MODEL DEVELOPMENT AND SYSTEM OPTIMIZATION TO MINIMIZE GREENHOUSE GAS EMISSIONS FROM WASTEWATER TREATMENT PLANTS

by

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ABSTRACT

DONGWOOK KIM. Model development and system optimization to minimize
greenhouse gas emissions from wastewater treatment plants. (Under the direction
of DR. JAMES D. BOWEN)

As greenhouse gas emissions (GHG) reduction has drawn considerable attention, various methods have been established to estimate greenhouse gas emissions from wastewater treatment plants (WWTPs). In order to establish a design and operational strategy for GHG mitigation, accurate estimates are essential. However, the existing approaches (e.g. the IPCC protocol and national greenhouse gas inventories) do not cover emissions from all sources in WWTPs and are not sufficient to predict facility-level emissions. The ultimate goal of this research was to improve the quantification of GHG emissions from WWTPs. This was accomplished by creating a new mathematical model based on an existing activated sludge model. The first part of the research proposed a stepwise methodology using elemental balances in order to derive stoichiometry for state variables used in a mass balance based whole-plant wastewater treatment plant model. The two main advantages of the elemental balance method are the inclusion of carbon dioxide (CO_2) into the existing model with no mass loss and ease of tracking elemental pathways. The second part of the research developed an integrated model that includes (1) a direct emission model for onsite emissions from treatment processes and (2) an indirect emission model for offsite emissions caused by plant operation. A sensitivity analysis of the proposed model was conducted to identify key input parameters. An uncertainty analysis was also carried out using a Monte Carlo simulation, which provided an estimate of the potential variability in GHG estimations. Finally, in the third part, the research identified an optimal operational strategy that resulted in minimizing operating costs and GHG emission, while simultaneously treating the wastewater at better levels. To do this, an integrated performance index (IPI) was proposed to combine the three criteria. The IPI was then incorporated into an optimization algorithm. The results obtained in this research demonstrated that the variation of GHG emissions is significant across the range of practical operational conditions. With system optimization, however, WWTPs have the potential to reduce GHG emissions without raising operating costs or reducing effluent quality. Further research should include a mechanistic examination of processes that produce methane (CH_4) in the wastewater treatment stream and nitrous oxide (N_2O) in the sludge treatment stream.

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LIST OF ABBREVIATIONS

ADM1	Anaerobic Digestion Model No. 1
ADT	anaerobic digester operating temperature
AE	aeration energy
AMO	ammonia mono-oxygenase
AOB	ammonia-oxidizing bacteria
ASMN	Activated Sludge Model-Nitrogen
ASMN_G	Activated Sludge Model-Nitrogen for Greenhouse gas
ASM1	Activated Sludge Model No.1
ASM(s)	activated sludge model(s)
ASP(s)	activated sludge process(es)
BNR	biological nutrient removal
BOD	biochemical oxygen demand
BSM	benchmark simulation model
C	carbon
$C_6H_{12}O_6$	glucose
CH_3COO^-	acetate
CH_4	methane
CO_2	carbon dioxide
CO_2e	carbon dioxide equivalent
COD	chemical oxygen demand
DO	dissolved oxygen
EC	environmental costs
ECD	external carbon dose

eGRID	Emissions & Generation Resource Integrated Database
EQI	effluent quality index
GGI	greenhouse gas index
GHG(s)	greenhouse gas(es)
GWP	global warming potential
H	proton or hydrogen
HE	heating energy
HRT	hydraulic retention time
IPCC	Intergovernmental Panel on Climate Change
IPI	integrated performance index
IR	internal mixed-liquor recycle
LCA	life-cycle analysis
LHS	Latin Hypercube Sampling
MCR	methane capture rate
MLE	Modified Ludzack-Ettinger
ME	mixing energy
N	nitrogen
N_2	nitrogen gas
N_2O	nitrous oxide
NH_4^+	ammonium
NO	nitric oxide
NO_2^-	nitrite
NO_3^-	nitrate
NOB	nitrite-oxidizing bacteria
OCI	operational cost index

P	phosphorus
PE	pumping energy
PI	proportional-integral
PST	primary settling tank
RE	revenues from biogas energy recovery
RS	relative sensitivity
RS	return sludge
RSM	response surface methodology
SP	sludge disposal
SRT	solids retention time
SS	suspended solids
TKN	total Kjeldahl nitrogen
TN	total nitrogen
TSS	total suspended solids
USEPA	U.S. Environmental Protection Agency
VC	violation costs
VSS	volatile suspended solids
WS	waste activated sludge
WWTP(s)	wastewater treatment plant(s)

CHAPTER 1: INTRODUCTION AND RESEARCH OBJECTIVES

1.1 Introduction

Due to increasing global concerns regarding climate change, much scientific effort over the last two decades has aimed at methods to estimate and minimize greenhouse gas emissions from wastewater treatment plants (WWTPs). Most current methodologies and estimates of GHG emissions for WWTPs are based largely on the IPCC protocol established by the Intergovernmental Panel on Climate Change (IPCC). As the IPCC protocol was developed for ease for comparison of national GHG emissions among countries including developing countries, this protocol provides a relative simple, straightforward calculation method based on national human activity data and emission factors for estimating emission inventories. Accordingly, the IPCC protocol is useful as an approximate method that can serve as guidance in establishing country-specific inventories (e.g. U.S. Greenhouse Gas Inventory). Although this method has been often used and may be suitable for national or regional scale estimation, it does not account for facility-specific treatment trains, which are unique to every plant, nor does it account for the varying operating conditions (influent organic material or nitrogen levels, the fraction of degradable organic material, temperature, oxygen concentration, sludge age, etc.). Furthermore, the current emission factors used provide incomplete information and are uncertain because they are based on the collected data from only some measurements of lab-scale and full-scale plants, and because most GHGs are microbially produced and consumed, which are affected by temperature, pH, available substrates, microbial competition and many other factors. The IPCC approach should therefore not be expected to provide accuracy for facility-level estimates, and the estimates may not reflect site-specific conditions of wastewater treatment systems that can significantly affect the extent of GHG production. An accurate estimation of the GHG emissions from a particular plant based on realistic site conditions and operational data is critical not only for the selection of a sustainable treatment process but also for the optimization of plant operations.

In addition, the existing IPCC and U.S. national GHG inventories are underestimating the contribution of WWTPs to global warming potential. For instance, according to the U.S. EPA's estimate (U.S. EPA, 2013), wastewater treatments account for approximately 0.4 percent of U.S. GHG emission profile. Also, wastewater treatments contribute 2.8% and 1.5% to the total CH_4 and N_2O emissions, respectively (Figure 1.1 and 1.2). However, this calculation represents only direct emissions that are actual on-site GHG generation from wastewater and sludge treatment processes, and non-fossil fuel combustion for heating or energy generation. Indirect emissions caused by the production of electricity, chemicals, fuels, and other materials used for the WWTP operation are not currently assigned to the wastewater treatment sector and instead they are included in other sectors (Energy and industrial processes). Recent research has revealed that in wastewater treatment facilities, the indirect emissions are much greater than the direct GHG emissions, indicating the potential for reducing overall GHG emissions at wastewater treatment plants through process optimization in design and operation (Sahely et al., 2006; Subramanian, 2010). Actual emissions could be much higher if indirect emissions are incorporated. For the rational assessment of the contribution of WWTPs, both direct and indirect emissions should be considered by the wastewater sector.

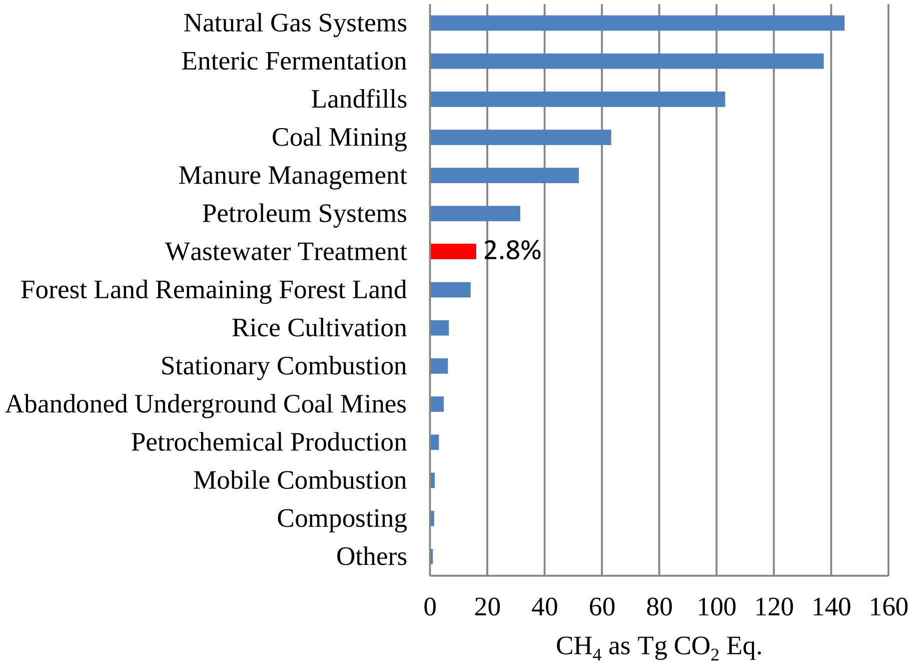

Figure 1.1: Contribution of wastewater treatment to total CH_4 emissions in the U.S. (EPA, 2013)

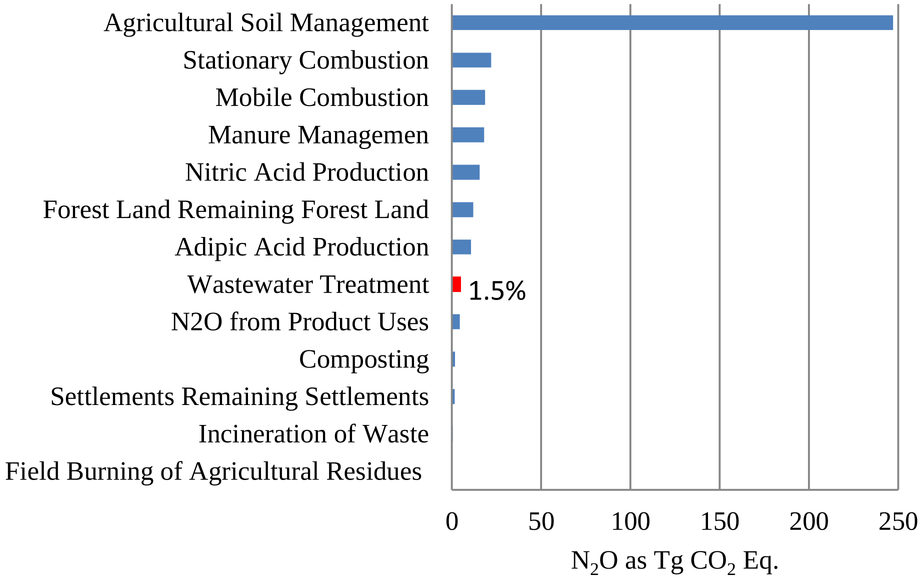

Figure 1.2: Contribution of wastewater treatment to total N_2O emissions in the U.S. (EPA, 2013)

1.2 Previous Studies on Estimating Greenhouse Gas Emissions from Wastewater Treatment Systems

WWTPs have been roughly evaluated regarding greenhouse gas production because the emission of greenhouse gases is not currently regulated and the contribution of WWTPs to global greenhouse gas budgets has been assumed to be small. Up to date, there have been numerous attempts to identify and estimate greenhouse gas emission, although there is a large uncertainty in accuracy of the prediction. In 2006, the Intergovernmental Panel on Climate Change (IPCC) established guidelines for national greenhouse gas inventories. In the IPCC Guideline, many inventories have been conducted at the national level. While many countries make use of the IPCC default methodology, some of them, especially in Europe, are developing more advanced methods that are tailored for specific country circumstances (IPCC, 2000; IPCC, 2006; EPA, 2013; EEA, 2010). In the IPCC methodology, CH_4 emission is estimated by multiplying the emission factors for each wastewater handling system by the total amount of organic material in the wastewater produced for each system. N_2O emission, on the other hand, is obtained through annual per capita protein consumption (IPCC, 2006; EPA, 2013). The U.S. Environmental Protection Agency (USEPA) has adopted and modified the IPCC protocol. U.S. greenhouse gas emission inventories indicate that process-related greenhouse gas emissions from wastewater treatment plants are on the order of 0.4% of the total U.S. emissions (EPA, 2013). As stated earlier, this figure is likely an underestimate, because emissions caused by indirect sources (e.g. electricity and fuel use) and biogenic CO_2 are not considered in these estimates (Greenfield and Bastone, 2005; Hara and Mino, 2008; Prendez and Lara-Gonzalez, 2008; EPA, 2013). In addition, this estimate ignores the possibility that wastewater treatment plants could be a net sink of GHGs if enough biomass is converted into CH_4 and then used as an energy source. There is in fact a major debate on whether biogenic CO_2 emission should be considered at all. The IPCC specifies that the CO_2 emission from biogenic sources should not be included in the GHG emission total due to the assumption that over time regrowth of biomass equals consumption (IPCC, 2006). That is, biogenic CO_2 emissions from wastewater are not considered in the IPCC Guidelines since the biodegradable organic fraction of biomass was assumed to be part of the renewable CO_2 cycle. Daigger et al. (2004) and most studies supported the recommendation of IPCC that wastewater treatment does not cause CO_2 emissions because if wastewater treatments plant did not exist, human wastes would be discharged to the environment where, presumably, they would eventually be oxidized to carbon dioxide and water. This issue has been debated by Keller and Hartley (2003); Cakir and Stemstrom (2005); Monteith et al. (2005); Sahely et al. (2006); Machado et al. (2007); Rosso and Stenstorm (2008). Sahely et al. (2006) argued that the concept of no net CO_2 resulting from biomass and from the production and combustion of renewable fuels is only applicable for those pursing national level studies. Rosso and Stenstorm (2008) believed that carbon from biogenic sources may contribute to the greenhouse effect and that the reduction of carbon from sustainable sources may retard its emission cycle and even global warming. Among the biogenic gases that are created by microorganisms, only biogenic CH_4 and N_2O are considered to affect global warming in most protocols. This issue is, however, still open to discussion. Although biogenic CO_2 emissions are not usually included in most protocols, the gross emissions including biogenic CO_2 could be significant, and thus there is a potential tradeoff in the overall GHG budget. Therefore, this study deals with this issue by counting biogenic CO_2 and separating this from other GHG emissions in order to look at the overall changes of emission at a facility.

Life-cycle analysis (LCA) methods have been employed to aid in determining the environmental burden of wastewater treatment plants. Many life-cycle based studies of WWTPs have been published during the past few decades (Emmerson et al., 1995; Tillman et al., 1998; Lundie et al., 2000; Bridle and Skrypski-Mantele, 2000; Suh and Rousseaux, 2002; Lundin et al., 2004; Houillon and Jolliet, 2005; Munoz et al., 2007; Higgins and Kendall, 2012). A literature review of previous studies that used the life cycle approach to examine WWTPs found that only a few studies have focused on GHG emissions (Lundin et al., 2000; Peters and Lundie, 2002; Kuber, 2006; Racoviceanu et al., 2007; Tripathi, 2007; Machado et al., 2007; Hospido et al., 2008; Lopez-Ridaura et al., 2009). Almost all of the previous studies have had different study scopes and did not look at the whole WWTP system; therefore, the emission results may differ from each other. In addition, estimating methods of GHG emissions from WWTPs use or modify empirical relationships and emission factors provided by the IPCC. Lundin et al. (2000) employed LCA for wastewater systems to demonstrate the influence of system boundaries and scale on the environmental loads. Kuber (2006) examined greenhouse gas emissions from municipal wastewater treatment plants under several energy supply scenarios. Racoviceanu et al. (2007) examined energy use and GHG emission inventory for water treatment systems, and noted the impact of the production and transportation of chemicals and electricity consumption for facility operations. In the study by Tripathi (2007), life-cycle energy and impact assessments were conducted for wastewater treatment plants in Michigan. This study concluded that the total life-cycle energy and emissions were mostly related to the electricity needed to operate the plant.

A few studies have examined different aspects of GHG emission from wastewater treatment processes in contrast to the research described above. In 1995, an attempt was made to understand N_2O emission from WWTPs. Czepiel et al. (1995) directly measured N_2O gas from a municipal wastewater treatment plant in Durham, NH. The IPCC protocol adopts N_2O emission factors from this study (IPCC, 2006). Cakir et al. (2005) estimated GHG emission and compared aerobic and anaerobic wastewater treatment technology through mathematical calculations. With a different approach from the IPCC method, Monteith et al. (2005) developed a procedure for the estimation of greenhouse gas emission from municipal wastewater treatment plants. To identify the carbon distribution of incoming biochemical oxygen demand (BOD), a mass balance for suspended solids in secondary treatment was used. Monteith et al. evaluated the procedure using full-scale data from sixteen Canadian wastewater treatment facilities and then applied it to all ten Canadian provinces. Prendez et al. (2008) estimated GHG emissions using existing models and applied the strategies for sanitation management in wastewater treatment plants for GHG emission control. Prendez et al. considered selected models proposed by the IPCC and some others published by different authors; these were modified according to national conditions, different sanitation, and temporal scenarios. Rosso and Stenstorm (2008) mathematically quantified CO_2 and CH_4 emissions of wastewater treatment in large urban areas using WHO/UNICEF datasets. Wei et al. (2008) analyzed indirect GHG emission from a WWTP based on emission factors as recommended by the IPCC (2000). They regarded combustion of fossil fuels, use of chemicals, and the transport of solid waste as indirect emission sources. Various research studies have been conducted to assess indirect emissions associated with electricity, fuel, or chemical use, and most of them have focused on electricity use because of its overwhelming domination of the CO_2 emission budgets for WWTPs (Emmerson et al., 1995; Clauson-Kaas et al., 2001; Bolzonella et al., 2002; Dones et al., 2003; Racoviceanu et al., 2007). More recently, several attempts has been made to use activated sludge models for estimation of GHG emissions within the wastewater treatment community (Flores-Alsina et al., 2011; Ni et al., 2012; Mampaey et al., 2013). Flores-Alsina et al. (2011) estimated CO_2 emissions using a simple model rather than activated sludge models. Ni et al. (2012) and Mampaey et al. (2013) focused on models for N_2O emissions. Overall, methodologies for estimating GHGs from indirect emission have been well developed, whereas a detailed, facility-specific protocol for WWTP process emissions has not yet been properly established and thus needs to be developed. Based on a review of the existing methods, this research will mainly focus on this area. Review of the research so far indicates that two separate advances need to be made. First, a model needs to be developed that can simultaneously account for both direct and indirect sources from all unit processes within a wastewater treatment plant. Second, this model needs to account for all three greenhouse gases (i.e. CO_2, CH_4, and N_2O) that are emitted from wastewater treatment plants. The literature review also indicates that GHG emissions from wastewater treatment process can be estimated with more detailed models using existing wastewater models that have been specifically tailored and modified for the purpose.

