population in all reactors adjusted to the pre-ozonation conditions. In order to compare the effects of ozonation between the temperature-paired reactors, the solids inventories must be in similar steady-state conditions in both reactors before ozonation can begin. The reactors and setup went through a number of refinements, both physically and operationally, to attempt to achieve the calculated expected solids inventories. This chapter presents the data from issues encountered during initial setup and the resulting modifications and optimization. As well, the results and characteristics of the attained biomass concentration in the reactors after these adjustments are presented.

4.2 Setup Adjustments

Throughout the experimental phase, the set up was constantly upgraded and improved based on results obtained during operation. Most of the major changes that led to the final layout presented in Chapter 3 (Materials and Methods) occurred during the first few months of operation. There were a significant number of minor changes to the set up and operation during this time, such as aeration plate modification, wasting frequency and sampling practices. Only the three most significant changes that corrected problems detrimental to operational stability are presented to demonstrate the methods used to find solutions when a challenge in the set up presented itself. These problems are feed stability, light infiltration and dissolved oxygen concentration in the early part of the reaction cycle.

4.2.1 Feed Recipe and Stability

Since a feed container was utilized over a three-day period, the COD levels in the feed needed to be maintained over the entire period. Two methods of COD stabilization, autoclaving and refrigeration, were used, and results were compared to COD concentrations in non-treated feed that was kept on the bench. The autoclaved and refrigerated feeds both maintained the initial COD level over the three days (only 8% reduction), while the non-treated feed had a significant drop in COD starting on the second day and had lost 42% of the initial COD by the third day (Figure 13). Therefore, both autoclaving and refrigerating the feed were judged acceptable methods of maintaining COD levels in the feed. Based on these findings, the feed was autoclaved a day before use and allowed to cool to room temperature. The feed pumped to the cold reactors needed to be refrigerated as well in order to reduce temperature increase in the reactors as the reactors were being fed.

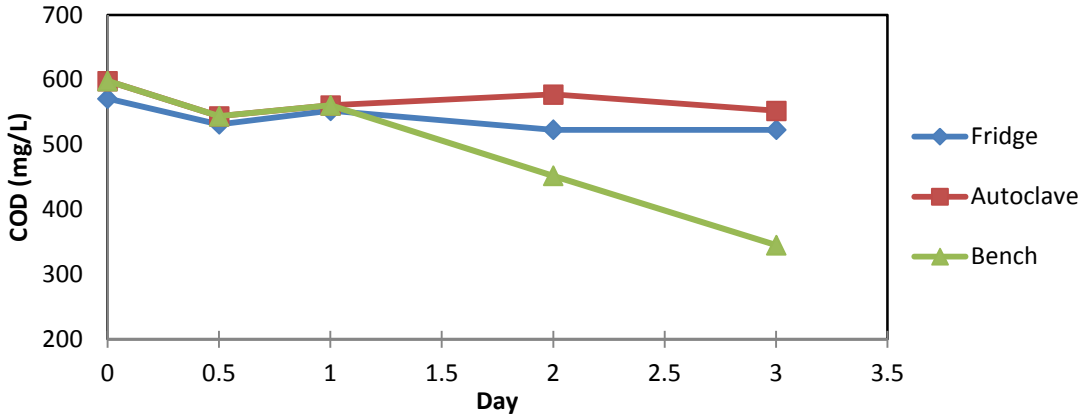


Figure 13. Feed COD stability for treated and non-treated feed over three days. Both autoclaved and refrigerated feed maintained COD levels over the 3 day period and were used in daily operation. Note, Y-axis does not start at 0.

4.2.2 Red Biomass and Reactor Covering

Early on in the experimental phase, a type of red biomass was noted during settling period of the warm reactors. After observations under the microscope, the biomass was determined to be red algae. While algae is a desired organism in other wastewater treatment set ups, such as constructed wetlands, in activated sludge wastewater treatment algae is considered an undesirable organism as excess algae can lead to surface scum and poor water clarity (Palmer 1977). The growth of algae in the reactors

was possibly due to high light penetration through the clear plexiglass sides. This does not reflect the conditions in the majority of wastewater treatment processes since wastewater treatment occurs in near darkness in large below-grade tanks. It was decided that the amount of light entering the reactors needed to be reduced. The clear plexiglass reactors were then covered with aluminum foil (Figure 14) to better simulate wastewater treatment conditions. The red algal biomass was not observed after this change.

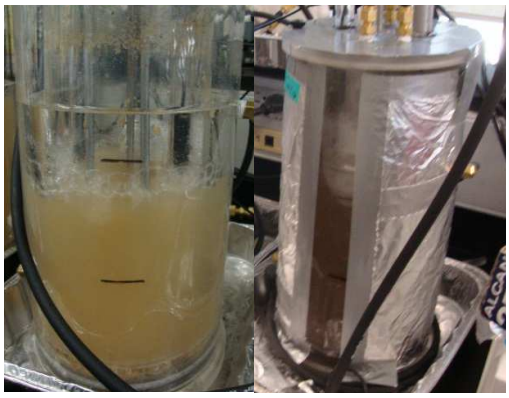


Figure 14. Reactors before and after they were covered to reduce light infiltration that promoted algae

4.2.3 Dissolved Oxygen and Cycle Adjustment

As the temperature decreased in two of the reactors, there was a noticeable difference in the biomass texture between the cold reactors and the warm reactors. The biomass from the cold reactors developed a grainy dense floc while the warm reactors developed a filamentous light floc (Figure 15). The dense grainy flocs of the cold reactors made collecting a representative grab sample of the MLVSS difficult as floc size varied greatly within the reactors. While initially the filamentous floc structure of the warm reactors did not present any issues, bulking issues later manifested and a high total suspended solids concentrations in the effluent resulted. The effluent TSS issue will be discussed in detail in Chapter 6.

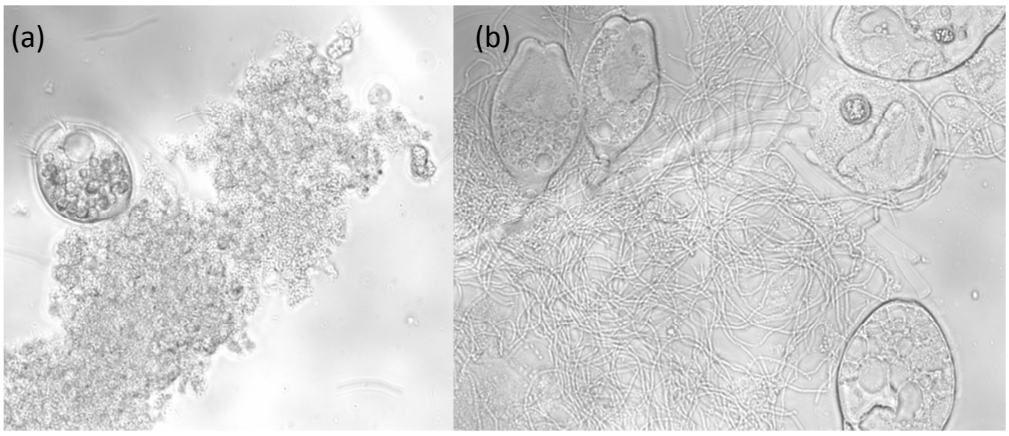


Figure 15. Particulate flocs in cold reactors (a) and filamentous flocs in warm reactors (b) at 100x magnification. Filamentous bacteria led to bulking in the warm reactors

While investigating the potential causes of the filamentous bacteria, the oxygen content throughout one cycle of the reactor was measured. It was noted that at the beginning of the cycle, directly after the previous effluent has been pumped out, the dissolved oxygen content was near 0 mg/L (Figure 16 (a)). This was due to the previous hour long settling period when no aeration occurred. As soon as the effluent pumps shut off, the influent pumps were turned on to dispense a fresh volume of feed into the non-aerated reactors. It was only after the influent pumps turned off that aeration began. This was crucial as the dissolved oxygen concentration in the reactors remained below 1 mg/L during the entire feast phase of the cycle (phase when the COD from the wastewater is consumed by the biomass). Note that the end of the feast phase (corresponding to a stabilization of the soluble COD concentration; data not shown) is marked by the rapid increase in dissolved oxygen concentration 10-15 min after the start of the feed fill period (Figure 16). Consumption of substrate at low dissolved oxygen concentrations is conducive to the growth of filamentous bacteria, which thrive in low oxygen conditions. However, they are undesirable for this project and wastewater treatment in general because they cause bulking problems interfering with solid-liquid separation during the settling phase (Jenkins et al. 2004).

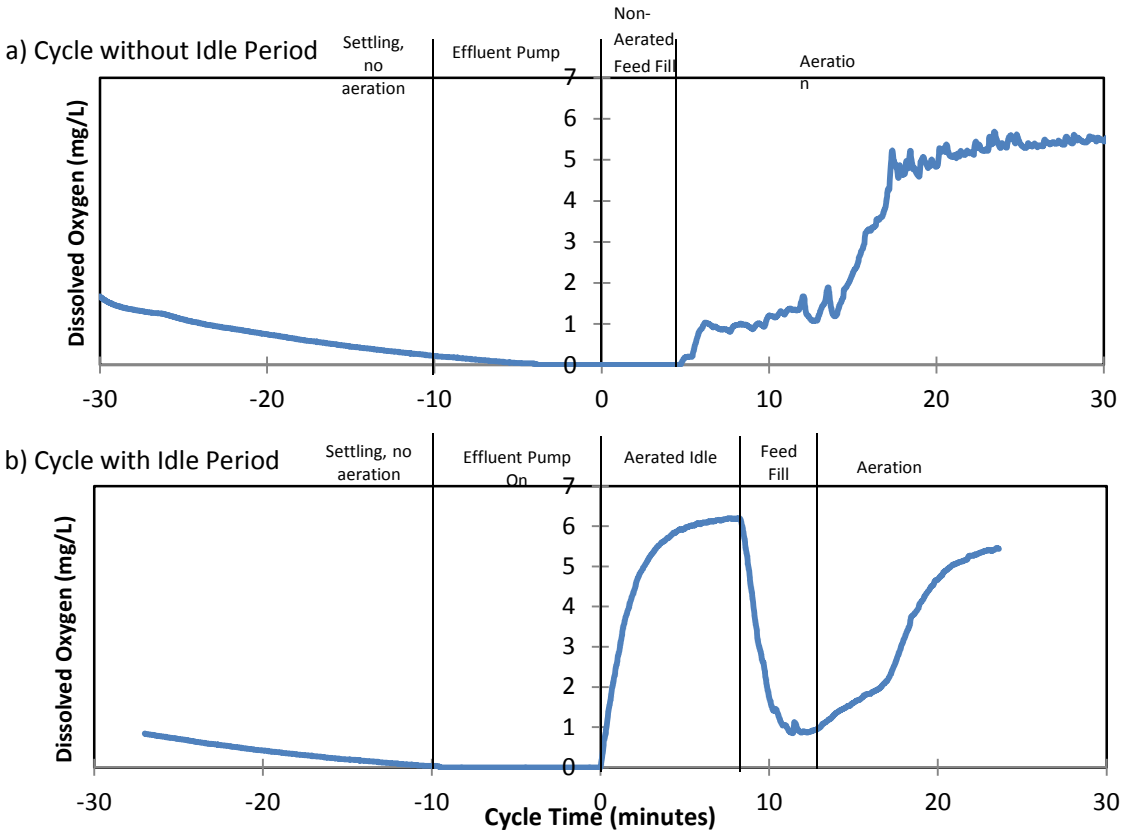


Figure 16. Online dissolved oxygen profiles of a warm reactor (a) before introducing an aerated idle period, and (b) after introducing idle period before the feeding phase. The idle period ensures DO concentrations do not go below 1 mg/L during the feeding phase, which can promote undesirable filamentous bacteria growth.

To correct this problem, the cycle was adjusted to remove this period of low oxygen feeding. In the final design, after the effluent pumps shut off, an 8 minute aerated idle period begins before feed is pumped into the reactors. A follow up cycle analyses of the dissolved oxygen content showed the reoxygenation of the reactor before the feed is added, the expected drop once the feed is added, and the slow increase back to saturation (Figure 16 (b)). Because the dissolved oxygen does not go below 1 mg/L, conditions favor the floc forming bacteria over the filamentous bacteria (Jenkins et al. 2004).

4.3 Biosolids Stabilization

4.3.1 Expected Biomass Concentration

The main objective after decreasing the temperature in the two cold reactors was to achieve the expected MLVSS in the reactors. Using eq. 4 (Rittmann and McCarty 2001)

and with the operational parameters and biological constants from literature, the expected MLVSS in the cold and warm reactors were 2,900 and 3,930 mg VSS/L, respectively. The influent microbial and inert (non-degradable) volatile solids fractions ($X_i{}^0$) were assumed to be 0 mg/L as there is no biomass fraction in the feed recipe, and it is autoclaved.

$$X_v = \frac{\theta_x}{\theta}\left[X_i{}^0 + \frac{Y(S^0-S)(1+(1-f_d)b\theta_x)}{(1+b\theta_x)}\right] \qquad (\mathbf{eq.4})$$

Table 4. List of variables used in eq.4

Notation	Description	Unit	Value
X_v	Volatile suspended solids	mg/L	
θ_x	SRT	day	15
θ	HRT	day	0.5
$X_i{}^0$	Influent inert biomass	mg/L	0
Y	Yield constant	g VSS/ g BOD	0.42*
S^0	Influent COD	mg-COD/L	550
S	Effluent COD	mg-COD/L	30
f_d	Biodegradable fraction	--	0.8*
b	Endogenous-decay coefficient	day^{-1}	0. 15*/0.06**

***Values from (Rittmann and McCarty 2001),**

****Value at 8 °C, used temp correction equation $b_8 = b_{20}(1.07)^{(8-20)}$**

Figure 17 shows the MLVSS levels (X_v) in all reactors before ozonation. The cold reactor averaged 3,400 mg VSS/L from Day −60 to Day 0, while the warm reactors averaged 1,750 mg VSS/L during the same time period. Although every aspect of operation and set up was examined and refined if possible, the biosolids concentrations in the reactors were consistently lower than expected.

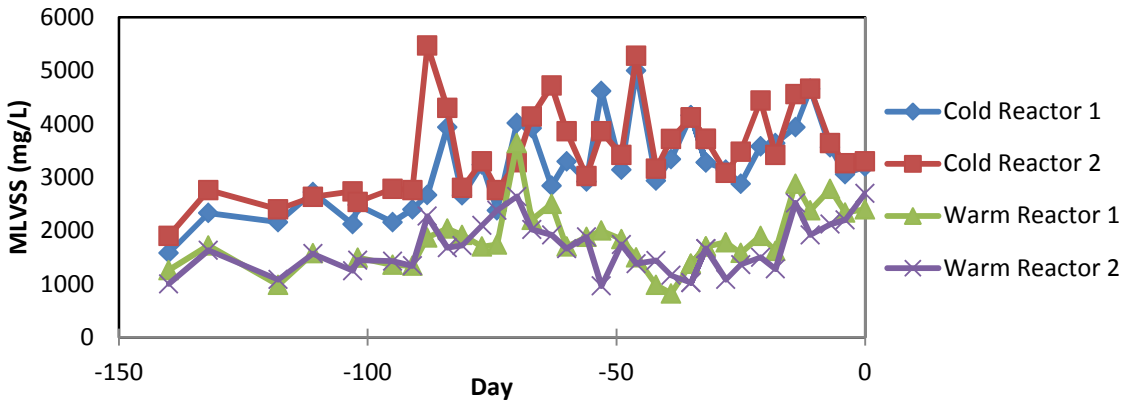


Figure 17. Mixed liquor volatile suspended solids concentration in all reactors 140 days prior to the start-up of ozonation. Temperature pared reactors maintain similar MLVSS concentration, although lower than expected.

It was theorized that the lower biomass concentration could be due, in part, to the small scale of the reactors. Eq. 4 was developed for full-scale basins and does not take into account issues that arise when working with small volumes. For example, the ratio of surface area of the reactor walls to volume is much higher than that of a treatment plant basin. This can affect settling performance as solids can stick and build up against the walls, increasing the solids concentration in the effluent. Also, factors such as decay rate, yield and influent inert biosolid had to be assumed when using eq. 4. Although values used were based in literature from Rittmann and McCarty (2001), there is still a range of possible values. Figure 18 shows the possible variations of the MLVSS concentration when the decay and yield coefficient are changed. With these graphs, the actual MLVSS concentrations in the cold reactors correspond to a decay rate of 0.09 and a yield constant of 0.4, and the warm reactors correspond to a range of combinations. If the decay rate for the cold reactor is corrected to 20 °C, and the yield is held constant at 0.4, the estimated MLVSS concentration in the warm reactor would be 2,500 mg VSS/L, which is still too high. It may be the biomass type in the warm reactors as discussed previously could be contributing to the low mass concentration in those reactors. Regardless of the reason, once the solids concentration stabilized, the main objective was achieved and the project moved into the ozonation phase.

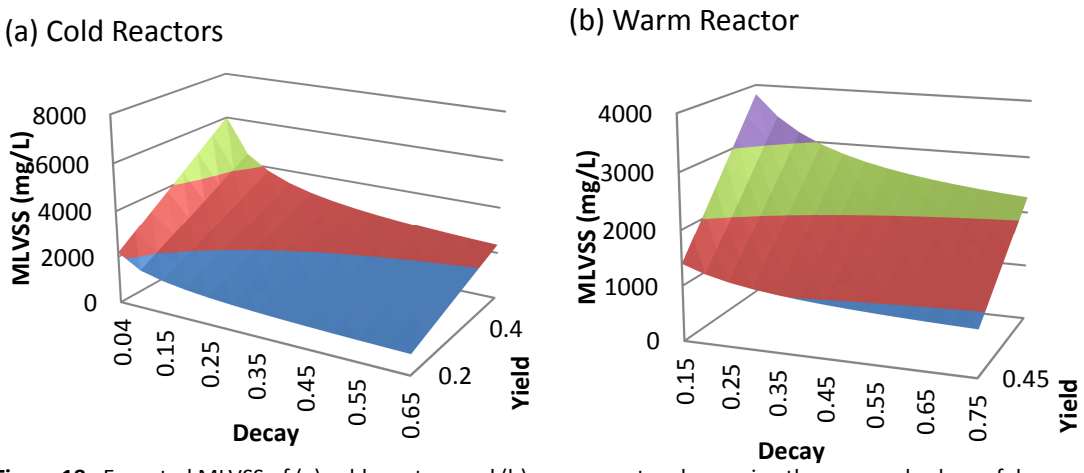


Figure 18. Expected MLVSS of (a) cold reactors and (b) warm reactors by varying the assumed values of decay and yield within the possible range at specific temperature.

4.4 Conclusion

The setup of the reactors went through a number of changes from its initial design to the final setup. Most of these improvements resulted from data generated during operation and from scientific and engineering knowledge. Specific biomass was selected for and certain undesirable bacteria reduced by manipulating the reactor environmental characteristics, such as maintaining the dissolved oxygen at higher concentrations and eliminating light penetration. The system optimization allowed the biomass concentration to reach a steady-state condition, although at a somewhat lower than the expected level, and generate baseline data before ozonation begins.

Chapter 5
Development of Ozonation Procedures

5.1 Introduction

Biosolids reduction by ozonation is a complex process that requires preparation and planning. The objective of this chapter is to show the development of the ozonation protocol used in this project. The development method included both experimental results and calculations to determine both the ozone dose and the waste MLVSS volume to be exposed to ozone, so as to achieve the desired reduction of waste biosolids while still maintaining similar inventory of biosolids mass in the reactors. Since the ozonated biosolids were added back into the reactor over three days, results on the COD and ammonium stability are also presented.

5.2 COD Solubilization Curve and Target Ozone Dose

Wasted mixed liquor collected from paired reactors was mixed and used to determine the COD solubilization curve by ozone for each set of reactors. Figure 19 illustrates the similar behavior of both the warm and cold MLVSS upon exposure to ozone. The resulting curves are made up of a linearly increasing portion, where the ozone dose is directly related to the amount of COD released, and a plateau portion, where no more COD is released despite an increase in ozone dose. The slope of the linear portion, or the solubilization efficiency, was found to be 3.46 g COD/g O_3, which is within the range reported in the literature: 0.7- 9.6 g COD/g O_3 (Labelle et al. 2011) .

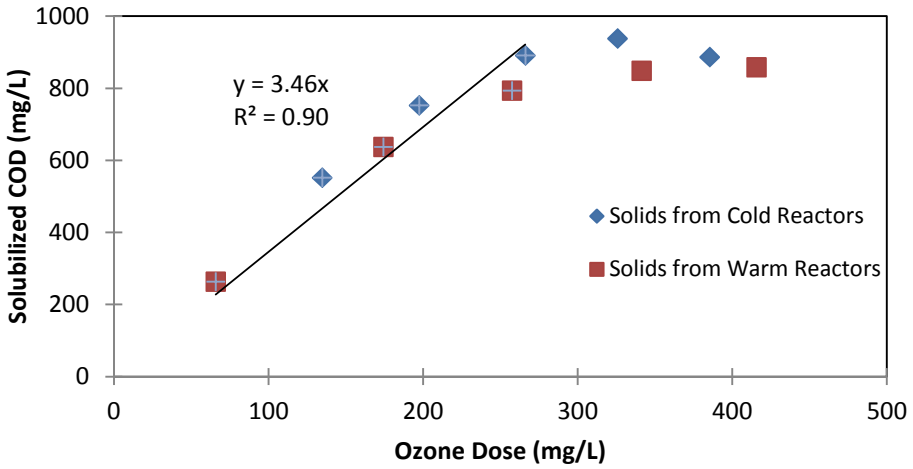


Figure 19. Solubilization curve relating solubilized COD to ozone dose applied to both MLVSS from warm and cold reactors. The relationship is linear until reaching the plateau region, where no more soluble COD is produced despite increasing the ozone dose.

The importance of this curve is to determine the target ozone dose the experimental reactors should receive. While a high ozone dose will release more COD and increase the amount of biosolids reduction achieved, too high of a dose will bring the reaction into the plateau region, which is inefficient. Therefore, the dose chosen for this experiment is an ozone dose of 225 mg/L of ozone, which corresponds to a COD release of about 800 mg/L.

5.3 Adjusting Volume of Wasted Excess Sludge

In order to achieve a significant sludge reduction while maintaining similar biomass inventories between paired reactors, a specific amount of solubilized COD per day must be returned into the experimental reactors. Using literature values for biological constants and predictions from a preliminary model developed (but not calibrated) similar to the one described in Section 3.6, this amount was determined to be approximately 330 mg COD per day that needs to be returned to the reactors to achieve a 40% reduction at 20 °C. This target reduction was chosen because it is large enough to highlight differences in treatment levels, but low enough to be achievable with the constraints of the laboratory-scale ozonation procedure used. It is also the typical target for industrial installations by Air Liquide Canada, the sponsor with NSERC of this research (M. Epiney, Air Liquide Canada, pers. comm.). These calculations were based off an un-calibrated model and assumed values of a number of variables. As such, the level of COD

to be returned to achieve 40% reduction should be considered an initial approximation. The actual reduction achieved will be determined in Chapter 6 and further modeling results will be presented in Chapter 7.

The initial strategy to obtain this COD amount was to continue wasting similar volumes of mixed liquor between the two paired reactors, as in the pre-ozonation stage, except then the portion of biomass required to achieve the reduction in the ozonated reactor would be exposed to ozone and returned back to the reactor. Initial calculations determined that for an SRT of 15 days, 133 mL/day of mixed liquor would need to be wasted from the control reactor. To achieve a 40% sludge reduction, 80 mL/day of mixed liquor would need to be wasted from the experimental reactor, and 53 mL/day would be ozonated and returned to the reactor. With this volume of mixed liquor and the required amount of COD returned per day, ozone would need to solubilize approximately 6,200 mg COD/L, which vastly exceeds the range of data. Since this amount would fall within plateau region of the solubilization curve, it would not be possible to reach this solubilization rate. Therefore, the amount of mixed liquor to be initially removed from the experimental reactors would need to be greater than that of the control. Of this removed sludge, the majority of it would be ozonated and returned back into the reactor, and the net amount of biomass leaving the system would be 40% less than the control. With the maximum possible COD solubilization of around 800 mg COD/L (Figure 19), the amount of mixed liquor to be wasted from the reactors, dosed and returned, was calculated to be 410 mL/day. With the addition of the 80 mL of mixed liquor to be actually wasted per day, the total amount of mixed liquor pumped from the reactors per day was 490 mL.