1.3 Research Objectives

The primary motivation behind this study is to improve the quantification of greenhouse gas emissions from wastewater treatment plants. The specific hypothesis of this research is that GHG emissions can be reduced without sacrificing effluent quality through process optimization. To date, research has shown that the magnitude and distribution of GHG produced is dependent on the characteristics of the influent wastewater, the required treated water criteria, the types of wastewater and sludge treatment processes used, and operational conditions (e.g. Keller and Hartley, 2003; Monteith et al., 2005; Sahely et al., 2006; Hospido et al., 2008; Shahabadi et al., 2009; Subramanian, 2010). A detailed research in this area could provide valuable information for trade-off of sustainability and regulation of the systems. Accordingly, careful attention to plant design and operation is required to minimize GHG production. Literature review has shown that there is potential for reduction of GHG emissions; however, few investigations of this have been reported with plant-wide simulation using activated sludge models, which is the most widely used wastewater treatment model. To test the hypothesis above, the development of more sophisticated means that reflect the real plant behavior under various design and operational conditions is absolutely essential. This study thus focuses on the development of a general methodology for a more accurate and comprehensive estimate of GHG emissions from wastewater treatment plants and the investigation of the effects of process operations and site-specific conditions on GHG emissions. The specific objectives of this study are divided in three main parts as follows:

- Develop and verify a plant-wide model that describes the complex interaction of wastewater substrates and GHGs in wastewater treatment systems (Chapter 2). Much of this dissertation was dedicated to performing this objective.
- Quantify GHG emissions from a WWTP by introducing a plant-wide elemental balance-based simulation and provide a quantitative analysis of uncertainty in a GHG model simulation to evaluate its accuracy (Chapter 3).
- Investigate the potential of minimizing GHG emissions through system optimization (Chapter 4).

1.4 Contributions of This Research

The three major contributions of this research corresponding to respective objectives are described below:

- Inclusion of CO_2 as a state variable into an existing activated sludge model, which allows us to predict all three major GHG emissions simultaneously in a mathematical model and advances understanding of carbon cycle in a wastewater treatment system.
- Development and simulation of a comprehensive mathematical model for predicting plant-wide GHG emissions in a biological nutrient removal (BNR) wastewater treatment plant.
- Implementation of model-based optimization of operational strategy for sustainable WWTPs using an integrated performance index, which

includes three performance criteria: operating costs, effluent quality and GHG emissions.

CHAPTER 2: ELEMENTAL BALANCE-BASED SIMULATION TO ESTIMATE PLANT-WIDE GREENHOUSE EMISSIONS FROM WASTEWATER TREATMENT PLANTS

Abstract

In this chapter, a stepwise methodology using elemental balances is presented to establish a more general and comprehensive stoichiometry for state variables in an activated sludge model. The derived stoichiometries can be applied to define and to verify a plant-wide mass balance-based model that can quantify plant-wide greenhouse gas emissions from wastewater treatment plant (WWTPs). The ASMN (Activated Sludge Model-Nitrogen) was adapted as the basic biological process model and then extended to incorporate all elements components within the system including carbon dioxide (CO_2) emissions and other components (e.g. nitrogen and water) from biological processes. Using the data obtained from steady-state simulations and calculations on a spreadsheet, plant-wide chemical oxygen demand (COD), carbon and nitrogen balances were performed on a designed WWTP. Based on the results of balance calculations, fates of carbon and nitrogen over a WWTP were investigated. The results of plant-wide simulation showed that the model is useful in tracking the fate of elemental components of interest. The elemental balance method proved to be a useful tool in extending and verifying a model where no or insufficient data are available to track the fate of elements introduced into the plant.

2.1 Introduction

Mathematical modeling and computer simulation of activated sludge processes (ASPs) are considered to be a valuable part of analysis and design of wastewater treatment systems, as they can assist engineers and scientists in capturing the features of the complex system and predicting the dynamic response of the system under a variety of operational conditions.

A number of models, such as the Activated Sludge Models (ASMs) (e.g. Henze et al., 2000), have been developed and widely applied in simulations of different types of biological wastewater treatment processes. Traditionally, the ASMs have been developed to assess water quality and to evaluate the process performance. As particular attention is devoted to the impact of wastewater treatment plants (WWTPs) on global climate change, attempts have been made to include the processes associated with the sources and sinks of greenhouse gases (GHGs, i.e. carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O)) in the activated sludge models (Snowling et al., 2006; Sin & Vanrolleghem, 2007; Hiatt & Grady, 2008). The existing ASMs can be extended with processes describing greenhouse gas emissions caused by the biochemical behavior of the system because of their important common feature, use of the so-called Petersen matrix consisting of a stoichiometry matrix for each process and state variable and a vector of kinetic process rates. In the ASM matrices, multiple reactions take place simultaneously and are generally written based on mass balance equations for each component involved in each process.

Using this approach to implement a plant-wide model simulation while incorporating gaseous emissions from the wastewater treatment plant poses some new challenges. First, the current ASM matrices have been developed based on mass balance equations for chemical oxygen demand (COD), nitrogen (N), charge, and/or phosphorus (P) and therefore, some components (e.g. nitrogen gas (N_2), CO_2 and H_2O) that have a unit COD of zero are ignored. Second, elemental mass continuities of other elements, such as carbon (C) and hydrogen (H), are not considered. In addition, in wastewater treatment plants water quality variables such as dissolved oxygen (DO), COD, total suspended solids (TSS), and total Kjeldahl nitrogen (TKN), are routinely measured to manage the system performance and effluent quality, while the formation and emission of greenhouse gases except for CH_4 generated from anaerobic sludge digesters have not been an operating point of concern, therefore data on their generation are very scarce. Thus, our recent interest in greenhouse gas emissions leads us to suggest that a new approach for modeling should be considered.

Biological wastewater treatment processes handle a complex consortium of bacteria and a wide range of organic compounds resulting from a variety of human activities. Understanding the compositions of organic matter (state variables) in terms of C, H, O, N, and COD is essential in modeling an activated sludge process since the elemental composition can substantially influence process operation & performance (e.g. solids retention time (SRT), aeration time, sludge production, temperature, and effluent quality) as well as greenhouse gas emissions. The stoichiometry of the activated sludge process demonstrates the relationships between the quantities of reactants and products, especially bacteria and compounds in biochemical reactions. This process and conservation-based description is generally used as a basis for building the stoichiometric matrix of activated sludge models. A general stoichiometric equation for aerobic growth of heterotrophic biomass fed on acetate is formulated as follows (Rittman & McCarty, 2000):

$$0.125\ CH_3COO^- + 0.0295\ NH_4{}^+ + 0.103\ O_2$$
$$\rightarrow 0.0295\ C_5H_7O_2N + 0.0955\ H_2O + 0.095\ HCO_3^- + 0.007\ CO_2 \qquad (2.1)$$

In defining the composition of the different compounds involved in a process, simple empirical formulas have typically been used that are obtained from experiments or the chemical compositions of well-known organic compounds, for example glucose ($C_6H_{12}O_6$), acetate (CH_3COO^-), etc., are used as shown in Eq.(2.1). However, in adding the processes that are needed to predict greenhouse gas emissions, and in coupling unit process models to produce a whole-plant simulation, it can be very difficult to define the composition of every state variable due to the lack of required information. Hence, a more general and powerful approach, which offers flexibility in establishing stoichiometry and is amenable to inclusion into the Peterson matrix based specification of a wastewater treatment plant process, is required

In the field of wastewater treatment process modeling, the elemental balance method has proven to be a very useful tool for verifying the results of a simulation model (Reichert et al., 2001; Gracia et al., 2006; Takacs & Vanrolleghem, 2006; Reichert & Schuwirth, 2010; Hauduc et al, 2010) and for combining different unit process models for plant-wide simulation (Volcke et al., 2006; Grau et al., 2007; Zaher et al., 2007; Ekama, 2009). This method is based on the principle of conservation of all elements. The method relies on two assumptions. First, it is assumed that all elemental compositions of all substances and organisms in the system are known. Second, in all biochemical reactions, elements cannot be formed or disappear, but only can be transformed, so that the total amount of every element is conserved. The main reason for using an elemental balance in this study is to quantify completely the overall carbon and nitrogen cycle in an entire WWTP system. The advantage of the elemental balance lies in the fact that it completely describes the fate of every element of every compound in the biochemical conversion system with no mass loss, providing researchers with improved information needed to analyze the system and facilitate integration of models using different state variables. Moreover, mass balancing is especially helpful in cases in which no or insufficient data are available to quantify process rates of interest. Using mass conservation constraints an unknown flow may be quantified from the residual of the available mass flux. For example, in estimating gaseous emissions, for which data are generally not available from WWTPs, mass conservation can provide a means for estimating emission rates.

The main objective of this study is to present a methodology to further improve an existing implementation of the ASM by adding elemental balances to plant-wide greenhouse gas simulations and to provide more accurate information concerning GHG emissions from a WWTP. In this context, the present study presents a comprehensive approach to derive the stoichiometry for all activated sludge processes. Stoichiometric coefficients in the matrix were re-derived as functions of the elemental mass fraction of organic compounds and organisms, and kinetic parameters. The derived stoichiometries are then compared with those of the original ASM to verify whether the use of the proposed method is suitable and applicable to various organic compounds. This paper first presents a stepwise methodology to extend an ASM with redefined stoichiometric coefficients. Next, the proposed method is tested using a plant-wide simulation in an activated sludge plant with anaerobic sludge digesting designed to remove organic carbon and nitrogen.

2.2 Methods

2.2.1 Model Selection

Nitrogen removal is commonly carried out in wastewater treatment systems by a two-stage biological process called nitrification and denitrification. This biological nitrogen removal process is believed to be a significant source of nitrous oxide (N_2O) emissions (Tallec et al., 2006). N_2O is an important greenhouse gas with a global warming potential of 310 over a 100-year period (IPCC, 2006). To consider N_2O production our model uses a modified version of the original ASM1 (Activated Sludge Model No.1) (Henze et al., 2000), called ASMN (Activated Sludge Model-Nitrogen) model proposed by Hiatt and Grady (2008). In this study we have adapted ASMN to reflect the current knowledge on nitrogen gas (N_2) and N_2O gas emissions during biological nitrogen process. Compared to the original ASM1, the ASMN model describes a more detailed nitrification/denitrification process that includes all nitrogen compounds, ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), nitric oxide (NO), N_2O, and N_2. The one-step nitrification and denitrification processes of the ASM1 model are further divided into two-steps ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$) and four-steps ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$), respectively. In this study the original ASMN model has been extended to incorporate a description of all elemental components, including H_2O, proton (H^+), CO_2, and N_2 gas emissions from biological processes. The resulting model that we have created allows us to consider elemental balances and simulate the three major greenhouse gases (CO_2, CH_4, and N_2O). The Anaerobic Digestion Model No. 1 (ADM1) presented by Batstone et al. (2002) is used in order to represent the biochemical and physiochemical processes in anaerobic sludge digestion. The biogas (mainly composed of CO_2 and CH_4) that results from the microbial degradation of organic matter can be predicted using the ADM1. Since its introduction, the ADM1 model has been successfully validated under dynamic conditions on numerous laboratory-scale and full-scale systems (Blumensaat and Keller, 2005; de Gracia et al., 2009; Thamsiriroj and Murphy, 2011).

2.2.2 Model Matrix

In general, activated sludge models consist of stoichiometric matrix and a vector of process kinetics. As an initial implementation of our method, the coefficient matrix of the selected model (ASMN) was reproduced using element balancing in a spreadsheet as proposed by Reichert et al. (2001) with some modifications. The method is based on the requirement that all model components (state variables) be defined by chemical formulas with prescribed stoichiometries. In addition, the formulations of stoichiometric coefficients of activated sludge processes in the model are expressed as functions of the elemental compositions of all organic and inorganic matter involved and the kinetic behavior of microbial biomass. In ASM1 and/or ASMN, the stoichiometric coefficients can be determined from elemental balancing of C, H, O, and N if kinetic parameters, such as yield coefficient (Y) and nitrogen content of biomass (i_XB) and organic particulate (i_XP), are specified. The proposed method for establishing an elemental balance-based model matrix relies on the following 5 steps (Figure 2.2):

Step 1. Define the generic and fixed compositions of model state variables

The first step in building a model matrix is to assign the chemical composition of all model state variables in terms of C, H, O, N, and charge. As mentioned above, the chemical compositions of organic matter state variables vary mainly depending on influent characteristics, so that in order to offer increased flexibility in the determination of stoichiometry, generic fraction formulas are assigned to organic matter in the form of an unknown generic composition ($C_cH_hO_oN_n$). Fixed stoichiometries are used for the inorganic matter (e.g. CO_2, NO_3^-, etc.). This strategy allows elemental balance equations to be written in the general form for any wastewater condition. The values of generic compositions are better determined during later plant-wide elemental balancing (step 5).

Step 2. Establish the stoichiometric coefficients

Before establishing elemental balance equations and stoichiometric coefficients, the following assumptions are made:

- All biological processes are completely balanced within the system in terms of mass of C, H, O, N, and charge.
- The alkalinity balance of the ASMs is replaced with a proton (H^+) balance equation. In this case, the signs of the terms in the proton balance equation become the opposite of the signs of the terms in the alkalinity balances found in original ASMs.
- The system is controlled under constant pH condition (i.e. pH 7). Thus, there are no transformations between bicarbonate (HCO_3^-) and CO_2 in the bioreactor and inorganic carbon exists in the form of CO_2.
- H_2O is included in reactions as a state variable, which allows closure of the oxygen mass balance over the system; however the changes in the amount of

water flow through the process reactions are neglected for the plant-wide simulation.

- There are no transformations between ammonium (NH_4^+) and ammonia (NH_3) in the system. Thus, ammonium is used as a nitrogen source for biomass growth and/or as an electron donor for energy production.
- In the anoxic growth process of heterotrophs, all oxidized nitrogen compounds are sequentially reduced to other inorganic nitrogen compounds, and are not utilized for biomass production.

First, based on the principle of mass conservation within the system, stoichiometric equations for model processes are constructed and elemental balance equations are set up as illustrated in Takacs et al. (2007). Formulating the relationships among biomass yield coefficients and elemental components of compounds is an important step toward developing stoichiometric coefficients. The requirement of this step is to set up the same number of independent algebraic equations as unknown coefficients so that the resulting system of equations has a unique solution. As an example, the first step of anoxic growth process of heterotrophs ($NO_3 \rightarrow NO_2$) needed for the production of 1 mole of biomass is presented as shown below:

$$\begin{aligned} &\gamma_{Ss} C_{c1} H_{h1} O_{o1} + \gamma_{NO3}\, NO_3^- + \gamma_{NH4}\, NH_4^+ \\ &\quad \rightarrow C_{c2} H_{h2} N_{n2} O_{o2} + \gamma_{NO2}\, NO_2^- + \gamma_{H2O}\, H_2O + \gamma_{CO2}\, CO_2 + \gamma_H H^+ \end{aligned} \tag{2.2}$$

where $C_{c1}H_{h1}O_{o1}$ represents the elemental formula of substrate; $C_{c2}H_{h2}N_{n2}O_{o2}$ represents elemental formula of biomass; the unknown stoichiometric coefficients of each compound are represented as γ_{Ss}, γ_{CO2}, γ_{NH4}, γ_{H2O}, γ_H, γ_{NO3}, and γ_{NO2}, respectively.

If the biomass yield coefficient is assigned to be 1, the rest of the stoichiometric coefficients can be determined by balancing of C, H, O, N, and charge and by assuming the relationships between compounds. In order to derive seven stoichiometric variables of the process reaction, seven algebraic equations are written according to the information in Eq. (2.2) as follow:

- CarbonBalance: $c_1 \times \gamma_{Ss} - \gamma_{CO2} - c_2 = 0$
- HydrogenBalance: $h_1 \times \gamma_{Ss} + 4 \times \gamma_{NH4} - 2 \times \gamma_{H2O} - \gamma_H - h_2 = 0$
- OxygenBalance: $o_1 \times \gamma_{Ss} + 3 \times \gamma_{NO3} - 2 \times \gamma_{CO2} - \gamma_{H2O} - 2 \times \gamma_{NO2} - o_2 = 0$
- NitrogenBalance: $\gamma_{NO3} + \gamma_{NH4} - n_2 - \gamma_{NO2} = 0$
- ChargeBalance: $-\gamma_{NO3} + \gamma_{NH4} + \gamma_{NO2} - \gamma_H = 0$
- NitrateExpression: $\gamma_{NO3} - \gamma_{NO2} = 0$
- YieldExpression: $Y_H - 1/\gamma_{Ss} = 0$

where Y_H refers to the yield coefficient of the heterotropic biomass.

A computational software, such as like Mathmetica (Wolfram research), can be used to solve the resulting system of equations. Each process reaction is therefore uniquely specified as a function of the elemental fraction of each compound, the yield coefficients of heterotrophic and autotrophic biomass (Y_H and Y_A, respectively), the nitrogen contents of biomass and particulate products from biomass decay (i_XB and i_XP, respectively), and the biodegradable fraction of biomass (f_p). Stoichiometric coefficients are calculated in molar units according to the elemental balance equation for each process. The stoichiometric reactions of all processes of ASMN that are derived from these calculations are provided in Appendix A. An example of the stoichiometric reaction derived for the anoxic growth of heterotrophs with nitrate as the electron donor ($NO_3^- \rightarrow NO_2^-$) is shown below:

$$\frac{1}{Y_H}C_{c1}H_{h1}O_{o1}+\frac{-4c_1-h_1+2o_1+(4c_2+h_2-3n_2-2o_2)Y_\mathrm{H}}{2Y_\mathrm{H}}NO_3^-+n_2NH_4^+$$
$$\rightarrow C_{c2}H_{h2}N_{n2}O_{o2}+\frac{-4c_1-h_1+2o_1+(4c_2+h_2-3n_2-2o_2)Y_\mathrm{H}}{2Y_\mathrm{H}}NO_2^-$$
$$+\frac{-h_1+(h_2-3n_2)Y_\mathrm{H}}{2Y_\mathrm{H}}H_2O+\frac{-c_1+c_2Y_H}{Y_H}CO_2+n_2H^+ \qquad (2.3)$$

To produce the information needed to specify ASM equivalent coefficients, the elemental compositions of all compounds considered and stoichiometric coefficients of processes derived above are programmed into a spreadsheet. Then they are converted into a new subsequent matrix in terms of gram equivalent (nitrogen compounds, and inorganic matter) and COD (organic matter) units following the ASM format.

Stoichiometries formulated into the two matrix spreadsheets (as molar and gCOD units) are evaluated using a continuity check of C, H, O, N, COD, and charge as presented in Reichert et al. (2001). This provides a straightforward way of guaranteeing the validity of the model. In order to make a proper check of COD and charge balance, the concept of electron equivalent is used for oxidized or reduced compounds like nitrogen compounds. Here, 1 mole of electrons is assumed to be equivalent to 8g of COD (Heijnen, 1999). Table 2.1 provides conversion values for different oxidation states of nitrogen compounds during biochemical operations. It should be noted that the conversion must be performed using a fraction, not a decimal equivalent number, otherwise the model can produce small but not zero errors in the elemental balances when applied to model simulated WWTP inputs and outputs as a result of round off errors.

Table 2.1: Conversion values used for checking COD and electron balance in ASMN

Conversions	Changes in oxidation state	Values of fraction	Approximate values
$NH_4^+ \rightarrow NO_3^-$	(-3) → (+5)	64/14	4.571
$NH_4^+ \rightarrow NO_2^-$	(-3) → (+3)	48/14	3.429
$NH_4^+ \rightarrow NO$	(-3) → (+2)	40/14	2.857
$NH_4^+ \rightarrow N_2O$	(-3) → (+1)	32/14	2.286
$NH_4^+ \rightarrow N_2$	(-3) → (0)	24/14	1.714
$NO_3^- \rightarrow NO_2^-$	(+5) → (+3)	-16/14	-1.143
$NO_2^- \rightarrow NO$	(+3) → (+2)	-8/14	-0.517
$NO \rightarrow N_2O$	(+2) → (+1)	-8/14	-0.571
$N_2O \rightarrow N_2$	(+1) → (0)	-8/14	-0.571

Step 3. Determine the elemental composition of model state variables

Once the complete model matrix is obtained, the unknown composition formula of organic matter ($C_cH_hO_oN_n$) can be determined by specifying a small number of additional parameters (yield coefficient, nitrogen content in organic matter, and fraction of biomass converted to inert matter). In order to reproduce the stoichiometry of the ASMN and to obtain the composition formula of organic matter, the default parameter values recommended in Hiatt and Grady (2008) are used to provide kinetic information of the model. In addition, there are six state variables of organic matter that have an unspecified composition and need to be determined: S_S (substrate), S_I (soluble inert organic matter), X_B (biomass), X_I (particulate inert matter), X_P (particulate products resulting from biomass decay), and X_S (slowly biodegradable matter). The following procedure is used to specify the stoichiometry of these state variables. First, a widely recognized empirical formula ($C_5H_7NO_2$) is assigned to chemically define bacteria biomass (X_B, see Metcalf & Eddy, 2003). The model includes two inert matter state variables (S_I and X_I) that neither react within the system nor affect the results of modeling but play an important role in interfacing between ASMN and ADM1. Their elemental compositions are determined later using elemental balanced applied between unit process models. In this step, default compositions are given for the inert matter. Finally, the elemental compositions of the remaining organic matter state variables (S_S, X_P, and X_S) are determined based on model parameters and best available scientific knowledge on the elemental composition of the different influent fractions.

Step 4. Conduct model simulation

The validity of the proposed matrix is tested by the model simulation. A simple biological nutrient removal (BNR) process configuration as reported in Benchmark Simulation Model no. 2 (BSM2) (Nopens et al., 2010) is used here. The inflow of wastewater is equal to 30,000 m^3/d, whereas the biodegradable COD load to the plant corresponds to 510 mg/L. The WEST software (Mike by DHI, Denmark) is chosen as the simulator with the modifications presented. A steady-state simulation is conducted for 500 days using a two-step nitrification /denitrification configuration, as illustrated in Figure 2.1. The steady-state simulation results are applied to a spreadsheet to check mass balances over the plant. The balances are made by considering all incoming and outgoing fluxes of elements and their internal conversions within the system. The balance is influenced by biologically produced or consumed compounds and mass transfer between the liquid and gas phases. The conservation of each element is checked along the system one by one unit. Under steady-state conditions, the equation for COD balance in bioreactors is represented by:

$$\frac{\partial \mathrm{COD}}{\partial \mathrm{t}} \cdot \mathrm{V} = \mathrm{COD_i} - \mathrm{COD_o} - \mathrm{COD_d} + \mathrm{COD_s} - \mathrm{Aeration} = 0 \qquad (2.4)$$

where COD_i is inflow COD (kgCOD/d); COD_o is outflow COD (kgCOD/d); COD_d is COD demand for the transformation of nitrogen compounds (kgCOD/d); COD_s is outflow COD by nitrogen gas stripping (kgCOD/d); Aeration (kgO_2/d); V is reactor volume (m^3).

$$COD_d = 1.714 \cdot \Delta N_2 + 2.286 \cdot \Delta N_2O + 2.857 \cdot \Delta NO + 3.429 \cdot \Delta NO_2 + 4.571 \cdot \Delta NO_3 \quad (2.5)$$

where ΔN_2, ΔN_2O, ΔNO, ΔNO_2, and ΔNO_3 are the differences of nitrogen compounds between inflow and outflow (kgN/d).

$$COD_s = 1.714 \cdot N_{2,g} + 2.286 \cdot N_2O_g + 2.857 \cdot NO_g \quad (2.6)$$

where $N_{2,g}$, N_2O_g, and NO_g are nitrogen gas flows released to the atmosphere via gas stripping (kgN/d).

The equation for COD balance in the digester reads as:

$$\frac{\partial COD}{\partial t} \cdot V = COD_i - COD_o - COD_{biogas} = 0 \quad (2.7)$$

where COD_{biogas} is COD transformed from organic matter to biogas (i.e. CH_4 and H_2) (kgCOD/d).

The equation for carbon and nitrogen balance in bioreactors and digester is:

$$\frac{\partial M}{\partial t} \cdot V = M_i - M_o - M_s = 0 \quad (2.8)$$

where M_i is inflow mass (kg/d); M_o is outflow mass (kg/d); M_s is outflow mass by gas stripping (kg/d).

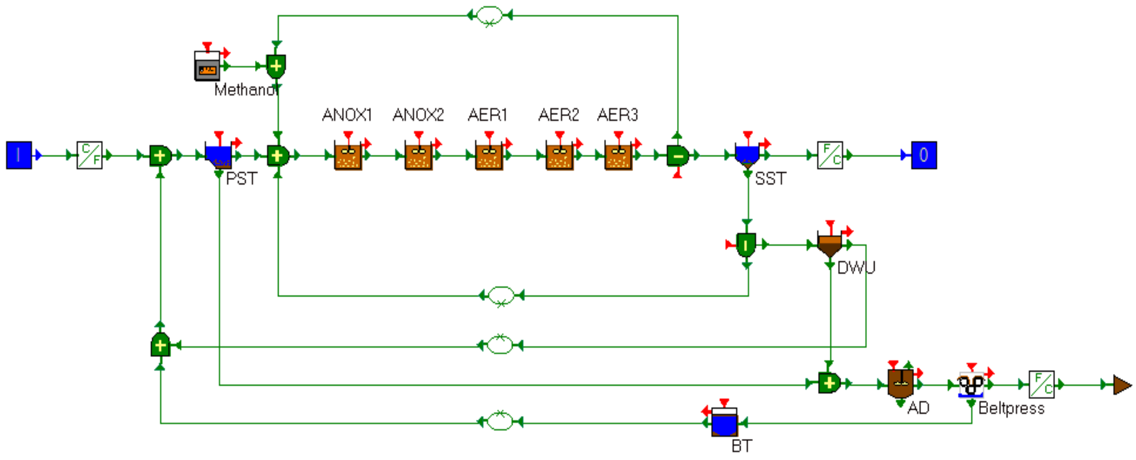

Figure 2.1: Configuration of the tested treatment plant. ANOX1 and ANOX2: anoxic reactors; AER1, AER2 and AER3: aerobic reactors; PST: primary settling tank; SST: secondary settling tank; DWU: dewatering unit; AD: anaerobic digester; BT: buffering tank.

Step 5. Finalize the composition of model state variables and stoichiometric coefficients

For a successful plant-wide simulation, interfaces between the activated sludge and the sludge digestion models need to be created (i.e. ASMNtoADM1 and ADM1toASMN were built to couple the two models). The interface must be able to connect the two models guaranteeing mass conservation. To define the interfaces, the method proposed by Nopens et al. (2009) was adopted with some modifications. This method was originally developed based on only COD and nitrogen balances, and a carbon balance was not considered. In our study, a particular effort is made to guarantee carbon continuity for interfaces. A modification of the ADM1 model is made by characterizing all model components of ADM1 using elemental composition in a similar way as applied to ASMN. The compositions of inert organic matter (S_I and X_I) in both models are adjusted iteratively until carbon mass balance is achieved. Production and release of GHGs are tracked from one unit process to the next. Through this approach it is possible to successfully construct the modified interfaces with the consideration of carbon and nitrogen balances, allowing plant-wide elemental balance over a WWTP.

Consequently, requiring an elemental balance of the complete plant-wide model, the chemical composition formulae for all state variables can be determined. Table 2.2 shows the chemical composition of the organic matter state variables given our choice of biomass stoichiometry and kinetic parameters. In general organic matter composition can vary depending on influent characteristics and system kinetics and be determined using our procedure. The stoichiometric coefficients as presented in ASMN are in agreement with the derived values utilizing our procedure. In practice, only the CO_2 state variable is newly incorporated into ASMN in conducting model simulations. The modified ASMN, including CO_2 related components is referred to as ASMN_G (Activated Sludge Model-Nitrogen for Greenhouse gas) in this study. Changes in CO_2 stoichiometric coefficients caused by variability in the composition of organic matter as shown in the next section provide an example of flexibility of the proposed model matrix to deal with a variety of influent compositions.

Table 2.2: Chemical composition of organic matter derived from elemental balances

Element (molar ratio)	Soluble inert organic matter (S_I)	Readily biodegradable substrate (S_S)	Particulate inert organic matter (X_I)	Slowly biodegradable substrate (X_S)	Particulate products from biomass decay (X_P)	Biomass (X_{BH}, X_{BA})
C	1.767	2.410	4.502	2.410	4.498	5.000
H	2.390	3.980	4.551	3.980	4.551	7.000
O	1.000	1.000	1.121	1.000	1.121	2.000
N	0	0	0.632	0	0.631	1.000

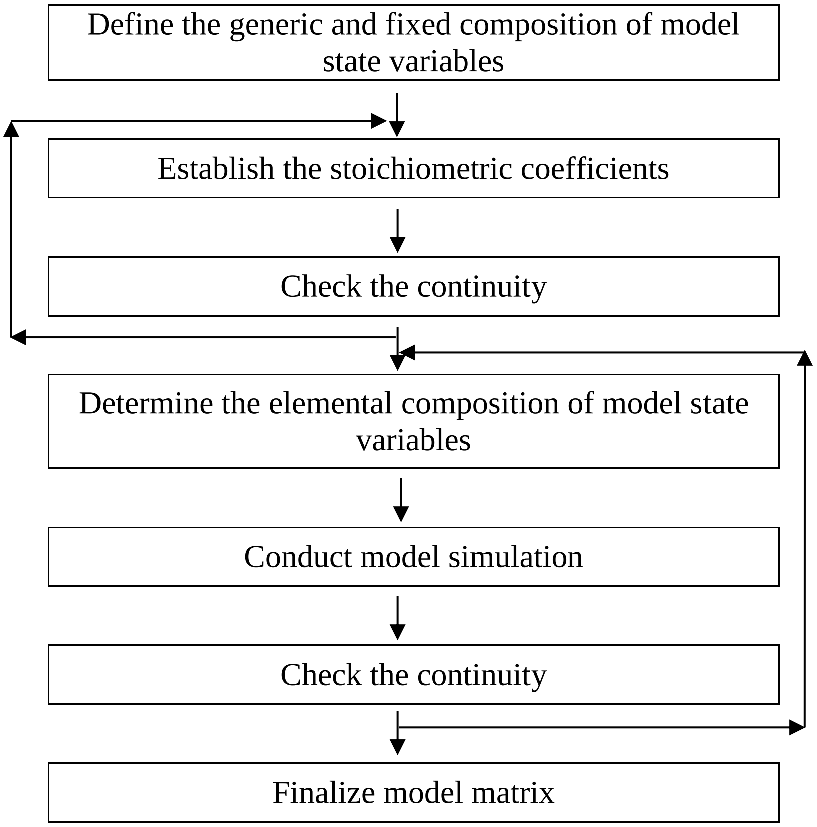

Figure 2.2: Scheme of the proposed procedure for the construction of the model matrix to implement plant-wide elemental balances

2.3 Results and Discussions

To test our procedure, the stoichiometry derived by our elemental balance method was compared with two alternative formulations. The first comparison was made to the original presentation of the ASMN model (Hiatt and Grady, 2008). The second comparison of derived stoichiometries was made to a stoichiometry determined using the electron equivalent-based method (Rittman and McCarty, 2011). In both cases, our method reproduced exactly the stoichiometry from these two methods when we used their values for stoichiometric and kinetic parameters such as yield coefficient. In both cases, elemental mass balances showed the plant wide models completely conserved mass.

CO_2 stoichiometric coefficients with two other carbon sources (glucose and acetate) were determined once the model matrix was determined (Table 2.3). It was assumed for this analysis, like the case giving the default parameter values of ASMN, 60% of carbon substrate as gram COD was utilized by biomass for its growth, while the remaining part was oxidized to CO_2 for energy production. This comparison revealed that the CO_2 production of each process could be significantly affected by the particular carbon source. For instance, when acetate was used as the carbon source rather than the baseline carbon source, CO_2 released per gram of biomass created increased by a factor of 2.36 for aerobic growth and 2.08 for anoxic growth (Table 2.3). Thus, the chemical compositions of organic matter and kinetic parameters like yield coefficients should be determined experimentally in practice to accurately predict CO_2 production.

The biomass composition may vary depending on operating conditions such as solids retention time (SRT). This composition is significantly correlated with biomass yield coefficient. As with most other studies, a fixed composition ($C_5H_7NO_2$) was used in this study assuming the elemental composition of the biomass would be much less variable than that of other organic compounds. It is apparent that if the chemical composition of biomass is fixed, its yield coefficient may be influenced strongly by the composition of organic substrate (Eq. (2.2)). For this reason, proper biomass yield coefficient should be considered for different substrates.

Table 2.3: Stoichiometric coefficients of carbon dioxide for different substrates

Process	CO_2 stoichiometric coefficients ($gCO_2/gCOD$ biomass)		
	This study ($C_{2.41}H_{3.98}O$)	Glucose ($C_6H_{12}O_6$)	Acetate ($C_2H_3O_2$)
Aerobic growth of biomass	0.5262	0.9167	1.2440
Anoxic growth of biomass	0.7374	1.1713	1.5351

The elemental balance method also provides us with the capability to retrieve more understanding about the fates of elements such as carbon and nitrogen. Figure 2.3 – 2.5 show the pathways of carbon, nitrogen, and COD in a WWTP for biological nitrogen removal under the steady-state condition described previously. As expected, the plant-wide mass balances for carbon, nitrogen, and COD over the system were closed with little residuals in a range of ± 0.00001%. On the other hand, it was impossible to define fixed elemental compositions of organic matter state variables under dynamic conditions because of the variations in carbon and nitrogen contents. Instead, the steady state values were used during dynamic simulations. A slight difference in the mass balance of C, N, and COD was recognized in the range of approximately ± 5%. According to mass balance calculations, approximately 46 % of influent carbon is released in the form of CO_2 (Figure 2.3) and less than 9 % of influent nitrogen is transformed into N_2O (Figure 2.4). A total COD removal of 95% is achieved: 38.8, 32.9, and, 23.4% from the bioreactor, digester, and sludge disposal, respectively (Figure 2.5). The amounts of organic carbon and nitrogen entering the receiving water body have been reduced greatly through the upstream of the plant. The pathway of each element may vary depending on operation conditions and system's performance. The results of plant-wide elemental balance are listed in detail in Appendix B.