In order not to shock the system, wasting was slowly increased over three weeks, with greater volumes of mixed liquor being ozonated and returned back to the system each time. Because of the large volume of mixed liquor removed from the reactors each day and the three to four days between ozonation, the wasted biomass was aerated in order to prevent any anaerobic digestion and loss of COD. As well, the wasted mixed liquor

from the cold reactors was kept at cold temperatures by isolating the receiving container with ice packs in coolers.

5.4 Ozonated Sludge Stability

After ozonation the mixed liquor is slowly returned to the reactors over the following three to four days. Because of the necessity of returning a specific amount of COD to the reactors, an experiment was done to determine the stability of the COD and ammonium in the ozonated mixed liquor in different storage conditions. One sample of each ozonated mixed liquor were placed either on the bench at room temperature non-agitated, on an agitated shaker at room temperature, or in the fridge non-agitated, and sampled every day for three days. The results are presented in Figure 20.

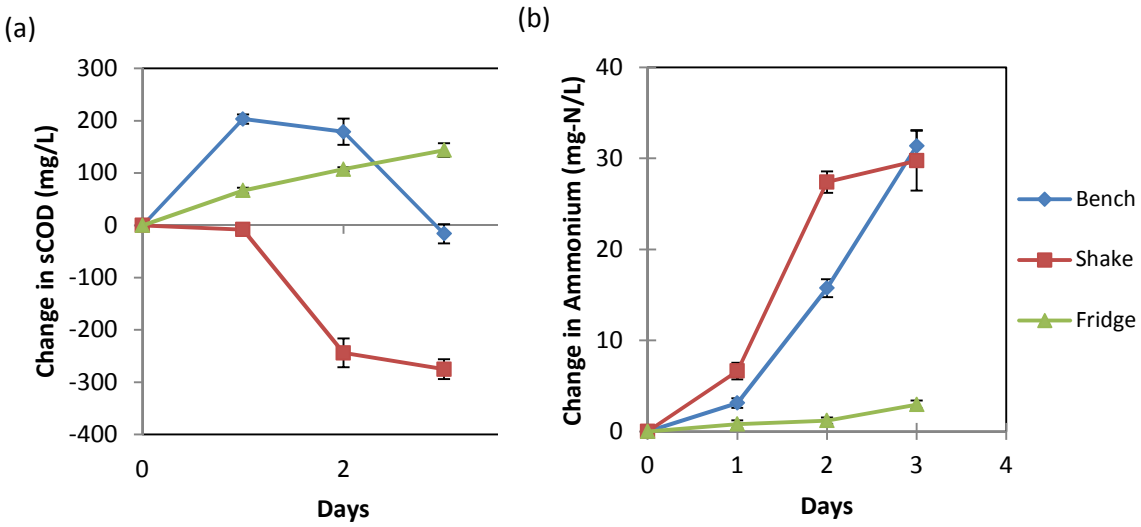


Figure 20. Soluble (s) COD (a) and ammonium concentrations (b) changes in ozonated mixed liquor over time in different storage conditions. Error bars show range of the two replicates. Note that the initial concentrations were adjusted to 0 on the graphs to facilitate comparisons. The initial concentrations were 560 mg sCOD/L and 7.0 mg

Initially, the sCOD increased by 203 mg sCOD/L over the first day in the mixed liquor samples kept on the bench, but a net decrease of 20 mg sCOD/L was observed over the full three days. This drop was more important in the samples incubated on the shaker with a decrease of 275 mg sCOD/L for the three-day period. The only sample with a slow and steady increase in COD is the samples in the fridge with a total increase of 143 sCOD/L for three days (or approximately 48 mg sCOD per day). These increases and decreases in sCOD over time indicate that there are continuing reactions occurring in the

solids over time. The increase seen initially in the bench sample and overall in the fridge sample could indicate continuing chemical reaction initiated by the ozone and releasing COD into the sample. The decrease of COD in the shaken sample and the later part of the bench sample suggests biological degradation of the COD, as typically a portion of microorganisms can be resistant to ozone and survive the ozonation process (Chu et al. 2009a, Paul and Debellefontaine 2007).

In all three samples, there is an increase in ammonium. The samples on the bench and the shaker released similar amounts, 31.5 mg NH_4^+-N/L and 30.0 mg NH_4^+-N /L, respectively, while the sample in the fridge release a small amount of 3 mg NH_4^+-N /L. The lower increase rate in the fridge and the steady increase of ammonium in the warm samples suggest a biological release of ammonium (ammonification) in the ozonated samples. During ozonation, there is a release of organic nitrogen molecules in cell material and the transformation of other non-biodegradable particles, and microorganisms that survive ozonation can transform these molecules into ammonium through hydrolysis.

The significance of these results is that there are continuing chemical and biological reactions occurring in the sludge after ozonation, and the method of storage has a large impact on the concentration of sCOD and ammonium in the samples. Therefore, after ozonation, the sludge was cooled down to 4 °C and maintained at this temperature throughout the 3 to 4 day of dispersion to minimize changes in COD and ammonium.

5.5 Conclusion

With the use of both experimental data and computer modeling, parameters for biosolids reduction with ozonation were developed. The solubilization limit of the system was lower than expected, and it required that the volume of biomass exposed to ozone be greater than the volume wasted in the control reactors. Although this seems counterintuitive, computer modeling predicted a steady-state with the determined numbers and supported this decision. Even after ozonation was complete, changes in COD and ammonium in the solids indicate that there are continuing reactions occurring,

and that further study is needed to understand what happens to ozonated samples over time.

Chapter 6
Reactors with Ozonation

6.1 Introduction

Once a stable MLVSS inventory was achieved in all reactors and a functional ozonation protocol developed, the stage of waste biosolids reduction by ozonation could begin. While the ozonation was being applied to the experimental reactors, three key elements of effluent quality (sCOD, suspended solids, ammonium) were monitored and compared to the control reactor at the same temperature. This chapter presents the biosolids inventories in all reactors and the actual reductions of biosolids achieved once ozonation began, as well as the values of effluent VSS, soluble COD and ammonium removal before and after applying ozone.

6.2 Waste Biosolids Reduction by Ozonation

Figure 21 shows the total biosolids inventories during the ozonation phase from Day 0 to Day 164. Results were monitored throughout operation, and slight adjustments to the solids retention time (SRT) and ozonation/wasting protocol were made in attempts to match biosolids inventories. Although the MLVSS concentrations of the ozonated reactors were consistently lower than the control reactors, there was a large volume of mixed liquor in the wasted/ozonated container. By adding this mass to the mass of solids in the reactor, the inventory of the system can be calculated and gives a better comparison of the biosolids between the control and ozonated reactors. Using the t-test statistical analyses for unpaired data (Ross 2009), the inventories of the cold reactors were determined not to be significantly different from each other ($p = 0.815$) over the presented time period (Figure 22). Due to the bulking issues that arose throughout operation in the warm reactors and since this issue was resolved in each reactor at different times, the results from the statistical analysis are skewed due to these experimental issues. Therefore, it is expected that the inventories were significantly different ($p = 0.004$) over the same time period. When comparing the average

difference before and after the commencement of ozonation, the cold reactors differ by 5% before ozonation and only 1% after ozonation. The warm reactors differ 8% before ozonation and 12% after. All the percent differences are below 20%, which is considered an acceptable level for experimental purposes. This comparison better describes the relation between the two paired reactors, as the paired t-test states the warm reactors are significantly different during ozonation due to the ozone reactor having a slight but consistently higher inventory than the control.

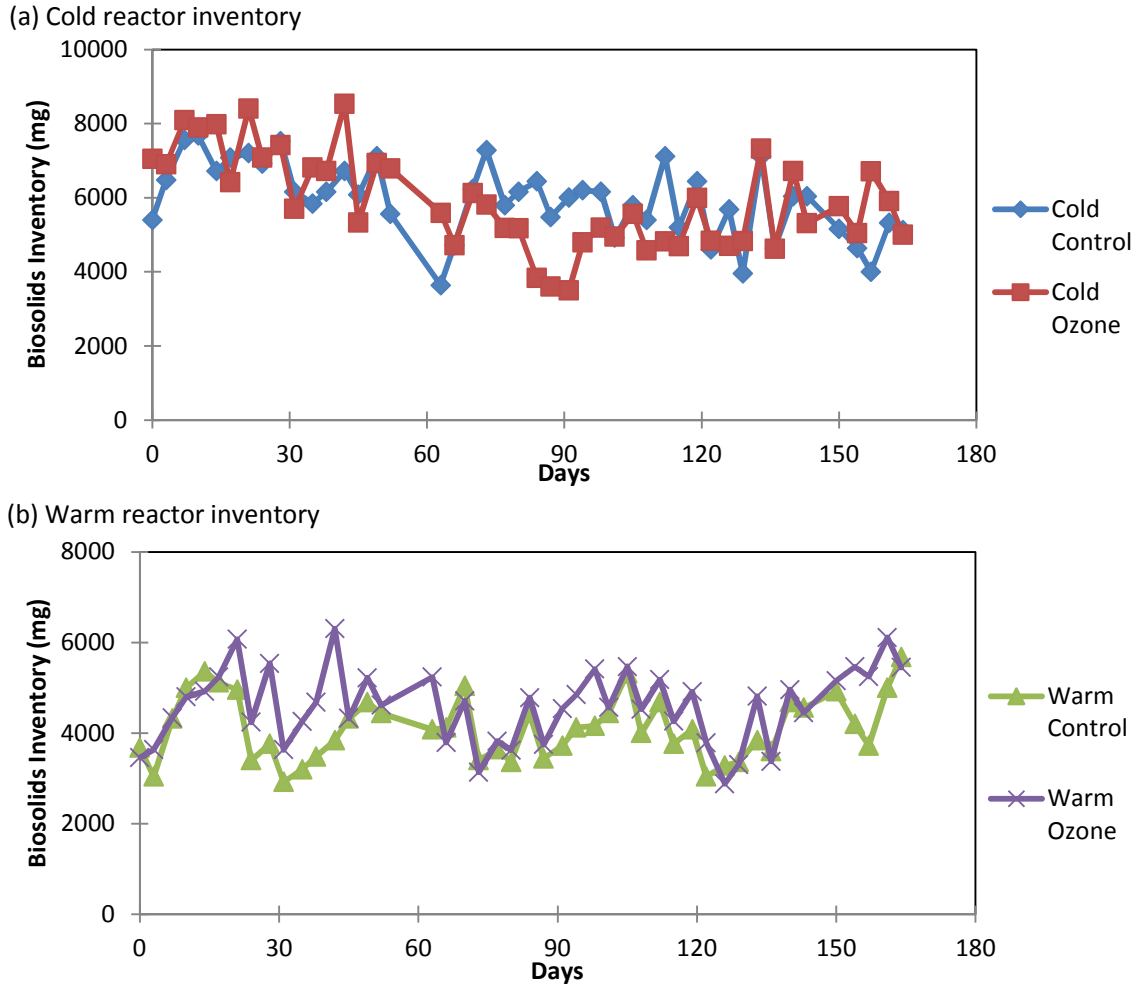


Figure 21. Total biosolids inventory in (a) cold reactors and (b) in warm reactors once ozonation began.

Because of the volume of the returned biomass and the lower net wasted biomass, the SRT of the ozonated reactors would be higher than the controls. With a biosolids reduction target of 40%, the SRT of the ozonated reactors would also be 40% higher;

therefore, a SRT target of 15 days for the controls would lead to a SRT of 21 days in the ozonated reactors. The actual SRT was measured by calculating a mass balance of the biomass around the reactors each day. This also includes the large return ozonated biomass volume for the ozonated reactors. As there is no control on the amount of biomass leaving the system in the effluent, the WAS volume is the only controllable factor in SRT maintenance. Therefore, a dynamic wasting schedule was adopted utilizing the most up to date solids data to control SRTs. As the wasting of the reactors was adjusted periodically, the resulting SRTs were not always at the targets of 15 and 21 days. Figure 22 shows the respective average inventories and SRTs of the reactors before ozonation (Day −140 to Day 0) and after ozonation began (Day 0 to Day 195).