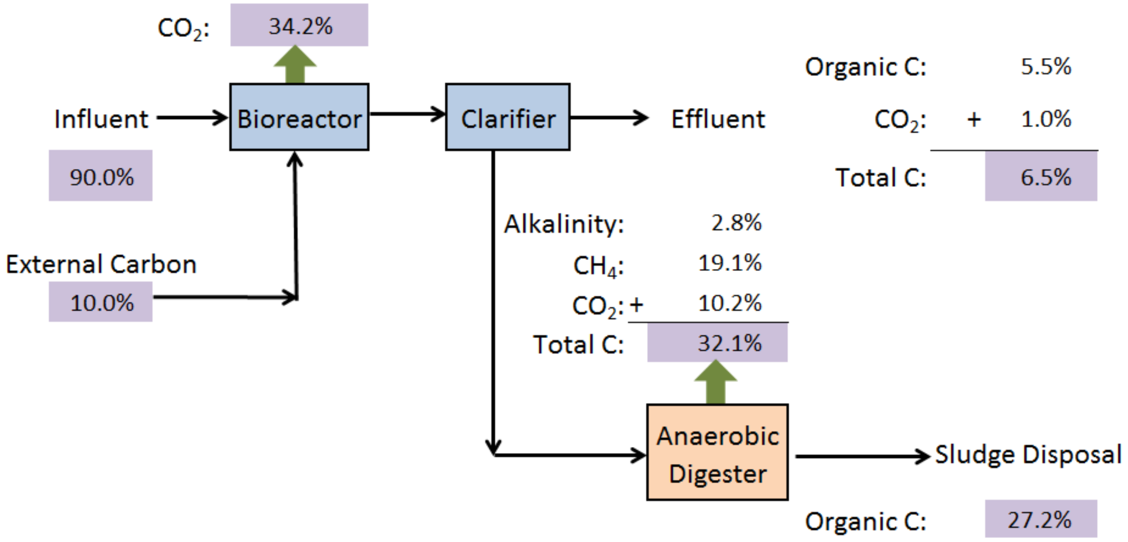

Figure 2.3: Fate of fed carbon derived from carbon mass balance over the two-step nitrification/denitrification wastewater treatment system with an anaerobic sludge digester

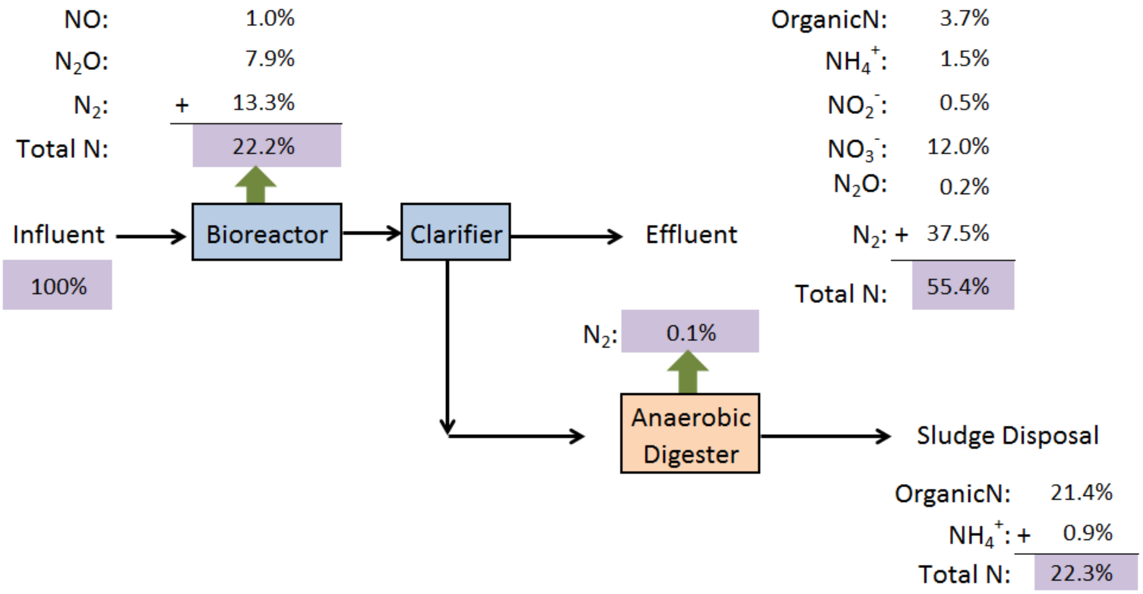

Figure 2.4: Fate of fed nitrogen derived from nitrogen mass balance over the two-step nitrification/denitrification wastewater treatment system with an anaerobic sludge digester

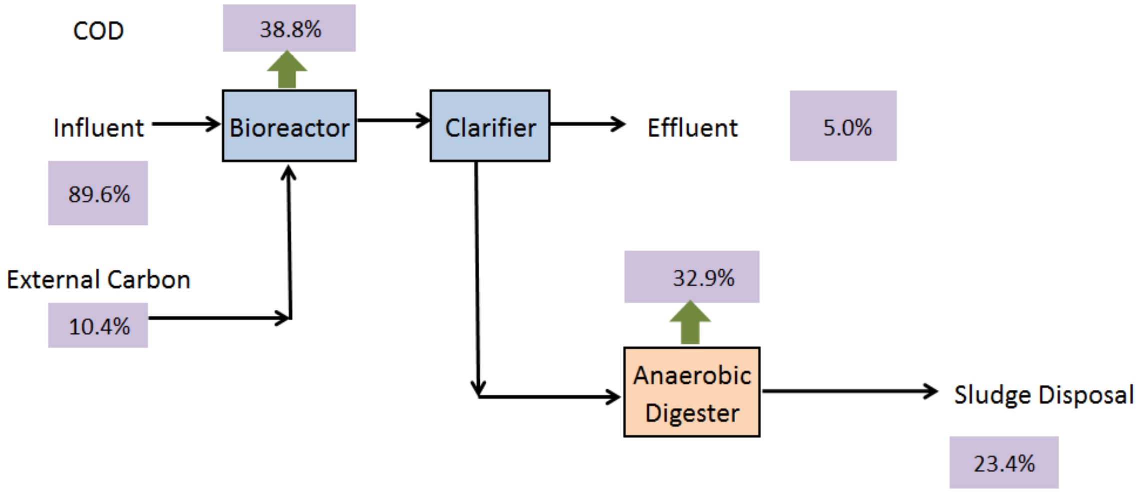

Figure 2.5: Fate of fed COD derived from COD mass balance over the two-step nitrification/denitrification wastewater treatment system with an anaerobic sludge digester

One of the critical considerations in developing this model was how alkalinity might be included into model formulation for better carbon dioxide estimation. In current ASMs, the alkalinity is generally calculated by the charge balance of several ions involved. Indeed, substantial increases in CO_2 production in proportion to the total alkalinity consumption were observed when defining the alkalinity as bicarbonate (HCO_3^-), which is generally accepted in the literature. To overcome this issue, the alkalinity was calculated using a proton balance.

The model parameters for the carbon and nitrogen fraction of organic matter are assumed to have unique values. However, in dynamic simulations it is not strictly correct to assign a unique value to the model parameters that are affected by varying influent. For example, for the same reason, the parameters proposed for the interface may cause unclosed elemental mass balances in dynamic simulations. Accordingly, stoichiometric and kinetic coefficients would need to be dynamically adjusted to reflect the characteristics of a given influent. Such a dynamic adjustment of model parameters is not an available feature of the current set of wastewater treatment plant models.

2.4 Conclusions

As outlined in the introduction, the focus of this chapter was to develop a new mathematical model with the aim to offer accurate evaluation of greenhouse gas emissions generated from WWTPs without restricting the analysis to a particular substrate composition. In contrast with existing model, the most important development of the new model is the inclusion of the mechanism of production and utilization of CO_2 in heterotrophic and autotrophic metabolism into an existing activated sludge model (i.e. ASMN). A stepwise procedure for developing an activated sludge model using elemental balancing was proposed. The stoichiometry derived from elemental balances was transformed into the equivalent stoichiometry of the ASMN model formulation. The model proposed was fully conservative in terms of carbon in addition to COD, oxygen, nitrogen, and ionic charge. The extension of the model was verified by detecting inconsistencies and closing elemental mass balances within the model matrix. This method was successfully tested on a complete wastewater system and can give a useful way to track certain components of interest in wastewaters; however, its validity still needs to be supported by applying to monitoring data obtained from full-scale activated sludge systems.

The advantage of the proposed approach is that the formulations of stoichiometric coefficients are determined as functions of elemental composition of compounds and organisms and that the model is created in a general form. As a result, the model development procedure described and tested here facilitates the application of the model to a broad range of wastewater and bacteria culture. With the presented methodology using elemental balancing, useful information on the pathways of elements of special interests (i.e. carbon and nitrogen) was provided. Moreover, this method could be used to generate kinetic parameters fitting to different characteristics of wastewater by assuming that state variable composition is independent of influent organic matter composition.

CHAPTER 3: COMPREHENSIVE MATHEMATICAL MODELING OF GREENHOUSE GAS EMISSIONS FROM WASTEWATER TREATMENT PLANTS

Abstract

This chapter describes a model that was developed in order to more accurately predict greenhouse gas (GHG) emissions from wastewater treatment plants (WWTPs). In the proposed model, an existing activated sludge model was extended to include carbon dioxide (CO_2) as a state variable and to include a nitrifier-denitrification process. The model was verified using the elemental balance method under steady-state conditions. The model includes (1) direct emissions from both biological wastewater treatment and sludge digestion processes and (2) indirect emissions caused by the consumption of materials such as electricity, heat, and chemicals used for plant operations. Using the proposed model, GHG emissions were evaluated in a biological nutrient removal (BNR) process. Direct emissions accounted for approximately 90 percent of total GHG emissions in the plant. Nitrous oxide (N_2O) and methane (CH_4) emissions were the two largest sources of emissions, representing 43 and 34 percent of total GHG emissions, respectively. Next, the effects of varying design and operational parameters on GHG emissions were examined under open-loop and control-loop systems. The dissolved oxygen (DO) controlled closed-loop system was found to reduce both sensitivity and uncertainty of the GHG emissions. Based upon the sensitivity analysis results, both the DO concentrations in the aerobic reactors and the aerobic reactor volume strongly

responded to increases of GHG emissions within the WWT system. In addition, N_2O emission was much more sensitive under different design and operating conditions, especially under the open-loop system, compared to CH_4 and CO_2 emissions. This indicates that N_2O emission has a significant GHG mitigation potential in the system. According to the results of the uncertainty analysis, it was concluded that the potential overall level of uncertainty in GHGs estimates could be significant and N_2O emissions dominant in both magnitude and uncertainty. With the information obtained from this study, operation and system design can be optimized with the aim of strategizing to reduce GHG emissions from a wastewater treatment system.

3.1 Introduction

As global warming has become a notable global concern, a number of efforts have been made to estimate greenhouse gases (GHGs) from wastewater treatment plants (WWTPs) over the last two decades (Czepiel et al., 1995; Keller and Hartley, 2003; Daigger et.al., 2004; Greenfield and Batstone, 2005; Kampschreur et al., 2008; Ahn et al., 2010). As a result, various tools and protocols for assessing GHG emissions are currently available in the area of wastewater treatment (e.g. IPCC, 2006; Cakir and Stenstron, 2005; Monteith et al., 2005; Sahely et al., 2006; Shahabadi et al., 2009; Subramanian, 2010; Flores-Alsina et al., 2011; Corominas et al., 2012).

To date, the Intergovernmental Panel on Climate Change (IPCC) protocol is recognized as the most widely-used accounting tool for GHG emissions inventories worldwide, and most current estimates of GHG emissions (e.g. U.S. Greenhouse Gas Inventory) follow the IPCC protocol with some modifications (U.S EPA, 2013). Originally, this protocol was developed to account for national-level emissions from wastewater treatment using generic calculation formulas and simple information such as emission factors, types of treatment employed, etc. It is now widely recognized that although the IPCC approach has been often used and may be suitable for national or regional scale estimations; it does not account for facility-specific treatment trains, nor does it account for the varying operating conditions in a WWTP. Indeed, wastewater treatment processes are unique to every plant and their operations vary depending on the plant configuration, influent characteristics, and environmental conditions (e.g. temperature). For this reason, a continuous research effort has been carried out on GHG estimations, particularly on nitrous oxide (N_2O) emissions. In recent studies, in order to improve accuracy and appropriateness for facility-level estimates, mechanistic models with a higher degree of detail like the activated sludge models (ASMs) have been used for estimating the GHG emissions from WWTPs to investigate the impact of system dynamics on GHG production (Hiatt and Grady, 2008; Flores-Alsina et al., 2011; Houweling et al., 2011; Corominas et al., 2012; Ni et al., 2012; Rodriguez-Garcia et al., 2012).

There is a major debate on whether biogenic carbon dioxide (CO_2) emissions should be considered in the site-specific emission estimation. The IPCC specifies that the CO_2 emissions that arise from biogenic sources should not be included in the GHG emission total due to the assumption that over time re-growth of biomass equals consumption (IPCC, 2006). That is, the biodegradable organic fraction of biomass is assumed to be part of the renewable CO_2 cycle in the IPCC Guidelines. Many studies have supported the recommendation of the IPCC that wastewater treatment does not cause CO_2 emissions (Daigger et al., 2004, Greenfield and Bastone, 2005; Hara and Mino, 2008; Prendez and Lara-Gonzalez, 2008). This issue has been debated by Keller and Hartley (2003); Cakir and Stemstrom (2005); Monteith et al. (2005); Sahely et al. (2006); Machado et al. (2007); Rosso and Stenstorm (2008); and Griffith et al. (2009). Sahely et al. (2006) argued that the concept of no net CO_2 resulting from the growth of biomass or from the production and combustion of renewable fuels is only applicable for those pursing national level studies. Rosso and Stenstorm (2008) stated that the carbon from biogenic sources may contribute to the greenhouse effect and that the reduction of carbon from sustainable sources may retard its emission cycle and even global warming. All current practices include biogenic methane (CH_4) and N_2O. The IPCC Guidelines assumes that all organic carbons that are present in the influent wastewater are not derived from fossil carbon sources, however, Griffith et al. (2009) showed that 25% of wastewater dissolved organic carbon is fossil carbon. This issue is still open to discussion. Although biogenic CO_2 emissions are not usually included in most protocols, the gross emissions including biogenic CO_2 could be significant and thus there is a potential tradeoff in the overall GHG budget. Hence, this study includes biogenic emissions, which are distinguished from anthropogenic emissions.

Biogenic CO_2 generated by wastewater treatment processes is a product of a series of microbial reactions such as biomass growth and decay, and its quantity can vary depending on influent characteristics and system kinetics. Biogenic CO_2 is also consumed by autotrophic bacteria as a carbon source. The CO_2 dynamics can be more accurately described when they are included in a simulation model. The biochemical mechanisms of N_2O production during biological nitrogen removal have also been included in activated sludge models in some recent studies (Hiatt and Grady, 2008; Houweling et al., 2011). On the other hand, probably due to the relatively clear understanding on the processes forming CO_2, few studies have bothered to extend the activated sludge models for CO_2 (Snowling et al., 2006). In most studies, biogenic CO_2 has been estimated by simple comprehensive models, which account for GHG emissions aroused from biodegradation of organic matter, endogenous respiration, and anaerobic digestion using a simple mass balance method (Monteith et al., 2005; Sahely et al., 2006; Flores-Alsina et al., 2011; Corominas et al., 2012; Ni et al., 2012). As a result, there is a need to include CO_2 emissions in a mechanistic model, thereby increasing the fundamental understanding of the overall GHG emissions under various conditions in a wastewater treatment system.

Following from above, the main objective of this chapter is to develop a plant-wide model for a more accurate and comprehensive estimation of GHG emissions from wastewater treatment plants. The model accounts for both the anthropogenic and biogenic emissions in order to look at the overall GHG emissions from a treatment plant. The model also encompasses three sub-models: two process models (i.e. an activated sludge model and an anaerobic sludge digestion model) and an indirect emission model. Conceptually, indirect emissions are released off-site as a result of the use of imported resources such as electricity and chemicals for the operation of WWTPs. The sub-models allow us to properly account for the plant-wide interactions between wastewater substrates and GHGs in a complex wastewater treatment system. A sensitivity analysis of the model output is performed to identify how key input parameters, including but not limited to aeration, sludge return, sludge retention time, and digester volume, contribute to overall GHG emissions over a system. The study is intended to provide a mechanistic framework for a more precise estimation of GHG emissions to be used for development of mitigation strategies, thereby highlighting the factors where GHG emissions are expected to be reduced. An uncertainty analysis is also carried out using a Monte Carlo simulation, which provides an estimate of the potential variability in GHG emissions. Among the various sources of uncertainties in the model, the uncertainties originating from key parameters are evaluated and compared.

3.1.1 Greenhouse Gas Production in Wastewater Treatment Plants

The aim of wastewater treatment systems is to minimize the adverse impacts of discharging untreated wastewater to the environment. However, wastewater treatment systems inadvertently create other negative impacts such as greenhouse gas emissions. The quantity and distribution of GHGs produced may depend on influent characteristics, effluent quality requirements, wastewater treatment processes used, etc. GHGs are produced directly or indirectly through wastewater and sludge treatment systems (i.e. direct emission) and activities required to maintain a facility, mainly for the use of chemicals and energy (i.e. indirect emission). Due to their biodegradability, most municipal wastewaters are commonly treated by different types of biological processes, ranging from a conventional activated sludge process to an advanced tertiary treatment technology for removing carbon and nutrients. In these biological processes, the removal of organic matter and nutrients is carried out by a biological degradation process utilizing biochemical metabolism of a variety of microorganisms (Figure 3.1). Here, different types of GHGs are naturally created as by-products, depending on process configurations, influent characteristics, and operating conditions. The amount of GHGs released is highly affected by the effluent quality requirements. Namely, as water quality regulations are tightened, a greater portion of the constituents removed are converted to GHGs and a smaller portion is discharged off-site through effluents or waste solids. The principal mechanisms of GHG production-reduction in wastewater treatment processes are reviewed in the following section.