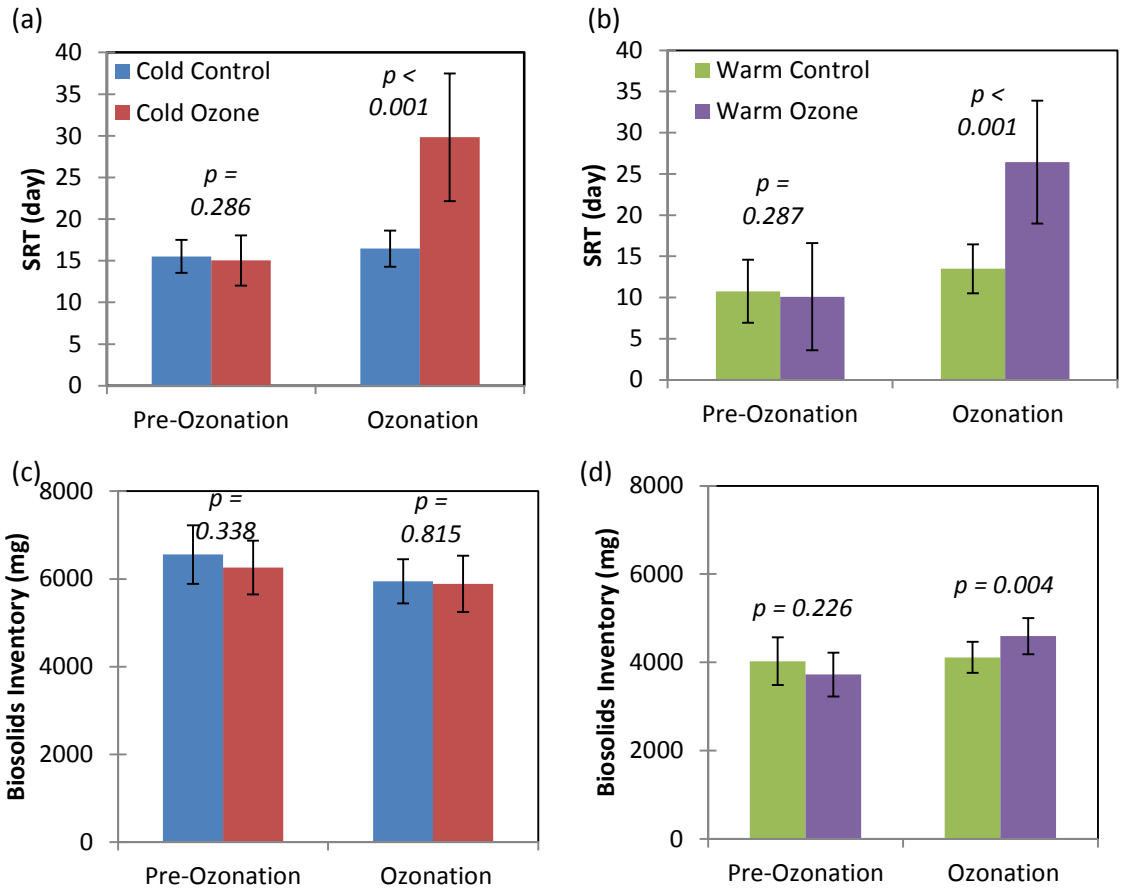


Figure 22. Average solids retention times (SRTs) in (a) cold reactors and (b) warm reactors and average inventories in (c) cold reactors and (d) warm reactors before and after beginning ozonation. Error bars represent the observed standard deviation and the probability of no difference between control and ozonated reactors' averages using an unpaired t-test are reported above the bar pairs.

Even with the dynamic wasting schedule, the actual average SRTs were higher than the expected SRTs, specifically 29.8 and 26.4 days for the cold and warm reactors, respectively. By assuming similar inventories and directly comparing the SRTs, the waste biosolids reduction can be calculated as 45% and 49% for the cold and warm reactors respectively. But as noted above, the warm reactors inventories were not always statistically the same, and there are variations in inventory in the cold reactors as well. So to account for this variation, each SRT calculated during the above time period is normalized by the inventory at that time and compared to its pair. Using this method, the average reduction accounting inventory variation is 45% and 43% for the cold and warm reactors. With both methods, the reduction is slightly higher than the expected 40%, although satisfactorily in its vicinity. The discrepancy is unsurprising as the technique used to calculate the volumes and ozone dose in Chapter 5 was based on an un-calibrated model with a number of variables assumed. It is also commonly observed that the suspended solids biomass floc structure will adapt to ozone after prolonged exposure, and treatment levels will change over time (Dytczak and Oleszkiewicz 2008).

During the ozonation process, the dose was constantly monitored and adjusted throughout in order to maintain the target 225 mg O_3/L dose. Although this dose was constant throughout the run of the experiment, the mass of solubilized COD generated during the ozonation process varied by day and by reactor (Figure 23(a)). This mass of sCOD is the change in soluble sCOD of the wasted biosolids before and after the ozonation process. The mass of sCOD generated can be normalized by the inventory (in mg COD) to generate the ratio $q_{Xtot,O3,sol}$, (Figure 23 (b)) as described in section 2.7. According to the unpaired t-test, the difference between the two reactors for both variables is not significantly different (p=0.119 and 0.498). This contrasts with observations made in the other cold temperature ozone study which found doubling the dose was necessary when operation temperature dropped from 15 to 10 °C to maintain constant reduction (Lee et al. 2005). This also contrasts with a sensitivity analyses on models of the ozonation process which states temperature as a significant parameter for sludge reduction (Isazadeh et al. in prep). However, it may be that temperature

sensitivity is hard to observe experimentally, especially with highly degradable substrate. Also, although it appears that temperature does not seem to have a significant effect on the ozonation process, the batch protocol used during this experiment allows the cold mixed liquor to warm up to room temperature before being ozonated, reducing any temperature effects during the actual ozonation of the biosolids. Therefore, the main difference during ozonation between reactors is the biomass and floc structure as reported in Chapter 4. Note that both ozonated mixed liquors are cooled before being returned to the reactors to stabilize the sCOD over time as discussed in Chapter 5.

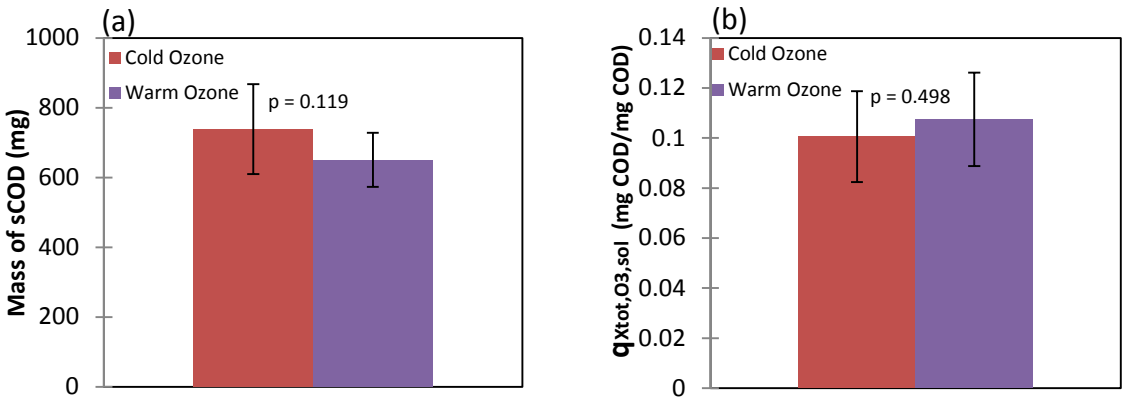


Figure 23. Average mass of solubilized COD generated by ozonation in both reactors (a) and the average ratio of the mass of the sCOD/mass of solids inventory. Error bars represent the observed standard deviation and the probability of no difference between control and ozonated reactors' averages using an unpaired t-test are reported above the bar pairs.

6.3 Effluent Quality

6.3.1 Effluent Soluble COD Concentrations

COD levels in the Syntho feed were maintained around 550 mg COD/L, with the majority (>95%) being soluble COD. In the pre-ozonation stage (Day -140 to 0), effluent soluble COD in all reactors were consistently below 30 mg sCOD/L, corresponding to 94.5% removal. Heterotrophic bacteria are quite resilient and adapt quickly to changes in environmental conditions, which is why COD removal is rarely effected by changes in operation or environmental conditions. For this project, the heterotrophic bacteria easily adapted to cold temperature, the ozonation and the resulting extra soluble COD entering the system. However, once ozonation was introduced to the experimental reactors, there was a slight increase in average soluble COD in the effluent shown in

Figure 24 representing data from Day 0 to 180. Using the t-test statistical analysis for unpaired data, the differences between the control and ozonated reactors is significant ($p < 0.001$). This is a common result found in many other studies (Lee et al. 2005, Salhi et al. 2003, Yan et al. 2009, Zhang et al. 2009) and is attributed to the increase of non-biodegradable soluble COD from cell material released due to ozonation.

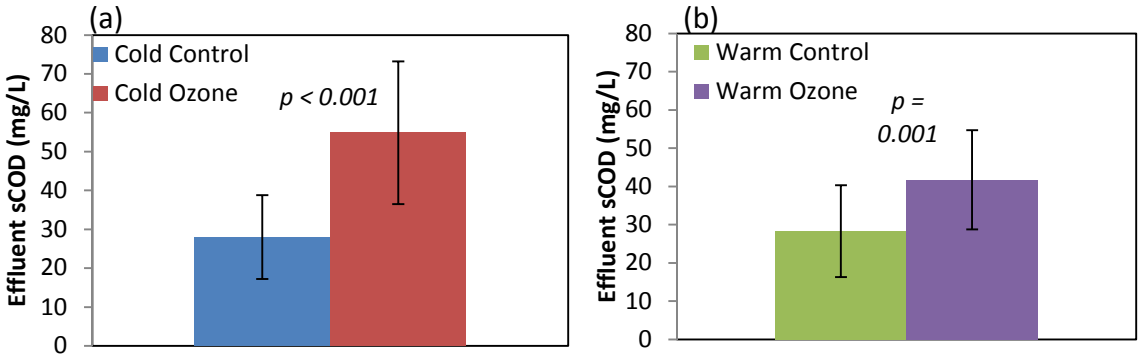


Figure 24. Average effluent soluble COD during ozonation in (a) cold reactors and (b) warm reactors. Error bars represent the standard deviation and the probability from t-test statistical analysis for unpaired data. There is an increase in sCOD in both ozonated reactors during the ozonation period, which is a commonly observed effect.

6.3.2 Effluent TSS Concentration and Bulking

While initially the filamentous floc structure of the warm reactors discussed in Chapter 4 did not present any issue in operation, bulking caused by filamentous bacteria was observed on Day 70 before ozonation began. The concentration of biomass in the effluent in the warm reactor went from below 50 mg VSS/L to over 200 mg VSS/L (Figure 25), even after the addition of the idle period to the cycle. During this time, the sludge blanket in both reactors did not settle below the effluent intake pipe after one hour of settling, resulting in high biomass concentrations in the effluent. Because of the mass of solids leaving the system, there was a significant decrease in the SRTs, and SRTs of 1-5 days were observed during periods of high effluent biomass concentration.

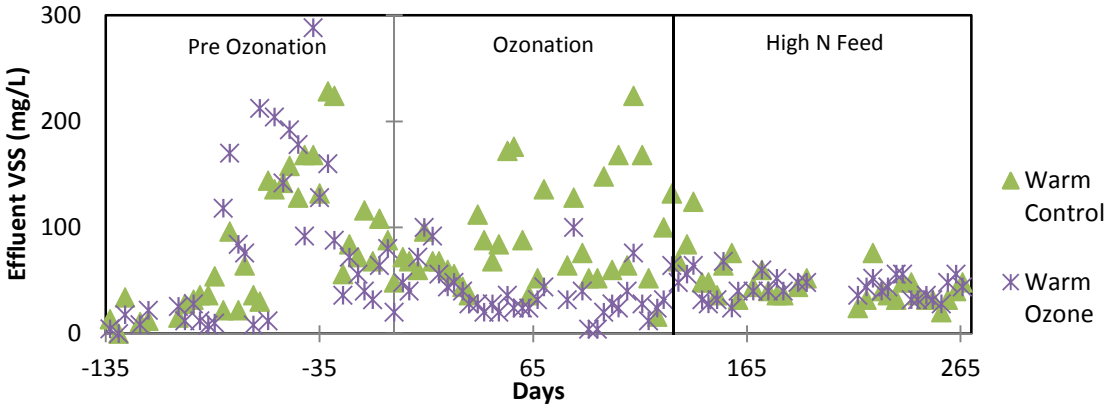


Figure 25. Effluent biomass concentration in warm reactors before and after ozonation began, and when high nitrogen feed was introduced. High levels of biomass in the effluent were caused by bulking due to filamentous bacteria. Levels dropped in the ozonated reactor once ozonation began and then in the control reactor once the nitrogen levels in the feed were increased.

Initially bulking was controlled by dosing small amounts of chlorine bleach into both reactors at a dose of 5 mg Cl_2/mg VSS as suggested by Foladori et al. (2010). However, chlorination was an undesirable long term method of bulking control, as it adds another oxidizing chemical to the system and it only treats the symptom and not the cause of the bulking. Bulking continued in both reactors in varying degrees until ozonation began on Day 0, after which the effluent biomass concentrations in the ozonated reactor dropped below 50 mg VSS/L on average. Because of its long filamentous cell shape with more surface area than floc-forming bacteria, the ozone will first attack the filamentous bacteria. This is the likely explanation for the reduction in bulking upon the start of ozonation. This is why ozone technology has been used in full-scale treatment plants for bulking control exclusively (Böhler and Siegrist 2004). Although bulking was controlled in the ozonated reactor, the issue still persisted in the control reactor.

The main conditions that support the growth of filamentous bacteria are low dissolved oxygen content, nutrient deficiencies and low food to microorganism (F/M) ratio (Rittmann and McCarty 2001). Filamentous bacteria also proliferate less in cold temperatures (Jenkins et al. 2004), which could explain the lack of bulking in the cold reactors. The first two causes were ruled out as the dissolved oxygen never reached below 1 mg/L with the new cycle, and the F/M ratio is always much higher (0.57-1.46) than the suggested limit of 0.4 (Chua et al. 2000). Therefore, the nutrient requirements

were further investigated. Prior to Day 130, the TKN of the feed was 16.25 mg N/L. Using the nutrient requirement data from Rittmann and McCarty (2001) and the measured MLVSS inventories, the estimated nitrogen requirement just for cell growth in the warm reactors was around 12 mg N/L. Therefore, the nitrogen in this feed recipe was only just sufficient and could be the cause of the bulking bacteria. The TKN of the feed was adjusted on Day 130 from 16.25 to 44.5 mg N/L, a more typical concentration for municipal wastewater. This increase was achieved by increasing the urea concentration as it would be the most common nitrogen source (Sedlak 1991) for municipal wastewater.

After one week at the high nitrogen concentration, a noticeable decrease in bulking and effluent VSS concentrations (Figure 25) was observed for the warm control reactor. Once the new feed was introduced on Day 130, the effluent biomass of the warm control reactor began to drop to below 50 mg/L, similar to the ozonated reactor. With this change in TKN in the feed, the MLVSS in all reactors slightly increased after Day 130: 34% and 12% in the cold control and cold ozone reactor, respectively; and 17% and 12%, in the warm control and ozone reactor, respectively.

6.3.3 Effluent Ammonium Concentrations

During the pre-ozonation stage, ammonium removal in all reactors reached 100%, although there was a significant adaptation period for the cold reactors to the initial drop in temperature. As such, when exposing the experimental reactors to ozonated biomass, it created a challenging environment for the nitrifiers, even when there is no temperature change. Figure 26 (a) shows the effluent ammonium concentration once ozonation began until the increase in nitrogen in the feed on Day 130. As ozonation began, the ammonium removal in both ozone reactors deteriorated, but while nitrification in the warm ozone reactor was able to recover within a month, full nitrification did not return in the cold ozone reactors.

At around Day 75, a break in ozonation due to equipment failure occurred, and wasting volumes for the ozonated reactors were returned to pre-ozonation levels for one week.

During this time, effluent ammonium in the cold ozonated reactors reached near zero levels. Once ozonation commenced and wasting volumes increased again, ammonium levels in the cold ozonated reactor returned to the high pre-failure levels. This indicates that the microorganisms capable of cold temperature nitrification are still present in the reactors, but are inhibited due to the enhanced mortality caused by the ozonation process.

Despite the many positive effects of increasing the level of nitrogen in the feed, such as reduced bulking and increased MLVSS, this increase had a very significant and detrimental effect on nitrification in both cold reactors. Figure 26 (b) shows effluent ammonium in all reactors after the change in feed. While the warm reactors quickly adapted to the increase in nitrogen, the ammonium levels in the cold reactors remained high. While the cold control reactor maintained a consistently lower effluent ammonium concentration compared to the ozonated reactor, it is most likely due to the higher MLVSS in the control reactor and the expectedly larger nutrient uptake by the heterotrophic bacteria. Although, a substantial adaptation time was expected for the nitrifiers to the higher nitrogen because of the low temperature, particularly in the ozonated reactor, neither reactor shows a substantial increase in nitrification after two months.

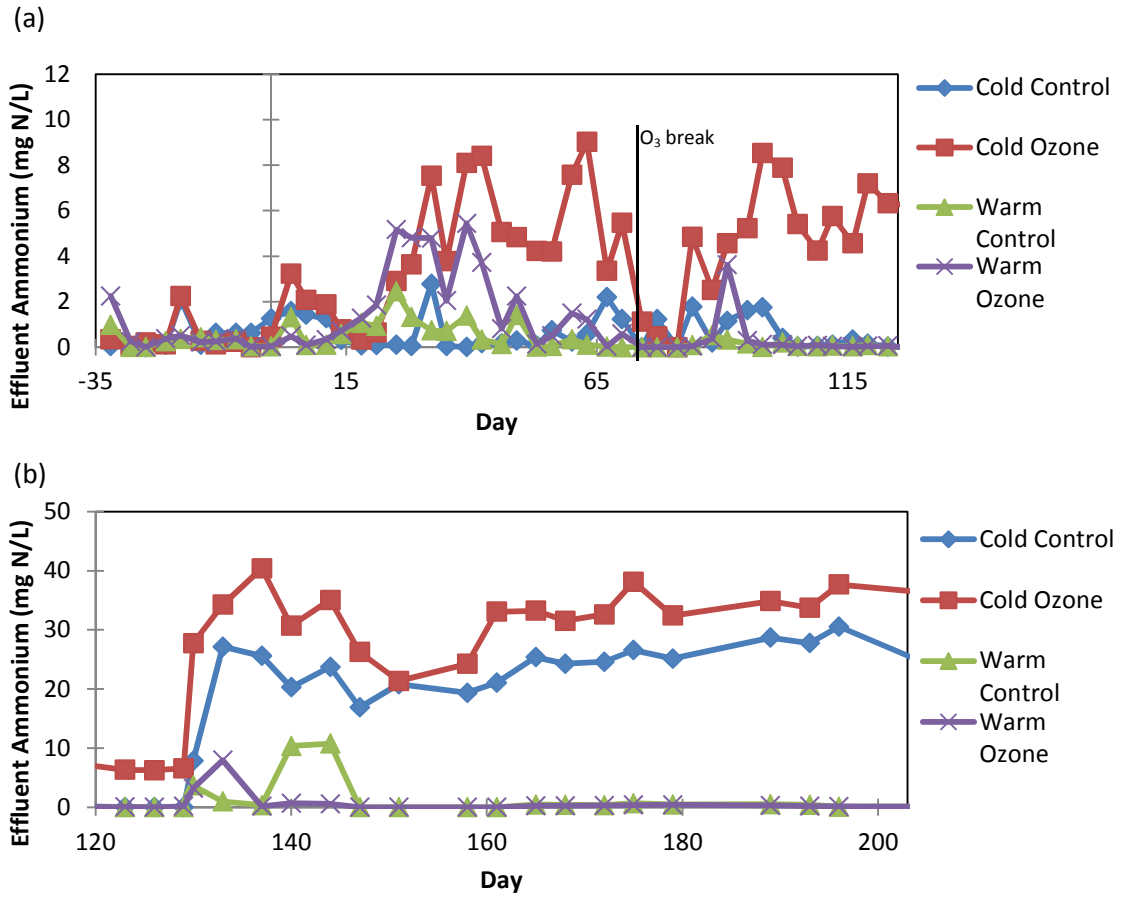


Figure 26. Effluent ammonium during ozonation at (a) low nitrogen level feed and (b) at high nitrogen level feed. Full nitrification was achieved in three of the four reactors at low nitrogen levels, but both cold reactors experienced a loss of nitrification at high nitrogen levels. Note the difference in scale of the effluent ammonium between the low and high nitrogen levels.

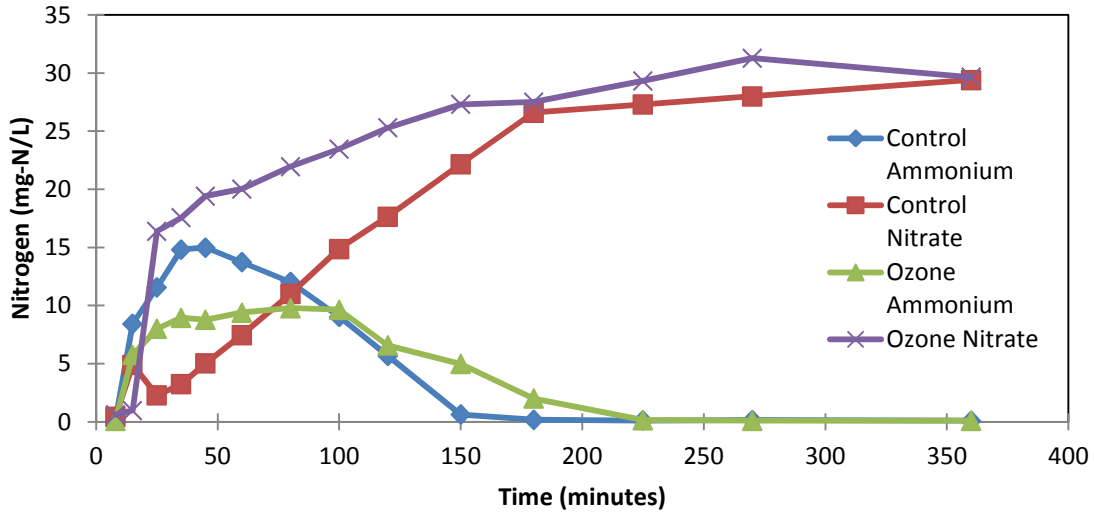
6.3.3.1 Nitrogen Species Cycle Analyses

Nitrification was further investigated in both the warm and cold reactors 30 days after increasing the nitrogen in the feed on Day 160 by measuring ammonium, nitrate and nitrite present throughout one cycle of the reactors. In both instances nitrite was measured and found to be near or below detection level throughout the cycle, and thus it was not included in the following figures. The low nitrite levels confirm that there is no nitrite build up during the cycle that could have inhibited nitrification.

Figure 27 (a) illustrates the conversion of nitrogen species in the warm reactors throughout one cycle. In both the control and ozonated reactor, the ammonium concentration increases during the first hour of the cycle, then is completely converted by Minute 225. This increase in ammonium in the first hour corresponds to the

conversion of the organic nitrogen, such as urea, in the feed into ammonium. As the ammonium is oxidized, there is a steady increase of nitrate produced from the nitrification process. As expected, the nitrate plateaus as the ammonium is completely oxidized. These results are typical of a well performing reactor and correspond to the low levels of effluent ammonium in both warm reactors.