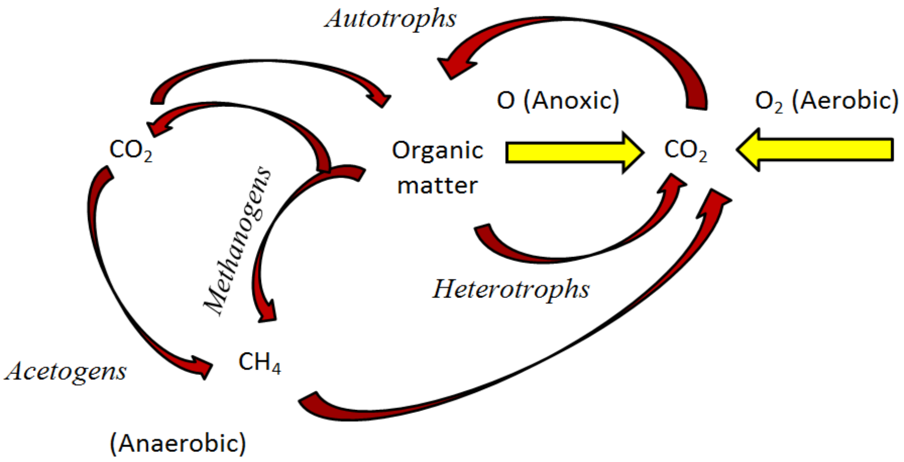

Figure 3.1: Conceptual diagrams of CO_2 and CH_4 production pathways in biological wastewater treatment processes

3.1.2 Aerobic Carbon Degradation Process

Aerobic treatment processes are usually preferred to handle relatively low concentrations of wastewater. Under aerobic conditions, biodegradable organic matter in the wastewater is stabilized by microbial metabolism. CO_2 is the main end product of aerobic degradation of organic matter in the process, and therefore the amount of CO_2 produced could be simply predicted by means of oxygen consumption in the carbon removal process. However, this approach is inappropriate for biological nutrient removal (BNR) processes since oxygen consumption may be much higher due to nitrification. In addition, a fraction of the organic carbon incorporated to biomass under aeration is converted to CO_2 via endogenous respiration. CH_4 can also be generated when aerobic processes are poorly managed. Aerobic operation is an energy-intensive unit process in most wastewater treatment plants because a significant amount of air is required for heterotrophic respiration and nitrogen oxidation. The greenhouse gas emissions from energy production processes (e.g. electricity) depend highly on the type of energy source. For example, electricity produced from hydropower or nuclear may contribute negligible greenhouse gas emissions (IPCC, 2006).

3.1.3 Biological Nitrogen Removal Process

Driven by water quality directives through enhanced government regulations, many WWTPs have been built or upgraded particularly to achieve intensive organic matter removal and biological nutrient removal. The biological nitrification and denitrification processes are considered feasible and practical ways to remove nitrogen compounds present in wastewater treatment systems in which two groups of bacteria (i.e. ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB)) are involved. However, these biological nitrogen removal processes have been revealed to be significant sources of N_2O emissions (Itokawa et al., 2000; Chandran and Smets, 2008; Butler et al., 2009). While the mechanisms of CO_2 and CH_4 production are quite well-known, those for N_2O production are relatively less understood and still open to question. Recently, due to its global warming potential, N_2O production, which was ignored in the past, is gaining more interest in the field of wastewater treatment. Early studies on N_2O in WWTPs focused on heterotrophic denitrification, which was thought to be a major source of N_2O emissions from nitrogen removal processes (Schulthess et al., 1994; Witcht, 1996; Barton and Atwater, 2002). However, recent studies have revealed that nitrification also plays a significant role in N_2O production, and NO_2 can also be produced by AOB (Tallec et al., 2006; Kamschreur et al., 2008; Chandran et al., 2011). No apparent potential for N_2O production by NOB is reported in the literature so far.

Complicating the prediction of N_2O emissions from a BNR process is the fact that there are several possible pathways of N_2O production during nitrogen transformations. To date, three main possible hypotheses for N_2O production from activated sludge processes have been presented in the literature (Colliver and Stephenson, 2000; Wrage et al., 2001; Tallec et al., 2006; Kamschreur et al., 2009), as shown in Figure 3.2: (1) hydroxylamine (NH_2OH) oxidation (2) nitrifier denitrification, and (3) heterotrophic denitrification. NH_2OH is a reactive intermediate of an ammonium oxidizing process by ammonia mono-oxygenase (AMO), which is generally further oxidized to nitrite (NO_2^-) or reduced to N_2O. In nitrifier denitrification, NO_2^- is first transformed into nitric oxide (NO) and then into N_2O by AOB where ammonia can serve as an electron donor under oxygen-limited conditions. In heterotrophic denitrification, fully oxidized nitrate (NO_3^-) is sequentially reduced to dinitrogen (N_2) by denitrifiers, and N_2O is produced as an intermediate of the catabolic pathway due to incomplete denitrification. Recent reviews of the literature by Itokawa et al. (2001); Tallec et al. (2006); Wu et al. (2009); Kampschreur et al. (2009); Lu and Chandran (2010) pointed out that N_2O production is closely correlated to several favorable operating environments such as low dissolved oxygen concentration during nitrification and denitrification, elevated nitrite concentration in nitrification and denitrification, and low chemical oxygen demand (COD)/nitrogen (N) ratio in denitrification.

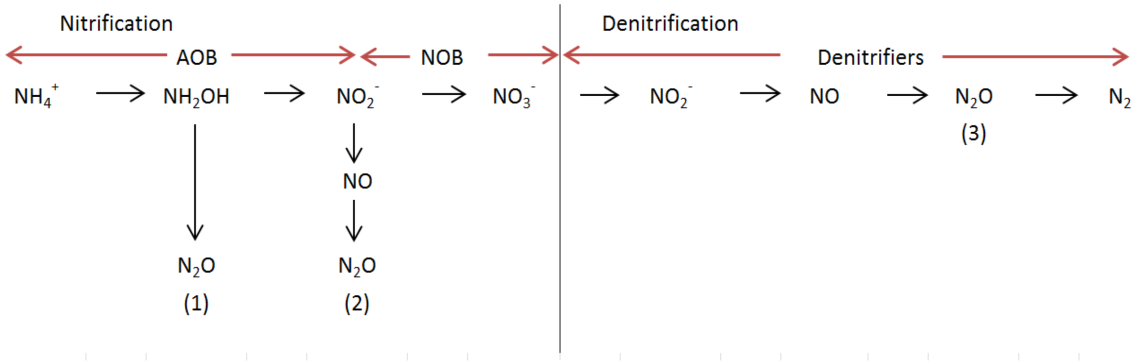

Figure 3.2: Conceptual diagrams of N_2O production pathways in biological nitrogen removal process (nitrification /denitrification)

While N_2O production from the denitrification process has a better-known mechanism (pathway 3), despite numerous studies demonstrating the potential for N_2O production during nitrification, the mechanisms for the production of N_2O from other pathways (1 and 2) remain unclear (Schuthess et al., 1994; Itokawa et al., 2001; Tallec et al., 2006; Kampschreur et al., 2007; Kampschreur et al., 2008). To date, several researchers have proposed models to quantify N_2O generation from nitrification, and work by several research groups is still being carried out in order to obtain a better understanding of the fundamentals of N_2O productions at various operating conditions (Ni et al. 2011; Chandran et al., 2011; Wunderlin et al., 2012; Mampaey et al., 2013). Accordingly, further knowledge of the microbial processes and the factors affecting N_2O production in wastewater treatment facilities is still needed.

N_2O can be emitted to the environment from wastewater treatment plants through gas stripping or effluents. According to the U.S. EPA estimates (2013), the majority of N_2O emissions from wastewater treatment plants are released from the treated wastewater effluent. When left untreated, discharge of nitrogen species into receiving water bodies may lead to aquatic problems (e.g. eutrophication). Both nitrification and denitrification processes also contribute to the generation of carbon dioxide since these two processes produce biomass and undergo endogenous decay. In addition, complete nitrification requires more energy to deliver the required amounts of oxygen via aeration. In most cases, the addition of alkalinity is required for the nitrification process, both of which are indirectly linked to GHG emissions. In most BNR processes, depending on the influent wastewater characteristics, an external carbon source (e.g. methanol) may be necessary to achieve complete biological nitrogen removal in the denitrification process, which may result in additional CO_2 production.

3.1.4 Anaerobic Process

In WWTPs, anaerobic processes are generally used for high-strength organic wastewater and sludge treatments. Anaerobic processes take place when organic matter is utilized as an electron acceptor in the absence of oxygen and nitrate. Three separate basic steps with multiple series and parallel reactions are included in the overall oxidation of complex biodegradable components in an anaerobic process: (1) hydrolysis, (2) fermentation, and (3) methanogenesis (Batstone et al., 2002). In the first stage, the particulate material is hydrolyzed to soluble compounds and simple monomers (i.e. amino acids, sugars, and fatty acids) that are used in the next stage by fermentation bacteria. During the second stage, amino acids, sugars, and fatty acids are degraded further. During this process, organic substances serve as both the electron donors and acceptors. The principal products of the fermentation are acetate, hydrogen, carbon dioxide, propionate and butyrate. The propionate and butyrate are fermented further to produce hydrogen, carbon dioxide, and acetate. Thus, the final products of fermentation are acetate, hydrogen, and carbon dioxide which bolster methane formation during the methanogenisis stage. In the final stage, methane is produced as a result of the growth of two different groups of organisms. The first is acetoclastic methanogens that transform acetate into methane and CO_2. The second is hydrogenotrophic methanogens that produce methane from the reaction of carbon dioxide and hydrogen by using hydrogen as an electron donor and CO_2 as an electron acceptor. When CO_2 is used as an electron acceptor, it is reduced to CH_4. As a result of anaerobic biodegradation processes, the produced GHGs are in the form of CO_2 and CH_4. Normally, the biogas produced during anaerobic processes contains 60-70% CH_4 and 30-35% CO_2 on a volume basis (Metcalf and Eddy, 2003).

The methane produced from anaerobic digesters is commonly combusted in large-scale plants to generate energy, or flared and converted to CO_2 in small plants to lessen the explosion hazard. In some cases, CH_4 emissions from these processes are not treated, but released directly into the atmosphere either intentionally or unintentionally. In a plant where fossil fuel is replaced by CH_4 for the digester and building heating, the indirect emissions by fuel consumption are avoided and CO_2 is emitted instead of CH_4, which has 25 times higher global warming potential compared to CO_2. Accordingly, the net GHG emission can be negative due to CO_2 savings. When the produced CH_4 is released into atmosphere due to accidental leakage of biogas, its impact on global warming could be considerable. Because the majority of methane produced is captured and treated to CO_2 under general operating conditions, the quantity of leakage is expected to be small. In addition to anaerobic processes, CH_4 is expected to be emitted when aerobic processes are poorly controlled.

3.2 Methods

In this study, a mathematical model quantifying greenhouse gas emissions from a wastewater treatment plant was developed using an activated sludge model based on the available knowledge from the literature. The comprehensive estimations included major direct and indirect sources of GHG emissions. The following sub-models were developed:

- The indirect emissions, which are caused by on-site use of heat, electricity, and chemicals.
- The direct emissions, which are generated due to the activated sludge wastewater treatment process and anaerobic sludge digestion.

Direct emissions from wastewater treatment processes were described by using mechanistic models, while indirect emissions were quantified by empirical models based on the available knowledge of the mechanisms of the system. The direct emission model covered two major process units associated with GHGs emissions, including the activated sludge process and the anaerobic digestion process. Overall estimates were normalized in global warming potential (GWP) unit as CO_2-equivalents after unit conversions in the model since GHGs have different heat absorbing capacities. The proposed model were codified and implemented in the WEST simulator software (MIKE by DHI, Denmark).

3.2.1 Direct Emission Model

3.2.1.1 CO_2 Emissions from Activated Sludge Process

The Activated Sludge Model-Nitrogen (ASMN) model proposed by Hiatt and Grady (2008) was selected as the base model since the ASMN has been widely used within the scientific fields for estimating N_2O emissions from biological nitrogen removal processes (e.g. Flores-Alsina et al., 2011; Porro et al., 2011; Corominas et al., 2012). In the WEST, the ASMN is simplified by removing less important processes and state variables, and then is renamed as ASM1_2N4DN. There are four main process reactions in the model related to CO_2 emissions: (1) CO_2 production due to heterotrophic growth, (2) CO_2 production arising from biomass decay, (3) CO_2 uptake for autotrophic growth, and (4) dissolved CO_2 stripping to the atmosphere. Such sinks and sources of CO_2 in activated sludge system can be taken into account by adding CO_2 as a state variable. The process stoichiometry of CO_2 was formulated based on the available knowledge in the literature (Henze et al., 2000; Rittman and McCarty, 2001). For simplicity's sake, the natural phenomenon of CO_2/bicarbonate equilibrium was neglected assuming the system is maintained at constant pH. In this study, the ASM1_2N4DN was further extended to include CO_2 as a state variable using the elemental balance method as presented in Chapter 2. All process stoichiometries were reproduced based on elemental mass continuity in terms of C, H, O, N, and charge. The elemental balance method has the advantage of avoiding any elemental loss in the development of the model, as well as being able to analyze the fate of carbon and nitrogen over the system. The modified ASM1_2N4DN including CO_2 related components has been referred to as ASMN_G (Activated Sludge Model-Nitrogen for Greenhouse gases) in this study.

3.2.1.2 N_2O Emissions from Activated Sludge Process

Although the mechanisms remain unclear, several studies have demonstrated the formation of N_2O during the nitrification pathway by AOB under limited oxygen concentrations (Kuai and Verstraete, 1998; Colliver and Stephenson, 2000; Schreiber et al., 2009; Kamschreur et al., 2009; Chandran et al., 2011; Wunderlin et al., 2012;

Mampaey et al., 2013). Recognizing the importance of nitrifier denitrification as presented in the literature, the ASMN_G incorporated the potential for N_2O production processes by AOB in the model (pathway (2) in Figure 3.1). The inclusion was based on the comprehensive understanding of the nitrifier denitrification provided by Bock et al. (1995) with several assumptions: (1) AOB use ammonium as the electron donor and oxygen, nitric oxide and nitrite as electron acceptors (Colliver and Stephenson, 2000); (2) in the presence of low concentrations of dissolved oxygen, nitrite or nitric oxide is a more preferable electron acceptor than oxygen; (3) under anoxic conditions, nitrite or nitric oxide is the only electron acceptor; and (4) the nitrifier denitrification is accompanied by the growth of AOB. In order to describe what proportion of the electron is provided to electron acceptors (O_2, NO_2^-, and NO), the fraction of oxygen dependence (f_o) was formulated with the Monod-type equation as:

$$f_o = \frac{S_O}{K_{OA}+S_O} \qquad (3.1)$$

where S_O denotes the concentration of dissolved oxygen and K_{OA} is the oxygen half-saturation coefficient for AOB.

In case that this switch function is used in process rates, the nitrifier denitrification would halt at DO = 0. For this reason, f_o is placed in the stoichiometry rather than in the process rates. As defined above, the value of f_o determines the oxygen dependence of AOB in the denitrification process. This means that AOB utilizes electrons: the fraction, f_o from oxygen and $(1-f_o)$ from nitrite. In this study, f_o was estimated at near 0.8 and less than 0.01 for aerobic and anoxic conditions, respectively.

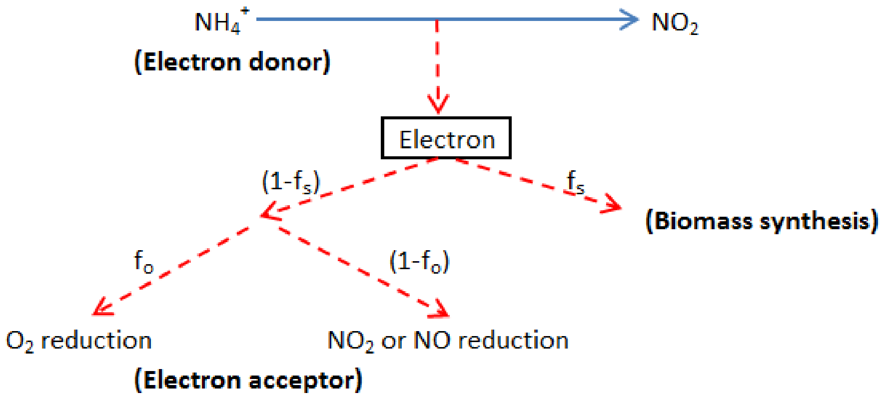

Figure 3.3: Schematic electron pathways in nitrifier denitrification. Dash lines indicate electron flows. f_s is the portion of electrons used for cell synthesis. f_o is the portion of electrons used for oxygen reduction.

The biological reactions for the two steps of nitrifier denitrification were derived on an electron-equivalent basis, considering all possible oxidation and reduction reactions that occur in the process (Rittman and McCarty, 2001). A full description to obtain the reactions is provided in Appendix C. Using the default value of AOB yield coefficient (0.18 gCOD/gNO_2^--N) in the ASMN_G, 32 % of the electron equivalents in an electron donor (ammonium) can be assumed to be used for cell synthesis (Hiatt and Grady, 2008). The nitrite reduction reaction by AOB was constructed:

$$(0.513-0.68f_o)\, NO_2^- + (0.347-0.68f_o)\, H^+ + 0.183NH_4^+ + 0.17f_oO_2 + 0.064CO_2 + 0.016HCO_3^- \rightarrow 0.016C_5H_7NO_2 + 0.68(1-f_o)\, NO + (0.34fo - 0.494)\, H_2O \qquad (3.2)$$

An important characteristic of this equation is that the stoichiometry may vary with the oxygen concentration in the system. For example, autotrophic denitrification relies more on nitrate than oxygen as an electron acceptor under limited dissolved oxygen concentrations. In the ASMN_G matrix, this reaction was formulated as a function of the

AOB (X_{BA1}) yield coefficient (Y_{A1}) and the nitrogen content of AOB (i_{XB}) by the following equation:

$$\left[\frac{1}{Y_{A1}} - (1 - f_o)\left(\frac{6}{Y_{A1}} - 1.75\right)\right] S_{NO2} + \left(i_{XB} + \frac{1}{Y_{A1}}\right) S_{NH} + f_o\left(\frac{24}{7Y_{A1}} - 1\right) S_O$$

$$+ \left(\frac{i_{XB}}{14} + \frac{1}{7\,Y_{A1}}\right) S_{alk}$$

$$\rightarrow X_{BA1} + (1 - f_o)\left(\frac{6}{Y_{A1}} - 1.75\right) S_{NO} \qquad (3.3)$$

Similarly, the nitric oxide reduction reaction by AOB was determined as:

$$0.68(1\text{-}f_o)\ NO + 0.183NH_4^+ + 0.17f_oO_2 + 0.064CO_2 + 0.016HCO_3^-$$

$$\rightarrow 0.016C_5H_7NO_2 + 0.34(1\text{-}f_o)\ N_2O + 0.167NO_2^- + 0.15H_2O + 0.33H^+ \qquad (3.4)$$

$$(1 - f_o)\left(\frac{6}{Y_{A1}} - 1.75\right) S_{NO} + \left(i_{XB} + \frac{1}{Y_{A1}}\right) S_{NH} + 1.375\ CO_2 + f_o\left(\frac{24}{7Y_{A1}} - 1\right) S_O$$

$$+ \left(\frac{i_{XB}}{14} + \frac{1}{7\,Y_{A1}}\right) S_{alk}$$

$$\rightarrow X_{BA1} + (1 - f_o)\left(\frac{6}{Y_{A1}} - 1.75\right) S_{N2O} + \frac{1}{Y_{A1}} S_{NO2} \qquad (3.5)$$

3.2.1.3 Biogas Emissions from Anaerobic Digestion

The use of the Anaerobic Digestion Model No. 1 (ADM1, Batstone et al., 2002) has been very common for a mathematical simulation of anaerobic fermentation of activated sludge, from which biogas production (e.g. CH_4, CO_2) has been successfully quantified (Blumensaat and Keller, 2005; Derbal et al., 2009; Thamsiriroj and Murphy, 2011). The biogas can be converted to energy in the form of electricity and heat. Since the ASMs and ADM1 use different sets of biological state variables, for plant wide simulation, the two different models need to be connected without any loss of elemental mass. Several interface approaches have been presented in the literature (Copp et al., 2003; Zaher et al., 2007; Grau et al., 2007; Ekama, 2009; Nopens et al., 2009) and the methodology proposed by Nopens et al (2009) is implemented in the WEST. Here, there is a practical issue related to the ASMN/ADM1 interface in terms of plant-wide carbon balancing. Due to the structures of the ASMN and ADM1, their interfaces have been built by considering only COD and N. Therefore, it is not possible to guarantee the elemental mass continuity of carbon. In order to overcome this limitation, the authors developed a method for the elemental compositions of state variables in both models as well as in both the ASM to ADM1 interface and the ADM1 to ASM interface, as illustrated in Chapter 2. Accidental methane production from primary treatment and sludge treatment due to poor operations were not considered as part of this work.

3.2.1.4 Gas Stripping

The model includes five gas components (i.e. O_2, CO_2, NO, N_2O and N_2). The supersaturated dissolved gases generated from processes are generally released from the system into the atmosphere by stripping. This liquid-to-gas transfer reaction may provide useful information on both the distribution of GHGs produced over the plant and the amount of GHGs presented in the effluent. The stripping out of gases due to aeration across the gas/liquid interface was calculated using the following formula:

$$Q_g = K_La \text{ x } (S - S^*) \text{ x } V \qquad (3.6)$$

where Q_g is the gas stripping rate (g/d) and K_La is the gas transfer coefficient in the liquid laminar layer (1/d). S* and S are gas concentrations at the air-liquid interface (saturated) and in the bulk liquid, respectively (g/m^3). V is the reactor volume (m^3).

The saturated concentrations of the gases in equilibrium with the gas phase pressure are proportional to their partial pressures in the atmosphere, and therefore the concentrations are calculated by using Henry's law constants provided by Sander (1999). Methane can be significantly supersaturated due to its low solubility and thus has a lower driving force when compared with CO_2. Molecular diffusion is a major transport pathway for dissolved gases into the atmosphere. Since the gas transfer coefficient can be expressed with its molecular diffusion coefficient (Merkel and Krauth, 1999), if the oxygen transfer coefficient is known, the mass transfer coefficient of each gas (K_La) can be estimated with:

$$K_La_{CO2} = K_La_{O2} \text{ x } \sqrt{\frac{D_{CO_2}}{D_{O_2}}} \tag{3.7}$$

where K_La_{CO2} and K_La_{O2} are the gas transfer coefficients for CO_2 and O_2, respectively. D_{CO2} and D_{O2} are the molecular diffusion coefficients for CO_2 and O_2, respectively (m^2/d).

3.2.2 Indirect Emission Model

The model considered three major indirect emission sources of greenhouse gases: electrical use, external carbon addition, and heating. Electricity consumptions for the process included in the model are for pumping, aeration, and mixing. The amount of required electricity for each unit was estimated by using the WEST simulator by means of oxygen transfer rates in aeration, flow rates, and tank volumes for aeration, pumping, and mixing, respectively. The indirect CO_2 emissions from off-site electricity generation were estimated on the basis of an emission factor (705.55 g CO_2e/kWh) provided by U.S. Environmental Protection Agency (EPA) database, Emissions & Generation Resource

Integrated Database (eGRID) 2012 Version 1.0 (U.S. EPA, 2012). Methanol was added into the anoxic bioreactor as an external carbon source for the denitrification process, and the amount was adjusted according to the desired level of effluent NO_3 concentration. The emission factor for methanol use (0.67 g CO_2e/g methanol) was based on data from IPCC (2006). Heat energy is needed for the anaerobic sludge digestion to maintain the optimal process temperature and is usually supplied from the biogas produced. The heating requirements were estimated from the calculation of heat loss through the wall structure of the digester and the heat required to raise the incoming temperature as presented by Zupancic and Ros (2003), using the formula:

$$HR = C \cdot A \cdot \Delta T + M_s \cdot H_s \cdot \Delta T \tag{3.8}$$

where C is the heat transfer coefficient ($W/m^2/^oC$) and A is the surface area of the digester through which heat loss occurs. The temperature difference term (ΔT) represents the temperature difference between the inside and outside of the digester (^oC), while M_s is the sludge mass load (kg/s) and H_s is the specific heat capacity of sludge (KJ/kg^oC).

The potential energy yield from the biogas was calculated using a lower heat capacity of methane (Zupancic and Ros, 2003), and then converted to CO_2 equivalent (CO_2e) to allow direct comparison to other emissions as well as to estimate carbon emission credit. All these descriptions for indirect emissions were combined with the process model to simulate system behavior.

3.2.3 Model Application

In order to apply the proposed model, a Modified Ludzack-Ettinger (MLE) process was evaluated using the configuration, as presented in the Benchmark Simulation Model 2 (BSM2) (Nopens et al., 2010) (Figure 3.4). The MLE process, which is designed for carbon and nitrogen removal, consists of two-stage anoxic and three-stage aerobic reactors in series. In this simulation, the volumes of each bioreactor are assumed to be 2,000 and 4,500 m^3 for anoxic and aerobic reactors, respectively. In the aerobic reactors (AER1-3), dissolved oxygen concentration (DO) is set up by different levels of oxygen transfer coefficients (K_{La}) for each aerobic reactor to maintain an optimal DO level (i.e. around 2 mg/L). The MLE process usually attained TN and TKN below their discharge limits without external carbon addition. However, when influent organic carbon level is low or excess influent organic carbon is removed from the primary settler, the system may require an external carbon source to support the denitrification process. In this study, methanol is added as the external carbon source to ensure stable nitrogen removal. Primary and secondary settlers are placed before and after the activated sludge reactors, respectively. Both the carbon-rich primary sludge and biomass-rich secondary sludge are sent to the anaerobic sludge digester. In the digester, most of the organic matter present in the sludge is degraded and part of it is transformed into biogas. The influent flow to the system is 30,000 m^3/d and the hydraulic retention time (HRT) is approximately 14 hours. The wastewater under study has an influent COD of 605 mg/ L and suspended solids (SS) concentration of 390 mg /L. A steady-state simulation was conducted for 500 days. During model simulations, under the solids retention time (SRT) of 17 days, approximately 450 days were required for the system to reach a steady state. The default parameter values presented in Hiatt and Grady (2008) and in the WEST were used, which correspond to a temperature of 20ºC.

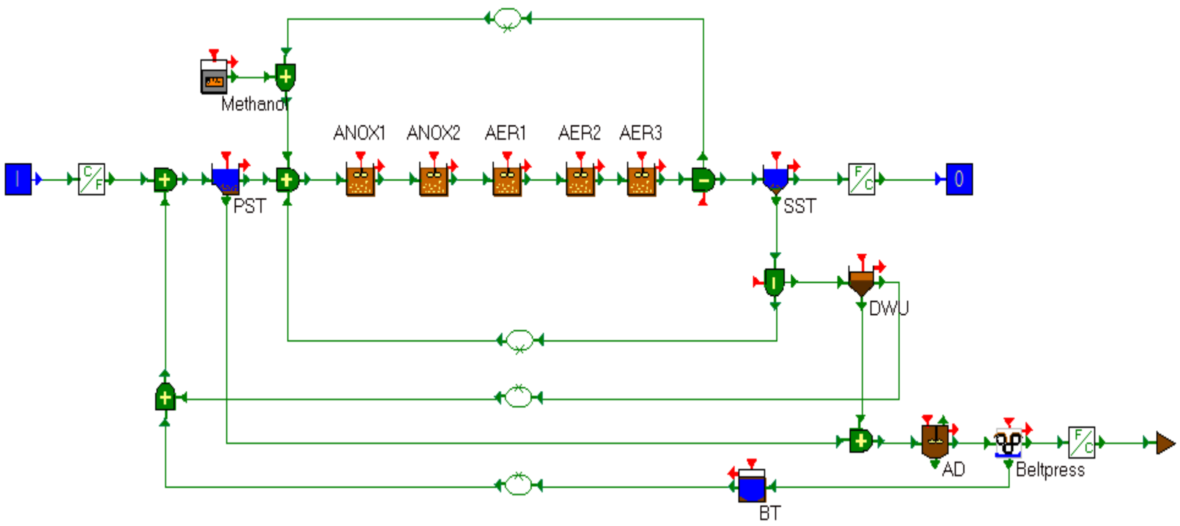

Figure 3.4: Configuration of the Modified Ludzack-Ettinger (MLE) under study. ANOX1 and ANOX2 : anoxic reactors; AER1, AER2 and AER3: aerobic reactors; PST: primary settling tank; SST: secondary settling tank; DWU: dewatering unit; AD: anaerobic digester; BT: buffering tank.

3.2.4 Sensitivity Analysis

Previous studies showed that physical configurations and operating conditions could influence GHG emissions from wastewater treatment (Kampschreur et al., 2008; Lu and Chandran, 2010; Porro et al., 2011). To determine the main factors influencing GHG emissions from a WWTP, the sensitivity of GHGs emissions to major input parameters was assessed. This analysis was carried out in open-loop (without controller) as well as closed-loop systems. In the open-loop operation, the system was modeled without any control strategy. All operational parameters such as aeration intensity in the aerobic reactors, internal recycle flow rate, and waste sludge flow rate were fixed at a value. In the closed-loop system, the dissolved oxygen level in each aerobic reactor was controlled with a proportional-integral (PI) control loop at a set point of 2 mg/L. Accordingly, aeration intensity may vary as concentrations of inflow COD into the aerobic reactors are altered. Several operational parameters can be controlled using closed-loop system, among which DO level substantially affects the production of GHGs. Overall 14 major input parameters were analyzed, including 10 operational parameters (i.e. (1) removal efficiency of COD for primary settler, (2) aeration intensity (open-loop) or DO set-point (closed-loop) in aerobic reactors, (3) operating temperature in anoxic/aerobic reactors, (4) internal recycle flow rate, (5) external carbon dose rate, (6) return sludge flow rate, (7) waste activated sludge flow rate, (8) removal efficiency of particulates in dewatering unit, (9) removal efficiency of particulates in belt-press, and (10) operating temperature in sludge digester) and 4 design parameters (i.e. (1) volume of anoxic reactor, (2) volume of aerobic reactor, (3) surface area of secondary settler, and (4) volume of sludge digester). These parameters were chosen among the major design and operational parameters that could be significantly influential in the model outputs. Model parameters were excluded from this simulation since the aim of this work was to identify the impact of changes in design and operations on GHG emissions. This information may be of value to those making decisions in process design and operation. A sensitivity analysis was performed in the WEST by perturbing each one of the 14 parameters. The influence of input parameters on GHG emissions was quantified using a relative sensitivity (RS) function because this sensitivity function is dimensionless and thus, facilitates comparison of the effects of different parameters on a target variable. The relative sensitivity can be expressed by the relative changes of model output for a given perturbation to input parameters:

$$\mathrm{RS} = \frac{\Delta \mathrm{M}_{\mathrm{GHG}}}{\Delta \mathrm{P}} \cdot \frac{\mathrm{P}}{\mathrm{M}_{\mathrm{GHG}}} \tag{3.9}$$

where P and ΔP, respectively, represent the reference value of input parameter and its variation. M_{GHG} and ΔM_{GHG}, respectively, is the reference value of model output (i.e. GHG emission) and its variation.

The sensitivity analysis was implemented by 500-day steady-state simulations in the WEST. The reference simulation with the default values of the input parameters was first run and 12 more runs were performed by varying each parameter with 1-10 percent perturbations. While running the model for sensitivity in each parameter, the other parameters were held constant without changing them from their default values. The combination of the 14 parameters and the 12 different variations for each parameter resulted in a total of 168 sensitivity functions. The results of the runs were saved into a spreadsheet for each run, and then the sensitivity functions were computed using Eq. (3.9).

3.2.5 Uncertainty Analysis

Although there are a variety of sources for uncertainty of GHG estimations in WWTPs, including model parameters, plant design, operating conditions, influent wastewater characteristics, etc, this uncertainty analysis focused on how the input parameters affect overall GHG emissions that were previously considered in the sensitivity analysis. For the open-loop system, the aeration density parameter was divided into three individual parameters for three sequential aerobic bioreactors because its value needs to be characterized by a specific value for each reactor rather than changed by percentages. Hence, in total 16 parameters were evaluated for the open-loop case. In the DO control loop system, a single DO level in the aerobic reactors was maintained at a same set point. Accordingly, 14 parameters were tested in this case. The uncertainty analysis using the Monte Carlo method was conducted by: (1) defining input parameters and their probability distribution functions, (2) generating sample input parameters, (3) calculating output variables through computer simulations, and (4) assessing the variation in GHG estimations. All of the input parameters were assumed to vary according to the uniform probability distribution function and their upper and lower bounds were assigned limits in the range of 3 - 65 % above and below their default values in order to avoid significant system disturbances that can lead to inhibition on microbiological activities, system malfunctions, or system failures. Ranges for these parameters represent the possibility of encountering fluctuations in process design or operation. Table 3.1 presents these parameters. Using these values, a sample of randomly selected values obtained by performing Latin Hypercube Sampling was generated using @RISK software version 5.7 (Palisade Corporation, 2011). A reasonable guide to determine the sample size was not found in the literature; thus in this study, the sample size was calculated by the number of testing parameters multiplied by 50 as presented by Benedetti et al. (2012).

Table 3.1: Ranges of input parameters specified for the uncertainty analysis

Parameter	Distribution function	Units	Default value	Lower bound	Upper bound
DO concentration in the first aerobic reactor	Uniform	g/m^3	2.0	0.5	5.0
Aeration intensity 1 (kla1)	Uniform	1/d	120	100	140
Aeration intensity 2 (kla2)	Uniform	1/d	90	70	110
Aeration intensity 3 (kla3)	Uniform	1/d	60	40	80
Methanol Dose	Uniform	m^3/d	3.5	2	5
Internal recycle	Uniform	m^3/d	86,000	30,000	120,000
Waste sludge	Uniform	m^3/d	400	200	800
Sludge underflow from secondary clarifier	Uniform	m^3/d	23,000	20,000	28,000
Operating temperature in bioreactor	Uniform	°C	15	10	20
Volume of a anoxic reactor	Uniform	m^3	2,000	1,500	2,500
Volume of a aerobic reactor	Uniform	m^3	4,500	4,000	5,000
COD removal efficiency in primary clarifier	Uniform	-	0.65	0.5	0.8
Particulate removal efficiency in dewatering unit	Uniform	-	0.98	0.95	1.0
Particulate removal efficiency in belt press	Uniform	-	0.98	0.95	1.0
Surface area of secondary clarifier	Uniform	m^2	2,500	2,000	3,000
Volume of sludge digester	Uniform	m^3	3,400	3,000	4,000
Operating temperature in sludge digester	Uniform	°C	35	30	40

3.3. Results

3.3.1 Estimation of GHG Emissions

Three operational scenarios were considered that may be encountered in estimating GHG emissions depending on the use of biogas produced from sludge digestion as presented in Figure 3.5. The total GHG emissions can be quantified from the sum of the greenhouse gases emitted into the atmosphere and those dissolved in the effluent at the steady-state condition. Scenario A assumes that biogas generated from anaerobic sludge digestion is released into the atmosphere without its recovery. Thus, this can be considered as the worst case scenario and as a reference case. The direct emissions, as a result of biological wastewater and sludge processes, accounted for about 90% of total GHG emissions, while indirect emissions were 10% of the total GHG emissions. Of the direct emissions, the contribution of biogenic CO_2, N_2O, and CH_4 to the total GHG emissions was approximately 10, 43, and 34 %, respectively. In Scenario B, biogas is captured from the anaerobic digester with no fugitive CH_4 emission, and 100% of the biogas collected is fully combusted to CO_2. This option would reduce the cumulative greenhouse gas emission by about 30%. Scenario C assumes that biogas is utilized for heating the sludge digester, and the surplus gains carbon emission credit. The results show the substantial potential of biogas recovery to contribute to mitigate GHG emissions in wastewater treatment as described by Greenfield and Batstone (2005). The best scenario results in a 45.3% reduction in total GHG emissions if all of the biogas could be captured and used for energy production.

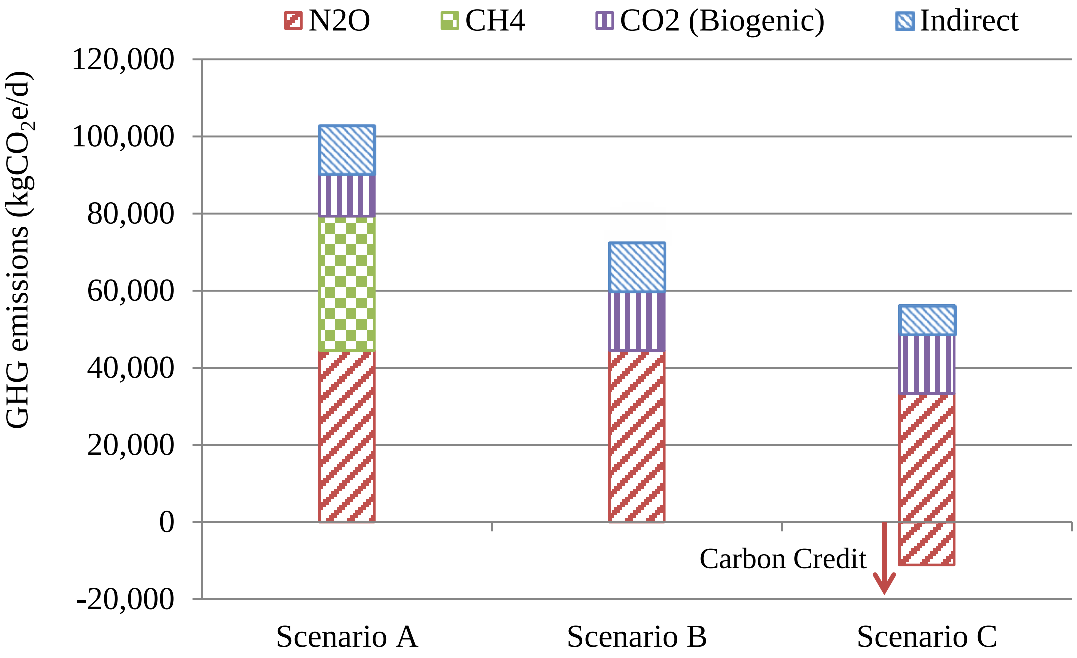

Figure 3.5: GHG emissions in different biogas usage scenarios in kgCO$_2$e/day. Scenario A: No CH$_4$ Collection, Scenario B: 100% CH$_4$ collection + Combustion, Scenario C: 100% CH$_4$ collection + Combustion + Energy recovery.