(a) Warm reactor nitrogen species



(b) Cold reactor nitrogen species

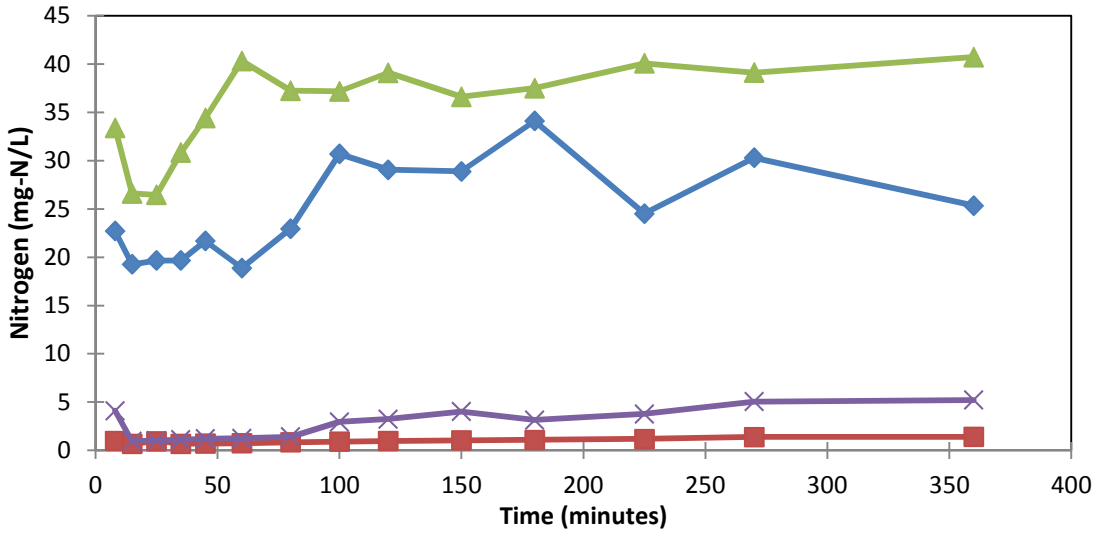


Figure 27. Nitrogen species over one cycle length in (a) the warm reactors, and (b) in the cold reactors on Day 160, 30 days after increasing nitrogen in the feed. Full nitrification can be observed in the warm reactors as all the ammonium is transformed to nitrate, but not in the cold reactors where the ammonium levels remain consistent.

In the cold reactors, the nitrification process is not as complete as in the warm reactors. In Figure 27 (b), an increase in ammonium concentration corresponding to the transformation of the organic nitrogen is observed, but unlike in the warm reactors, there is very little decrease in ammonium concentration over the cycle length. Because of this absence of nitrification in the cycle, the ammonium concentration remains high in the reactor after the effluent is removed, leading to the high levels seen at time zero. Nitrate levels in the cold reactors remain low, but there is a noticeable increase at the end of the cycle, indicating that some nitrification is occurring. These results do not indicate any inhibition or any other unexpected reactions occurring during the cycle that could be contributing to the loss of nitrification. The lack of complete nitrification in the cold reactors remains puzzling as a number of studies have achieved nitrification at this temperature (Komorowska-Kaufman et al. 2006, Oleszkiewicz and Berquist 1988, Shammas 1986). Komorowska-Kaufman et al. (2006) also achieved nitrification at low temperature, but found it was only stable at a COD/N ratio of 4 or lower. With a feed COD of 550 mg/L, the ratio in the cold reactors is 12, which could explain the lack of nitrification. So according to this research, nitrification could be improved by decreasing the COD or increasing the nitrogen. Regardless, further studies need to be conducted to fully understand the loss of nitrification in the cold reactors.

6.4 Conclusion

A stable biosolid inventory was achieved with biosolid reduction of 40% at both cold and warm temperatures. In addition to reducing the amount of biomass discarded, ozonation had other beneficial effects, such as bulking reduction in the warm reactor. There was a slight increase in effluent soluble COD at both temperature when ozonation was applied. However, nitrification at low temperatures becomes unstable once the ozonation process begins. Even with low nitrogen levels, full nitrification did not occur in the cold ozonated reactor within 4 months. This indicates that with ozonation at low temperatures and high COD/N ratio, the conditions are adverse for nitrifier growth, and nitrification is unstable. When the nitrogen levels are further increased, full nitrification is lost almost completely in both cold reactors and do not return within 2.5 months.

Since this loss is seen in both cold reactors and there is no inhibing nitrite build-up in the reactors, it can be concluded that it is due to other factors, such as the cold temperatures, and not just ozonation.

Chapter 7
Preliminary Model Simulations

7.1 Introduction

Since biosolids ozonation is still a relatively new technology, plant operators need to be convinced of its benefits before deciding to use it. A calibrated model of a treatment plant is a powerful tool for predicting performances, and current research is perfecting a model of the ozonation processes that can be used to demonstrate possible biosolids reduction and changes to effluent by implementing this technology. The benefit of these simulations is the ability to easily change the virtual environment to estimate conditions that could achieve the treatment and waste biosolids reduction goals. As every plant is different, a single model cannot be used for multiple locations without modification. But once calibration data is imputed, accurate simulations can be run for the range of temperatures and conditions experienced in Canadian treatment plants to determine accurate reduction rates.

This chapter presents model simulations of the sequencing batch reactors' operation data for the cold temperature using the International Water Association-Activated Sludge Model 3 (IWA-ASM3) (Gujer et al. 1999) and a previously developed extension describing the reactions of biosolids with ozone (Frigon and Isazadeh 2011, Isazadeh et al. *submitted* 2013). The main objectives of the modeling exercise are (1) to develop the proper physical layout description/abstraction and (2) to calibrate the model for the use of the synthetic wastewater Syntho. To simplify this process, only data from Day 30 to Day 130 were used for calibration, corresponding to the steady-state period with low nitrogen concentration in the feed. The main focus of the simulation was to capture the inventory and the soluble COD concentration in the effluent of both the cold control and ozone reactors. With the current available data, it was impossible to calibrate for the effluent ammonium concentrations, but still remains an available avenue for future work.

7.2 Approach and Methodology

The model is composed of a series of interacting COD mass balances that are used to calculate the dynamic results based on a number of imputed values. The model normalizes many of the parameters such as biomass as g-COD/m^3 in the calculations. In fact, the models are over parameterized, allowing for a number of assumptions to simplify calibration, such as holding biological parameters constant. This was the approach used in this model calibration. Laboratory data were imputed and the COD fractioning was adjusted to match the measured observations.

Laboratory data imputed in the model include the measured influent COD levels, the calculated SRTs of both the control and ozonated reactors, and the calculated relative COD solubilisation rate ($q_{Xtot,O3,sol}$) value. The first parameters calibrated were the COD fractions of the influent, which were compared to the measured inventory and effluent soluble COD of the control reactor. Once these were satisfactory, the COD fractions resulting from the ozone reaction parameters were calibrated to adjust the simulated and observed inventory and effluent soluble COD in the ozonated reactor. For simplicity, the non-biomass transformation rate constant and the biomass inactivation rate constant were considered equal and calculated according to eq. 1. Detailed description can be found in section 3.6.

7.3 Calibration Results

In the following results and simulation Day 30 and Day 130 in the general time line presented in Figure 1, corresponds to Day 0 and Day 100 of the simulation timeline.

The initial parameter calibrated was the total inventory and soluble COD in the control reactor. Once the actual SRT and influent COD were put into the model, the influent COD fractions (Table 5. Calibrated model parameters.) were adjusted to obtain the results presented in Figure 28. Unsurprisingly since the feed was synthetic and specifically designed, it had a high fraction of biodegradable COD, with only 10% of the total COD being undegradable. The average overall trend across the time period for the total biosolids inventory and soluble COD in the control reactor is captured satisfactorily

with a root mean square error (and % error compared to average of that time period) of 1300 mg/L (15%) and 8.65 mg/L (30%), respectively. The ozonated reactor was then calibrated using the ozonation reaction parameters to capture the trend of the total biosolids inventory and soluble COD (Figure 29) with a root mean square error (and % error compared to average of that time period of 2100 mg/L (25%) and 6.15 mg/L (11%), respectively. As reported in previous sections of this report, there was a week period in which ozonation was halted due to equipment malfunction that corresponds to Days 42-48 in simulation. To represent this, the relative COD solubilisation rate ($q_{Xtot,O3,sol}$) value for that time was set to zero and the SRT lowered. The higher variation in the measured biosolids inventory data in the ozonated reactor corresponds to the higher root mean square error of the model than in the control reactor. As with the feed fractions, the ozonation process produced a high percent of biodegradable COD with only 7% being undegradable and 4% being completely oxidized.

Not only do these results show a good description of COD fractioning, but it also indicates a good model representation of the waste/ozonated biosolids return system of the ozonated reactors. Because the model describes the wasting and return of the large volume of ozonated mixed liquor as a continuous process, it was imperative that SRT and volumes were as accurate as possible.

Table 5. Calibrated model parameters.

Parameter	Unit	Lab Value
Influent COD fractions		
Soluble biodegradable organics (f_{SB})	g-COD_{SB}/ g-COD_{total}	0.500
Soluble undegradable organics (f_{Su})	g-COD_{SU}.m^{-3}	0.065
Particulate undegradable organics (f_{XU})	g-COD_{XU}.m^{-3}	0.035
Particulate biodegradable organics(f_{XCB})	g-COD_{XCB}.m^{-3}	0.400
Ordinary heterotrophic organisms (f_{XOHO})	g-COD_{XOHO}.m^{-3}	0
RAS-ozonation fractions		
Soluble undegradable COD ($f_{SU\_O3\ trans}$)	g-COD_{SU}.g-COD_X^{-1}	0.070
Soluble biodegradable COD ($f_{SB\_O3\ trans}$)	g-COD_{SB}.g-COD_X^{-1}	0.550
Particulate biodegradable COD ($f_{XCB,O3\ trans}$)	g-COD_{XCB}.g-COD_X^{-1}	0.340
Oxidized COD ($f_{mnr,O3}$)	g-COD_{mnr}.g-COD_X^{-1}	0.040

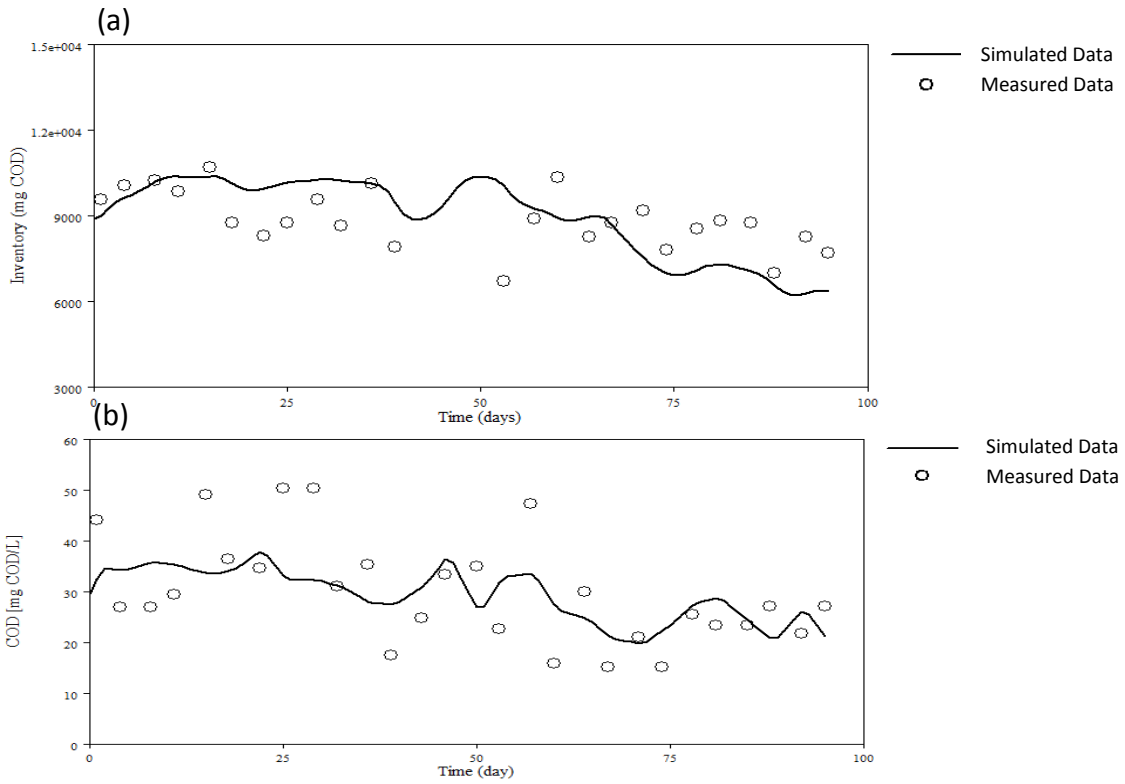


Figure 28. Calibration results of the cold control reactor of (a) total biosolids inventory and (b) effluent soluble COD. All results are presented in COD units.

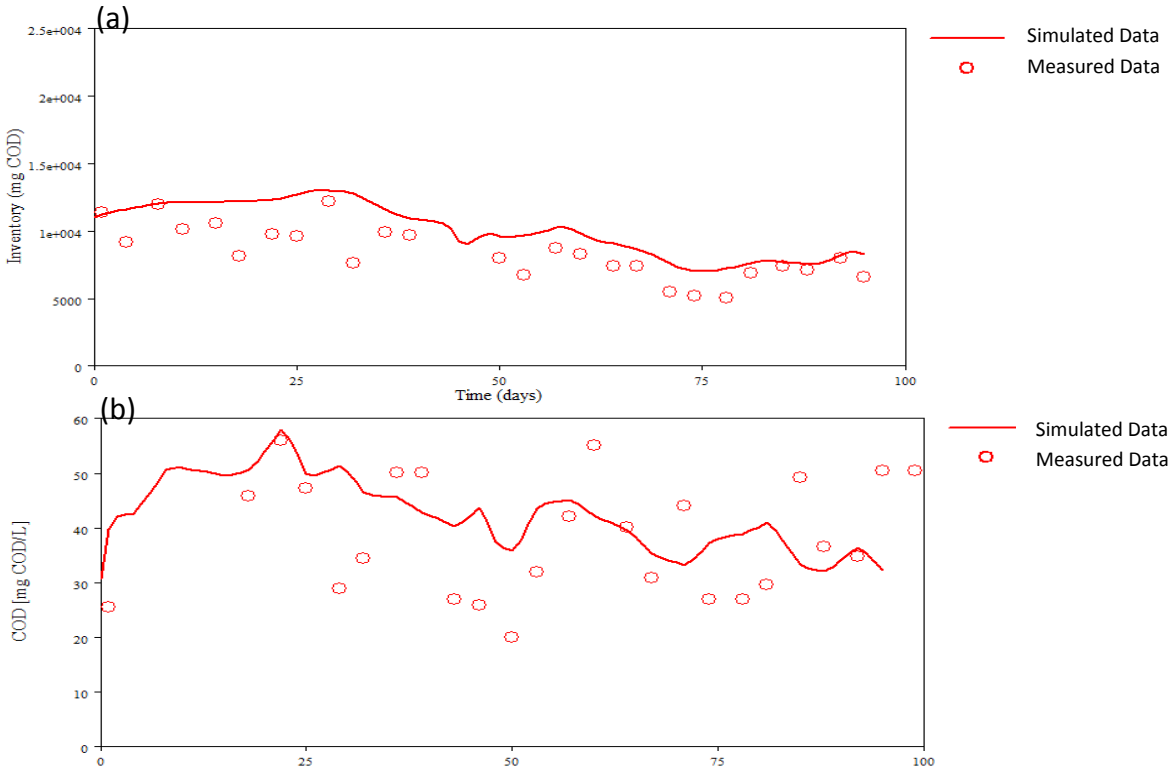


Figure 29. Calibration results of the cold ozonated reactor of (a) total biosolids inventory and (b) effluent soluble COD. All results are presented in COD units.

7.3.1 Effluent Ammonium

Although the nitrification process is the focus of much of the work done in this report, capturing the measured results in simulation remains challenging. With no additional calibration than what was reported previously, the model predicts full nitrification in both the control and ozonated reactor for the first half of the time period, and then under 5 mg N/L for the later time period for the ozonated reactor. In reality, ammonium remained higher in the ozonated reactor as shown as points in Figure 30 and near zero in the control. This discrepancy between the model prediction and the observations demonstrates that the model is incomplete and requires further calibration in order to accurately predict nitrification.

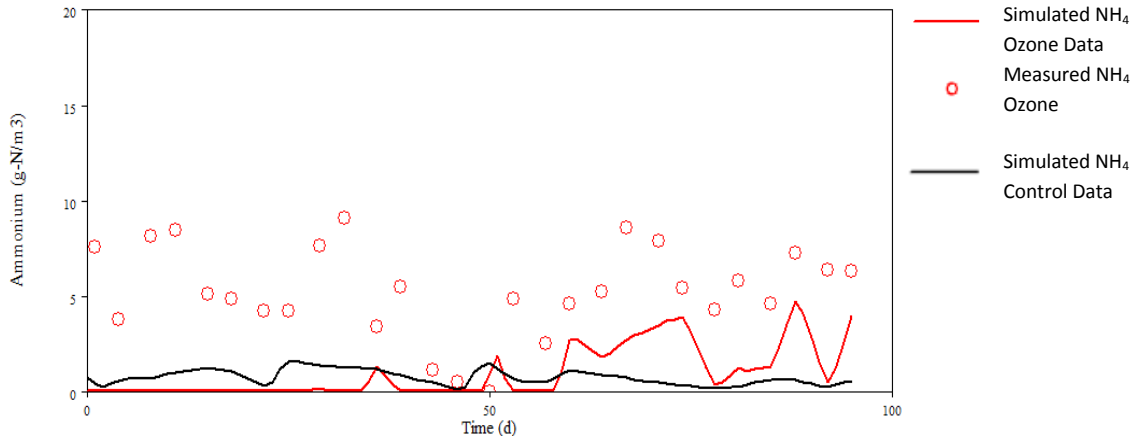


Figure 30. Uncalibrated effluent ammonium simulated results for the cold control and ozonated reactors. Lab results of the control reactor remained near zero, while measured ozonated reactor data is presented as points on graph

7.4 Discussion

The synthetic influent Syntho has been used in a number of studies for wastewater treatment, but its *influent* COD fractioning is only mentioned in one of the original papers on its development (Boeije et al. 1999). Although the recipe of the feed is known, how the bacteria consume the COD is open to interpretation. Acetate is well known for being a soluble biodegradable organic, but other compounds such as the starch and beef extract are less defined. Yet, this paper describes the Syntho COD fractions using ASM2, and so is not directly translatable to fractions for the ASM3 model used in this study because of differences in model structures. Although ASM2 fractions

the COD differently, it still describes high amounts of biodegradable particulate matter and soluble substrates, which is similar to the calibrated ASM3 fractions (Rottiers et al. 1999).

Table 6. Comparison of COD fractions

Parameter	Syntho/Lab-scale study values	Real Wastewater /Pilot-scale study values*
Influent COD fractions		
Soluble biodegradable organics (f_{SB})	0.500	0.39 ± 0.04
Soluble undegradable organics (f_{Su})	0.065	0.05 ± 0.02
Particulate undegradable organics (f_{XU})	0.035	0.25 ± 0.03
Particulate biodegradable organics (f_{XCB})	0.400	0.31 ± 0.06
Ordinary heterotrophic organisms (f_{XOHO})	0	0
RAS-ozonation fractions		
Soluble undegradable COD ($f_{SU\_O3\ trans}$)	0.070	0.216 ± 0.0305
Soluble biodegradable COD ($f_{SB\_O3\ trans}$)	0.550	0.418 ± 0.0652
Particulate biodegradable COD ($f_{XCB,O3\ trans}$)	0.340	0.366 ± 0.0720
Oxidized COD ($f_{mnr,O3}$)	0.040	0.0402

*(Isazadeh et al. *submitted* 2013)

Table 6 compares the ozone reaction COD fractions used in the calibration to the fractioning reported in Isazadeh et al. (*submitted* 2013). This study describes RAS ozonation for a pilot plant receiving real wastewater. The influent COD of real wastewater feeding the pilot plant had a much higher fraction of particulate undegradable organics (f_{Su}) (31%) than the synthetic feed used in the current laboratory-scale study (3.5%). This difference seems to correspond to an important difference in how the ozone reacts with the biosolids from each location. The soluble undegradable fraction resulting from ozonation ($f_{SU\_O3\ trans}$) was much higher for the pilot-scale plant study (21.6%) than for the current lab-scale study (7%). This is the COD fraction accounting for the slight increase in soluble COD in the effluent that was observed during the ozonation (Figure 24), and any change to this fraction would increase the model's effluent soluble COD prediction. This suggests that non-degradable particulate COD may be more likely lost to the effluent, which could be a positive effect of ozonation. While the fractions of biodegradable particulate COD from ozonation

($f_{XCB,O3\ trans}$) were similar for both studies, the biodegradable COD fractions ($f_{SU\_O3\ trans}$) accounted in opposite directions for the differences in non-degradable soluble COD fractions (Table 6). These differences suggest that on the whole biosolids produced in the current laboratory-scale study were more biodegradable than the ones in the pilot-scale study. While this explaination is based on of general observation, and more study is needed to fully understand COD fraction during ozonation, the purpose of this chapter is to develop a prelimary model, and experimentally determining COD fractions is out of the scope of this project .

7.5 Conclusion

Although the initial model used for estimation in Chapter 5 had a similar layout to the final model presented in this chapter, no data was available to calibrate it to this specific operation, and so its ability to accurately predict the reduction of biosolids was low. In order to obtain accurate predictions, data on operational and environmental parameters (SRT, relative COD solubilisation rate [$q_{Xtot,O3,sol}$], influent COD, temperature) and adjustment of the parameter values describing the COD fraction resulting from ozonation was needed. The presented calibrated model of the laboratory-scale reactors demonstrates that the set up can be accurately modeled and predict the biosolids inventory and effluent soluble COD of both cold temperature reactors. At this point, data is not available to calibrate the model to predict the nitrification processes, but the goal of this chapter was to create an initial model that can be used and built upon by future researchers, which has been achieved.

Chapter 8
General Discussion and Conclusions

The amount of waste biosolids produced at biological wastewater treatment plants across Canada has steadily increased, and new regulations on its handling will require a change to the current disposal methods. The reduction of waste biosolids by ozonation is an attractive alternative addition to conventional disposal methods as it operates in line and reduces solids from within the system. However, plants in North America are hesitant to install a system without knowing precisely how much reduction can be achieved. The economic risk remains high compared to Europe due to lower disposal costs in North America. Furthermore, little data is available on how this process will work in colder temperatures that occur during Canadian winters, and how it will affect treatment performance in these conditions. Until now, pilot-scale studies were needed to determine these conditions, but mathematical modeling could quickly and more economically predict the biosolids reduction levels and the other effects on treatment performances. Yet, the modeling approach needs to be validated and this project is part of a greater program aiming at developing the modeling concepts and validating them.

The development of the modeling concepts and their initial validation was done with the help of a pilot-scale study conducted with real wastewater (Frigon and Isazadeh 2011, Isazadeh et al. *submitted* 2013). Yet, the pilot-scale was not ideal to evaluate the RAS ozonation process and its mathematical model at low temperatures. However, laboratory-scale SBRs are well suited for this purpose as the small size allows for greater environmental control. Thus, the objectives of this research were to: (1) design and construct 4 mainly automated SBRs that could operate at specific temperatures, (2) observe changes in treatment performances at high and low temperatures caused by RAS ozonation to achieve a specific (40%) reduction in waste biosolid production, and (3) use this data to test the capacity of the mathematical model of ozonation to predict the

total solids inventory/biomass production and the changes in effluent compositions at low temperatures.