The influence of the plant configuration on the GHG level can be readily observed from the plot of dissolved CO$_2$ and N$_2$O gas concentrations in a series of reactors (Figure 3.6). In the anoxic zones (ANOX 1 & 2), heterotrophic activity leads to an increase of dissolved CO$_2$ concentration, whereas in the aeration zones (AER 1, 2, & 3), CO$_2$ stripping by aeration gives rise to a dramatic decrease in aqueous CO$_2$. In addition, although both CO$_2$ production by heterotrophic bacteria and CO$_2$ consumption by autotrophic bacteria simultaneously occur in the aerobic reactors, the CO$_2$ production is the predominant process in the aerobic system, and the net CO$_2$ production is always positive. The first anoxic reactor has a higher N$_2$O concentration compared to the second anoxic zone due to incomplete denitrification caused by entering DO presented in the internal recycle flow. Less strictly anoxic conditions may cause inhibition of denitrifying community's activity. N_2O concentration is highest in the first aerobic reactor and decrease in the following aerobic zone due to the increased DO concentration and gas stripping. Relatively low DO levels (< 1 mg/L) during the transition from anoxic to aerobic condition in the first aerobic reactor lead to the development of a steep change in N_2O concentration by AOB in which the DO level is favorable for N_2O production.

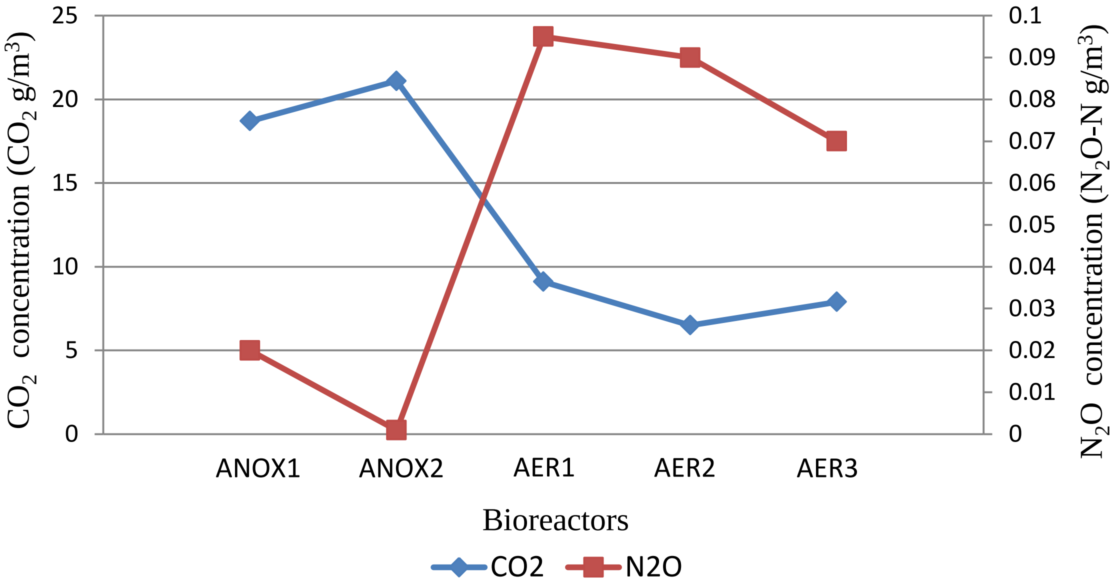

Figure 3.6: Dissolved carbon dioxide and nitrous oxide profiles in anoxic (ANOX 1 & 2) and aerobic zones (AER 1, 2 & 3) resulting from the 500 days of steady-state simulation.

3.3.2 Sensitivity Analysis

In order to identify the key design and operational parameters influencing GHG emissions, the sensitivity of the model was evaluated under open-loop and closed-loop systems. In the closed-loop system, only DO concentrations in the aerobic reactors were controlled since a preliminary sensitivity analysis revealed that DO was the most sensitive to the GHG emissions without control and that it must be controlled to minimize GHG emissions. Using the outputs from the simulations, sensitivity functions between each of the input parameter and the output variable were calculated. The sensitivity trajectories resulting from parameter changes in the range of ± 10% are presented in Figure 3.7, with the relative parameter percent changes ($\Delta P/P$) on the horizontal axis and the relative changes in overall greenhouse gas emissions ($(\Delta Q_{GHG}/Q_{GHG})/(\Delta P/P)$) on the vertical axis. The plots illustrate how the magnitude of the sensitivity for GHG emissions is affected as the parameter change ($\Delta P/P$) varies. The sign of the sensitivity function shows the relationship between each of the input parameter and the output variable. The positive value of the sensitivity function implies that the emission rate increases as a parameter increases. Conversely, the negative value indicates when a parameter increases, the emission rate decrease. In general, parameters with greater than 1 of relative sensitivity are considered very influential on a certain model output. In this context, in the open-loop system, five out of fourteen most influential input parameters on GHG emissions can be categorized as highly influential parameters: aeration intensity (or DO), volume of the aerobic reactor, operating temperature in the bioreactors, operating temperature in the sludge digester, and removal efficiency of the primary setting tank. The sensitivity levels of external carbon addition and internal recycle are relatively small (around 0.2 - 0.3%), and those of the remaining parameters have a negligible effect (less than 0.01%).

Figure 3.7 also shows how the estimated GHG emissions from the open-loop system can vary when DO control is implemented in the aerobic reactors. The upward trend in sensitivity is quite clear in the open-loop system. The sensitivities between the two systems differ greatly by a factor of 10, with higher sensitivity in the open-loop system. This variation is strongly related to the effects of DO level on the activity of

N_2O-producing bacteria (i.e. AOB). In the open-loop system, the sensitivity trajectories of most parameters have similar directions; however those for aeration and aerobic reactor volume reveal changes from linear to exponential with decreasing parameter values. This is mainly due to both the inherent nonlinearity of the model used and the high sensitivity of N_2O production to oxygen concentration. The sensitivity of N_2O emission is greatest because of its highest GWP and hence predominately impacts the sensitivity of total GHG emissions. The reason for the nearly identical sensitivity trajectories of the two parameters, aeration and aerobic reactor volume, is that changes in these two parameters without DO control lead to similar DO levels in the reactors. The sensitivity functions of most parameters except for these two parameters stay almost stable. From these calculations, the relative changes in emissions of the open-loop operation are in the range of -46 % to +13% when parameters vary in the range of ± 10% from their default values, while implementation of the DO control loop can lead to a sensitivity reduction by about 90%.

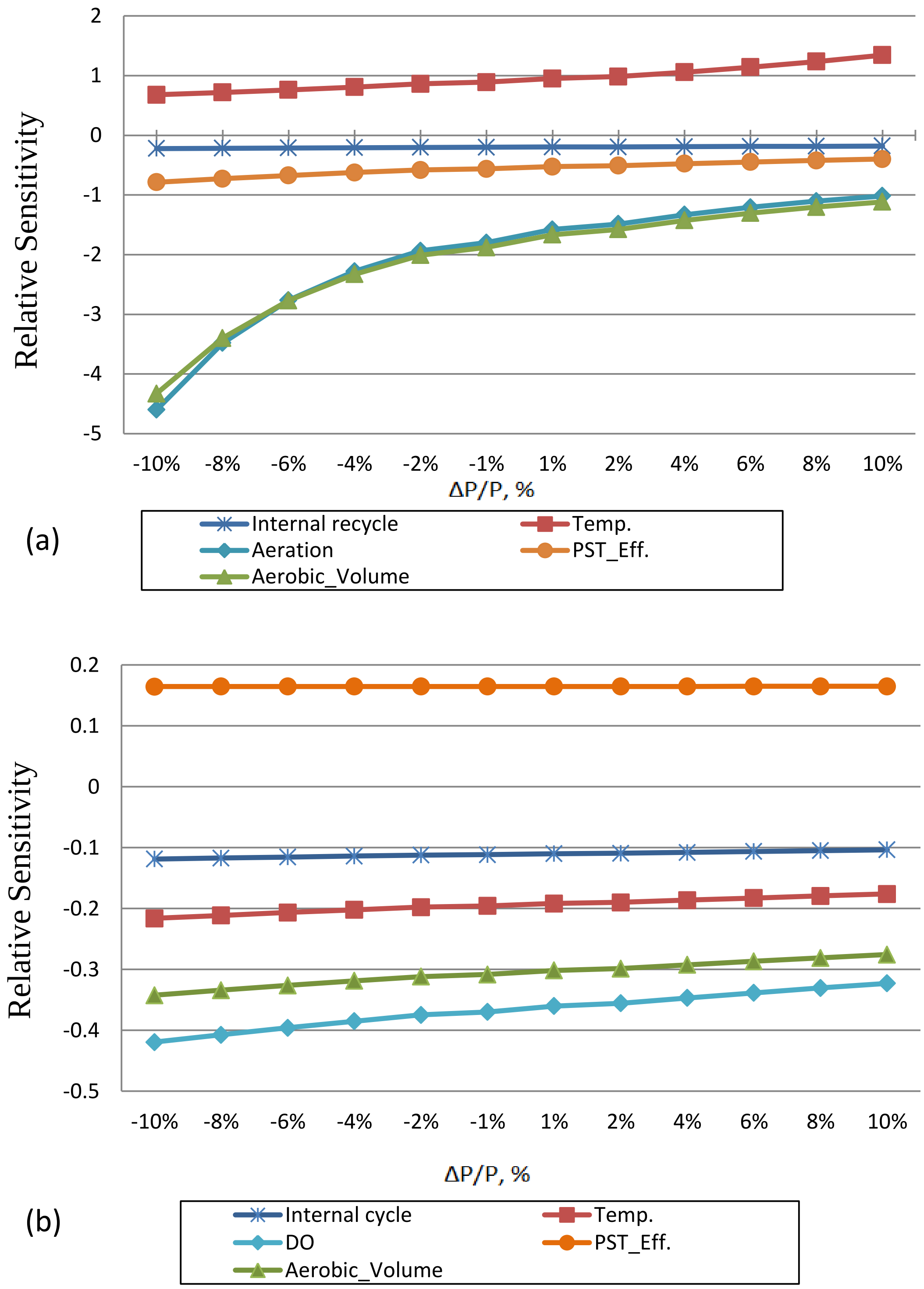

Figure 3.7: Simulations of relative sensitivity of GHG emissions with % variation of the input parameters. The top 5 highly sensitive parameters are plotted under (a) open-loop and (b) closed-loop (DO control) systems.

Figure 3.8 and 3.9 depict the percent changes in each individual greenhouse gas component with 1% variations in each input parameter. This information provides insight into which of the input parameters are the most important in terms of their contribution to the predicted GHG emissions total. With the use of DO control-loop the sensitivity of each emission is considerably reduced and the order of significance of parameters is slightly changed. Without DO control, aerobic reactor-related parameters including reactor volume and aeration intensity are most responsible for variation in the total GHG emissions, mainly due to the correlation between DO and N_2O production, while the total GHG emissions are moderately sensitive to the removal efficiency of COD in the primary settling tank, the operating temperature in the bioreactor, the internal recycle, and the external carbon dose. In terms of the sensitivity of each gas emission, N_2O emissions are very sensitive compared to CH_4 and CO_2. N_2O emissions are most significantly affected by aeration intensity (or DO level) and aerobic reactor volume. The sensitivity of indirect emissions to the operating temperature in the anaerobic digester is very high due to its high energy demand for heating. In regards to the process unit, the aerobic bioreactor is most sensitive to GHG emissions, followed by anaerobic digester and primary settling tank.

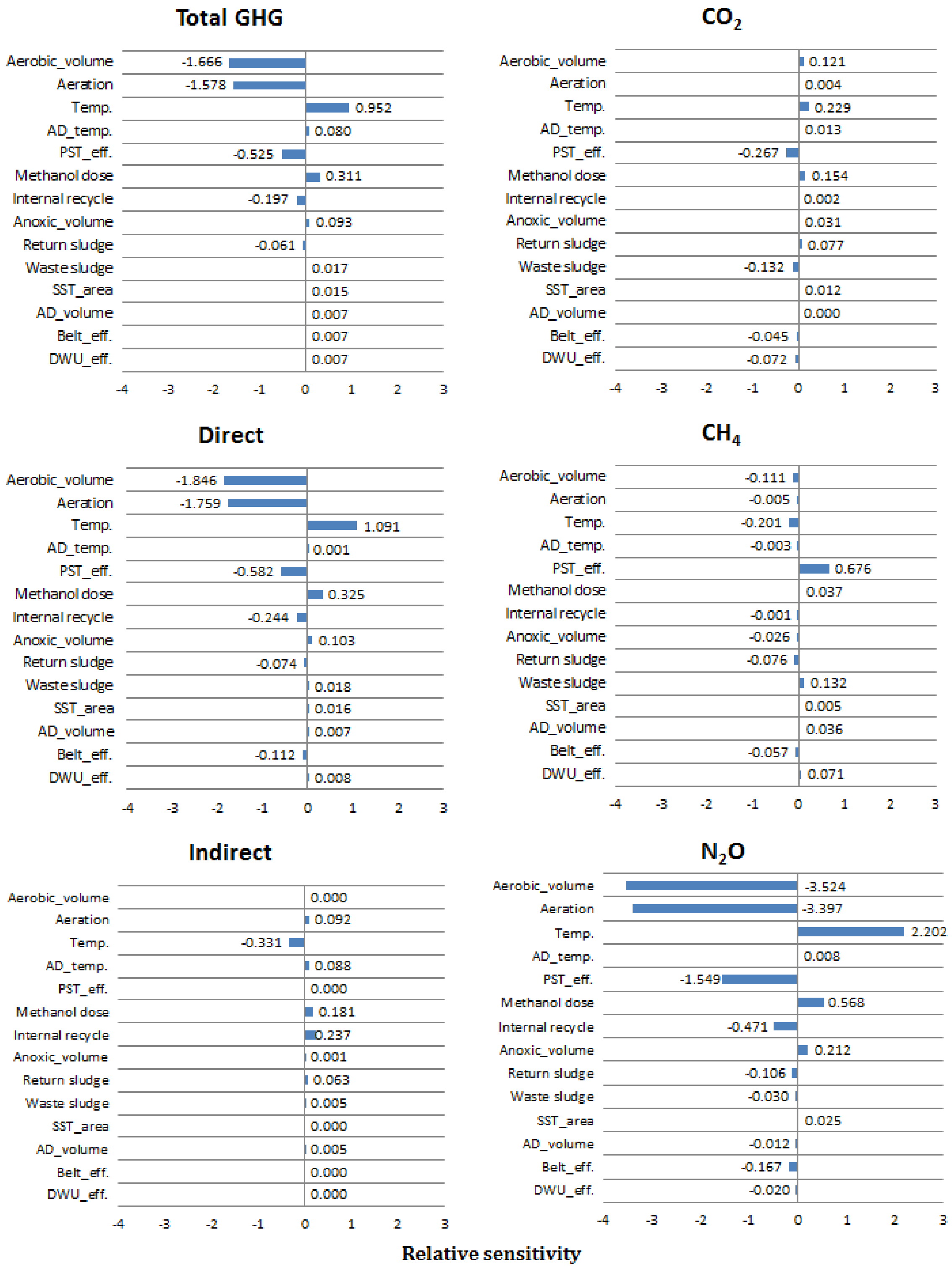

Figure 3.8: Relative sensitivity of GHGs with 1% change of parameter in the open-loop system.