8.1 Objective 1: Design and Construct of SBRs

Designing and building four laboratory-scale SBRs to maintain a steady MLVSS inventory required an equal amount of research and trial work. This type of reactor is highly flexible in its configuration, and the best setup for a specific experiment may not be the same as ones described in literature or available for purchase commercially. The design used in this project was able to maintain a steady MLVSS inventory at both warm and cold temperatures, and with and without ozonation. Because it was self-designed and produced, modifications and additions were extremely easy. Although the size was adequate to produce results, the small mixed liquor volume (only 2 L) required a careful consideration and meticulous recording of the sampling volumes so as not to disrupt the system. While the design was easy to use in daily operation, representing it in the digital model in Chapter 6 was complex. The challenges of the design and implementation of four SBR were overcome, and the resulting reactors operated as expected to produce meaningful results.

8.2 Objective 2: Observe Changes in Treatment Performances

In addition to building the SBRs, an accompanying batch ozonation protocol was developed and applied to MLSS from the reactors to determine the effects on the solids production dynamics and the effluent quality. Solubilization experiments were run to understand how the ozone affected the reactor biosolids. Using this data and a generalized, uncalibrated mathematical model, the dose of ozone and volume of biosolids was determined. Due to the batch nature of the protocol, this aspect of reactor operation was the least automated and required a sizable number of man hours a week to complete. An automated, semi-constant flow ozonation set up would have been ideal, but impossible with this project setup. However, due to the manual operation of the ozonation protocol, the ozone dose was activity monitored and adjusted for, leading to a very stable ozone dose throughout the entire run of the project. The target biosolid inventory reduction of 40% was achieved in both reactors

using the developed protocol. No temperature effects were noted in the effluent sCOD treatment levels. Temperature also does not seem to affect the ozonation process as both the rate of solubilization per total solids inventory and the achieved rate of reduction were similar in both ozonated reactors. Nitrification loss occurred in the cold ozonated reactor at low nitrogen levels and in both ozone and control reactor at high nitrogen levels. This result was unexpected as literature data (Oleszkiewicz and Berquist 1988) suggest the possibility of good nitrification at 8 °C. Side experiments were run to explore the reason behind this loss of nitrification, but no clear explanations were found. So, while biosolid reduction ozonation is possible at 8 °C and does not have a negative effect on effluent sCOD treatment, the low temperature had a destabilizing effect on nitrification.

8.3 Objective 3: Test the Mathematical Model at Low Temperatures

The last objective was to model the cold reactor operation data using the ASM3 ozonation extension from Frigon and Isazadeh (2011). The most challenging aspect was modeling the physical layout of the reactors. Once the layout was complete, the model of the processes was very robust, and using the data generated, the calibration process was relatively straight forward. Default biological values from the literature could be used for parameters that were not measured, and the model still produced meaningful results. An example of the strength of the model is its uncalibrated use, with very little input data, to generate the ozonation protocol in Chapter 5 that satisfactory reached the target reduction of 40% in Chapter 6. The subsequent calibrated model was able to predict the total solids inventory and effluent soluble COD in both cold reactors. The COD fractions in both the influent and the ozonation process used for calibration were both low in undegradable COD when compared to a study receiving real wastewater (Isazadeh et al. in prep). However, the prediction of nitrification was a second layer of complexity in the model that could not be captured with the available data. Therefore, a preliminary model of the SBR was successfully developed using the ASM3 extension, but further study is required to completely describe all processes occurring in the reactors.

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Appendix A: Additional Modeling Information

Full Gujer stoichiometry matrix for the IWA-ASM3 model from Gujer et al. (1999)

j	Component i >	1	2	3	4	5	6	7	8	9	10	11	12	13
	Process	S_O	S_I	S_S	S_{NH}	S_{N2}	S_{NO}	S_{HCO}	X_I	X_S	X_H	X_{STO}	X_A	X_{TS}
v	expressed as >	O_2	COD	COD	N	N	N	Mole	COD	COD	COD	COD	COD	TSS
1	Hydrolysis		f_{SI}	x_1	y_1			z_1		-1				$-i_{XS}$
Heterotrophic organisms, denitrification														
2	Aerobic storage of COD	x_2		-1	y_2			z_2				$Y_{STO,O2}$		t_2
3	Anoxic storage of COD			-1	y_3	$-x_3$	x_3	z_3				$Y_{STO,NO}$		t_3
4	Aerobic growth	x_4			y_4			z_4			1	$-1/Y_{H,02}$		t_4
5	Anoxic growth (denitrification)				y_4	$-x_5$	x_5	z_5			1	$-1/Y_{H,NO}$		t_5
6	Aerobic endog. respiration	x_6			y_6			z_6	f_I		-1			t_6
7	Anoxic endog. respiration				y_7	$-x_7$	x_7	z_7	f_I		-1			t_7
8	Aerobic respiration of X_{STO}	x_8										-1		t_8
9	Anoxic respiration of X_{STO}					$-x_9$	x_9	z_9				-1		t_9
Autotrophic organisms, nitrification														
10	Nitrification	x_{10}			y_{10}		$1/Y_A$	z_{10}					1	t_{10}
11	Aerobic endog. respiration	x_{11}			y_{11}			z_{11}	f_I				-1	t_{11}
12	Anoxic endog. respiration				y_{12}	$-x_{12}$	x_{12}	z_{12}	f_I				-1	t_{12}
Composition matrix $t_{k,j}$														
k	Conservatives													
1	COD g COD	-1	1	1		-1.71	-4.57		1	1	1	1	1	
2	Nitrogen g N		i_{NSI}	i_{NSS}	1	1	1		i_{NXI}	i_{NXS}	i_{NBM}		i_{NBM}	
3	Ionic charge Mole +				1/14		-1/14	-1						
	Observables													
4	TSS g TSS								i_{TSXI}	i_{TSXS}	i_{TSBM}	0.60	i_{TSBM}	

Process rates for the IWA-ASM3 model (Gujer et al. 1999)

j	Process	Process rate equation ρ_j, all $\rho_j \geq 0$
1	Hydrolysis	$k_H \cdot \frac{X_S / X_H}{K_X + X_S / X_H} \cdot X_H$
Heterotrophic organisms, denitrification		
2	Aerobic storage of COD	$k_{STO} \cdot \frac{S_O}{K_O + S_O} \cdot \frac{S_S}{K_S + S_S} \cdot X_H$
3	Anoxic storage of COD	$k_{STO} \cdot \eta_{NO} \cdot \frac{K_O}{K_O + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \cdot \frac{S_S}{K_S + S_S} \cdot X_H$
4	Aerobic growth	$\mu_H \cdot \frac{S_O}{K_O + S_O} \cdot \frac{S_{NH}}{K_{NH} + S_{NH}} \cdot \frac{S_{HCO}}{K_{HCO} + S_{HCO}} \cdot \frac{X_{STO} / X_H}{K_{STO} + X_{STO} / X_H} \cdot X_H$
5	Anoxic growth (denitrification)	$\mu_H \cdot \eta_{NO} \cdot \frac{K_O}{K_O + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \cdot \frac{S_{NH}}{K_{NH} + S_{NH}} \cdot \frac{S_{HCO}}{K_{HCO} + S_{HCO}} \cdot \frac{X_{STO} / X_H}{K_{STO} + X_{STO} / X_H} \cdot X_H$
6	Aerobic endogenous respiration	$b_{H,O2} \cdot \frac{S_O}{K_O + S_O} \cdot X_H$
7	Anoxic endogenous respiration	$b_{H,NO} \cdot \frac{K_O}{K_O + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \cdot X_H$
8	Aerobic respiration of X_{STO}	$b_{STO,O2} \cdot \frac{S_O}{K_O + S_O} \cdot X_{STO}$ $\quad b_{STO,O2} \geq b_{H,O2}$
9	Anoxic respiration of X_{STO}	$b_{STO,NO} \cdot \frac{K_O}{K_O + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \cdot X_{STO}$ $\quad b_{STO,NO} \geq b_{H,NO}$
Autotrophic organisms, nitrification		
10	Nitrification	$\mu_A \cdot \frac{S_O}{K_{A,O} + S_O} \cdot \frac{S_{NH}}{K_{A,NH} + S_{NH}} \cdot \frac{S_{HCO}}{K_{A,HCO} + S_{HCO}} \cdot X_A$
11	Aerobic endogenous respiration	$b_{A,O2} \cdot \frac{S_O}{K_O + S_O} \cdot X_A$
12	Anoxic endogenous respiration	$b_{A,NO} \cdot \frac{K_O}{K_O + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \cdot X_A$

Default biological values used in the model suggested in Hauduc et al. (2011)

Parameter	Unit	Value
Stoichiometric Parameters		
$Y_{Stor\_OHO,Ox}$	g X_{OHO} g X_{Stor}^{-1}	0.8
$Y_{Stor\_OHO,Ax}$	g X_{OHO} g X_{Stor}^{-1}	0.7
$Y_{SB\_Stor,Ox}$	g X_{Stor} g S_B^{-1}	0.8
$Y_{SB\_Stor,Ax}$	g X_{Stor} g S_B^{-1}	0.65
Conversion coefficient		
i_{N_XU}	g N g X_U^{-1}	0.04
i_{N_XCB}	g N g X_{CB}^{-1}	0.03
Kinetic parameters		
Hydrolysis		
$q_{XCB\_SB,hyd}$	g X_{CB} g X_{OHO}^{-1} d^{-1}	9
q_{SB_Stor}	g X_{CB} g X_{OHO}^{-1} d^{-1}	0.1
Ordinary Heterotrophic Organisms		
$\mu_{OHO,Max}$	d^{-1}	3
$\eta_{OHO,Ax}$	--	0.5
$K_{SB,OHO}$	g S_B m^{-3}	10
K_{Stor_OHO}	g X_{Stor} g X_{OHO}^{-1}	0.1
$m_{OHO,Ox}$	d^{-1}	0.3
$m_{OHO,Ax}$	d^{-1}	0.15
$m_{Stor,Ox}$	d^{-1}	0.3
$m_{Stor,Ax}$	d^{-1}	0.15
$K_{O2,OHO}$	g S_{O2} m^{-3}	0.2
Autotrophic Nitrifying Organisms		
$\mu_{ANO,Max}$	d^{-1}	1.3
$m_{ANO,Ox}$	d^{-1}	0.2
$m_{ANO,Ax}$	d^{-1}	0.1
$K_{NHx,ANO}$	g S_{NHx} m^{-3}	1.4

Appendix B

Programming of each outlet of the Apex AquaController

Fast Pumps

Fallback OFF
Set OFF
If Time 00:10 to 00:12 Then ON
If Time 06:10 to 06:12 Then ON
If Time 12:10 to 12:12 Then ON
If Time 18:10 to 18:12 Then ON

pH 2 Control

Fallback OFF
OSC 000:00/000:02/000:58 Then ON
If pH_2 > 07.45 Then OFF
If Time 04:50 to 06:15 Then OFF
If Time 10:50 to 12:15 Then OFF
If Time 16:50 to 18:15 Then OFF
If Time 22:50 to 00:15 Then OFF

WAS

Fallback OFF
OSC 640:00/001:00/799:00 Then ON

Effluent Pumps

Fallback OFF
Set OFF
If Time 05:50 to 05:59 Then ON
If Time 11:50 to 11:59 Then ON
If Time 17:50 to 17:59 Then ON
If Time 23:50 to 23:59 Then ON

Aeration

Fallback OFF
Set OFF
If Time 00:00 to 04:50 Then ON
If Time 06:00 to 10:50 Then ON
If Time 12:00 to 16:50 Then ON
If Time 18:00 to 22:50 Then ON

pH 1 Control

Fallback OFF
OSC 000:00/000:02/000:58 Then ON
If pH_1 > 07.45 Then OFF
If Time 04:50 to 06:15 Then OFF
If Time 10:50 to 12:15 Then OFF
If Time 16:50 to 18:15 Then OFF
If Time 22:50 to 00:15 Then OFF

CO_2

Fallback OFF
Set OFF
If Time 00:00 to 04:50 Then ON
If Time 06:00 to 10:50 Then ON
If Time 12:00 to 16:50 Then ON
If Time 18:00 to 22:50 Then ON