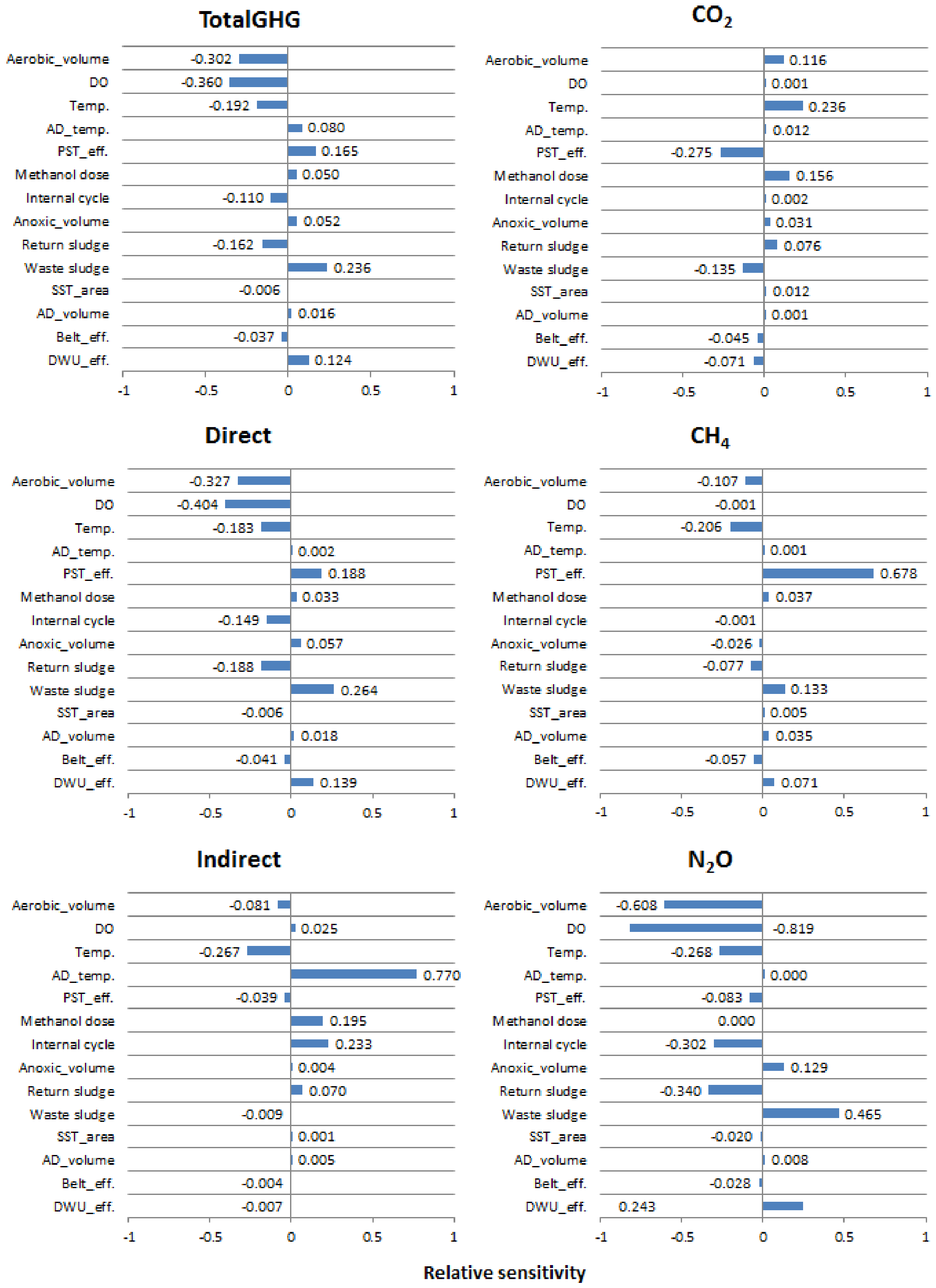

Figure 3.9: Relative sensitivity of GHGs with 1% change of parameter in the DO control-loop system.

3.3.3 Uncertainty Analysis

The GHG emissions generated from WWTPs are highly dependent on how the process is designed and operated. In order to quantify the uncertainty related to design and operational parameters, uniform distribution was used for all input parameters, whose importance was examined in the sensitivity analysis. Steady-state simulations were done for both open-loop and closed-loop systems. The results of the Monte Carlo simulations using LHS are summarized by means of box-plots (Figure 3.10) and histograms (Figure 3.11 and 3.12). These two figures show the likely variability in GHG estimates corresponding to the defined input parameters and the effects of DO control on the uncertainty of GHG estimates in the two systems. As expected from the results of the sensitivity analysis, there is significant variability in GHG estimates predicted by the model. The results also show that there is a difference in uncertainty between open-loop and closed loop systems. For instance, as can be seen in Figure 3.10 (a), the 25 to 75 percentile boxes of the open-loop system are skewed to the upper bound and their variations are higher. This difference is highly related to the effects of DO level on emissions, as observed before in the sensitivity analysis. In addition, the uncertainty in both direct and indirect emission estimates is decreased when DO levels in the aerobic reactors are controlled. Thus, it can be said that uncertainty caused by operational parameters can be reduced through optimum control strategy. It can be noticed from the box-plots that the uncertainty in the N_2O estimate, which is responsible for more than 85% of the total uncertainty, is dominant and most influential to the total GHG estimates,. According to the results of the sensitivity analysis, this high uncertainty of N_2O estimate is mainly due to the aeration intensity (or DO) and the aerobic reactor volume. Figure 3.11 and 3.12 show an alternative uncertainty display that describes the probability distribution of GHG emissions due to uncertainty in the input parameters. The use of DO control contributes to the reduction of the range of the probability distribution and its impact on the shape of the distribution is small. From these distribution figures, one might deduce that a significant variation in the total GHG estimate is caused by N_2O estimate because these two emissions have similar shapes of probability distribution for estimate uncertainty.

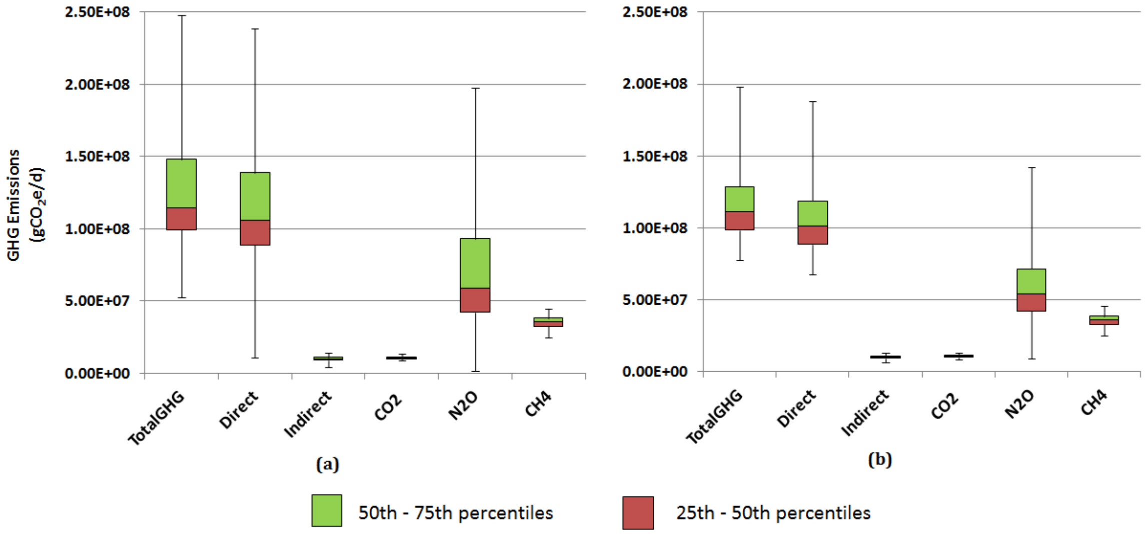

Figure 3.10: Box-plot of estimated GHG emission for open-loop (a) and closed-loop (b). The vertical line within the box represent the median. The bounds of the box-plot are 25th and 75th percentiles. Error bars extend to the minimum and the maximum of estimations.

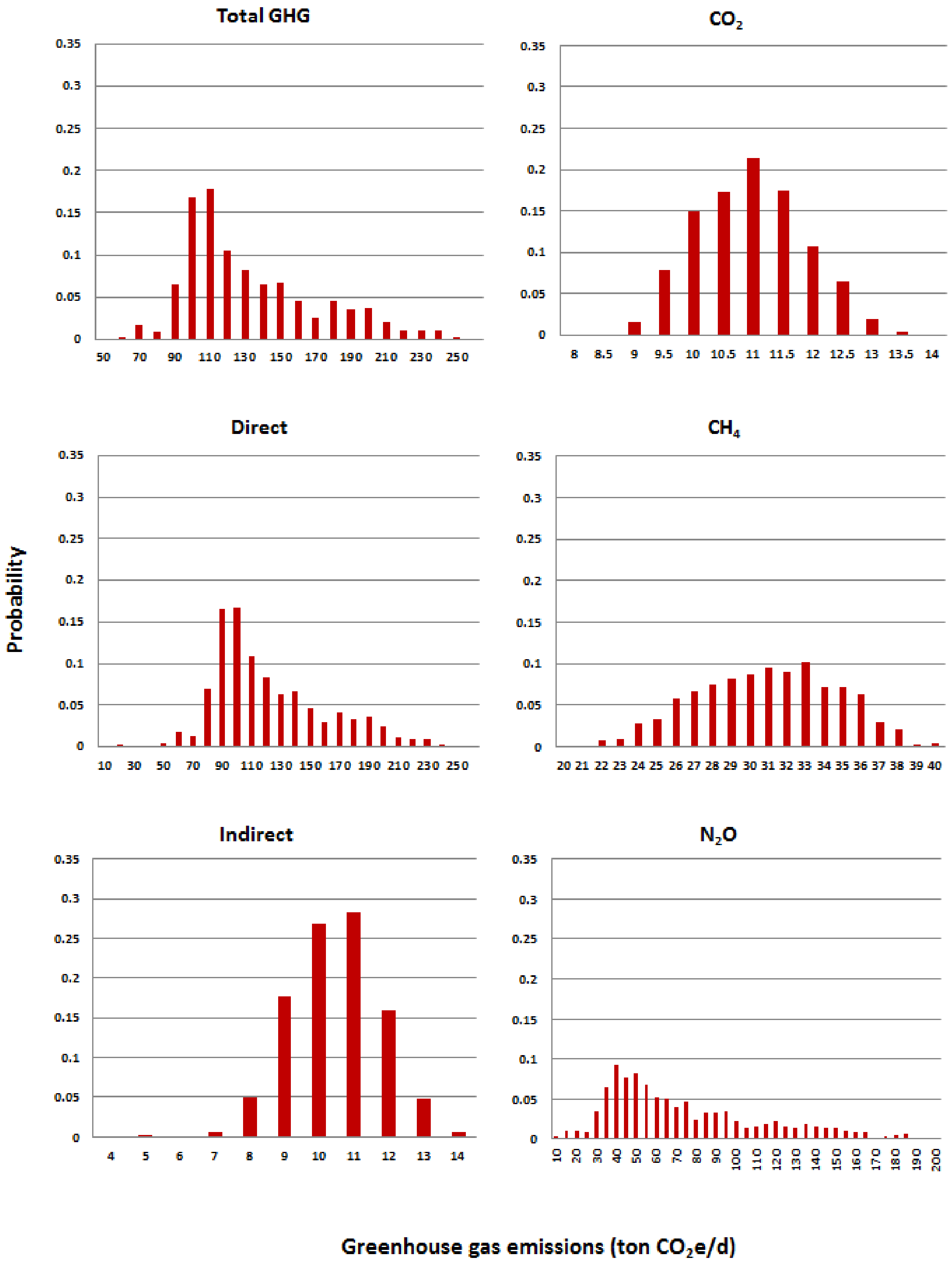

Figure 3.11: Probability distribution of GHGs emissions due to uncertainty in input parameters for open-loop system.

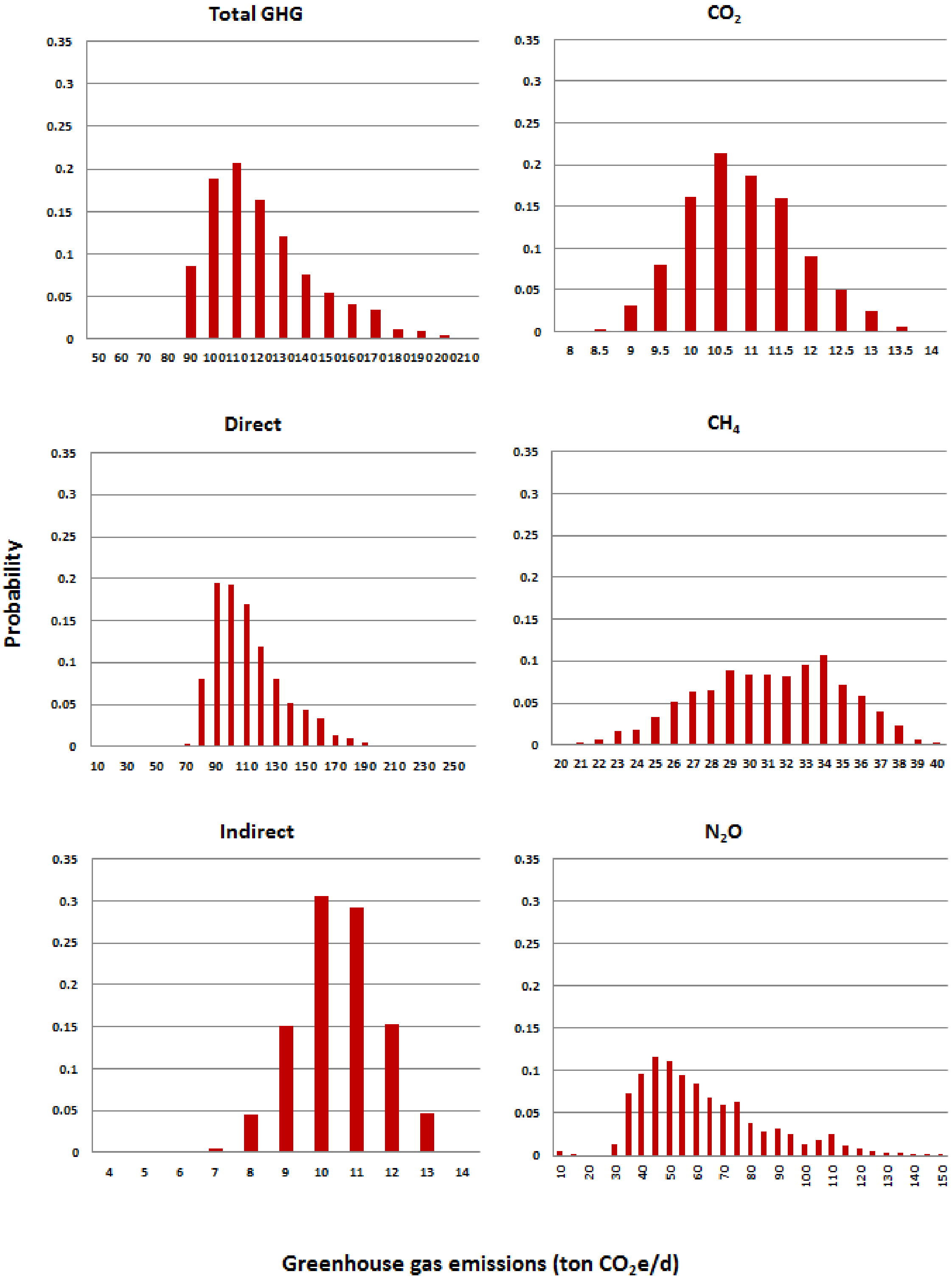

Figure 3.12: Probability distribution of GHGs emissions due to uncertainty in input parameters for closed-loop system.

3.4 Discussion

To evaluate the acceptability of the estimated results, the values of Scenario A were compared to those of previous studies. To compare with previous studies, estimated emissions from this study was computed according to the units used in the literature (Table 3.2). Overall, the estimates using the model presented were within the range of the values reported in the literature. Even though there are differences in the system boundary definition among the studies, CO_2 emission from COD oxidation was approximately 0.86 $kgCO_2$/kgCOD oxidized, which is slightly below the value presented in Hartley and Lant (2006). CH_4 production from anaerobic digestion was estimated 0.25 $kgCH_4$/kgCOD removed. This is the same as the theoretical estimation using chemical stoichiometry (Foley et al., 2008). N_2O generation accounted for about 8.0 % of the influent nitrogen load to the system, which is in the range of 0 - 14.6 % reported from several full-scale plants (Kampschreur et al., 2009). In addition, the percentage of generated N_2O-N out of denitrified nitrogen was 17.7 %, which is in the range of 0.6 - 25.6% as estimated from 3 full-scale MLE processes in Australia by Foley et al. (2010). However, more full-scale field measurements are necessary to produce robust data since the data are based on only a few field studies.

Table 3.2: Comparison of direct greenhouse gas emissions with previous studies

Type of emissions	Unit	GHG emissions		Reference
		This study	Previous studies	
Carbon dioxide	$kgCO_2/kgCOD$ oxidized	0.86	1.1	Hartley and Lant (2006)
Methane	$kgCH_4/kgCOD$ removed	0.25	0.18-0.25	Foley et al. (2008)
Nitrous oxide	$kgN_2O\text{-}N/kgN$ loaded	0.08	0-0.146	Kampschreur et al. (2009)
	$kgN_2O\text{-}N/kgN$ denitrified	0.18	0.006-0.256	Foley et al. (2010)

Gas stripping is thought to play a role in the release of dissolved gases from the system. As described in Eq. (3.4), the gas stripping rate is proportional to the gradient between the bulk liquid concentration of gas and the equilibrium concentration, and the aeration intensity. Thus, the dissolved greenhouse gases may be stripped to the gas phase during aeration until the aqueous gas reaches its equilibrium point. The gas stripping process was a major transport pathway for CO_2 and N_2O. Around 40% of influent carbon and 20% of influent nitrogen were discharged to the atmospheric environment via this process. All of the three major greenhouse gases have relatively low equilibrium points due to their low partial pressures in the atmosphere (< 0.04%) compared to nitrogen (78%) and oxygen (21%). For this reason, the dissolved greenhouse gases were highly supersaturated in all five bioreactors of the MLE configuration and even in the effluent, and thus it provided enough mass transfer driving force for gas stripping.

It is important to point out the close relation between inorganic carbon (CO_2, bicarbonate (HCO_3^-), and carbonate (CO_3^{2-})) and nitrification. In nitrification, inorganic carbon serves as the carbon source for AOB and nitrite-oxidizing bacteria (NOD). Some studies reported that AOB activity was limited due to a lack of inorganic carbon (Wett and Rauch, 2003; Guisasola et al., 2007). Guisasola et al. (2007) found that AOB growth is limited at inorganic carbon (< 3mol-C/m^3). Nevertheless, limitations of the nitrification by inorganic carbon have not yet been fully investigated, and thus further studies are needed to elucidate this issue. The carbon limitation is closely connected with alkalinity presented in the wastewater. The alkalinity level may vary depending on the process operation. Theoretically, for the nitrification process, about 7.14 g of alkalinity (as $CaCO_3$) are required for each gram of nitrogen oxidized. Thus, a sufficient level of alkalinity is needed to maintain approximate to neutrality (pH 6.5-8.0) for the nitrification process despite the denitrification results in the recovery of 3.6 g of alkalinity per gram of NO_3-N reduced. The alkalinity level in the reactor is also affected by aeration. As the dissolved inorganic carbon (CO_2) in the wastewater is stripped out from the liquid in the aeration zone, the proton concentration increases and consequently affects alkalinity. In this study, the amount of CO_2 produced through the metabolism by heterotrophic bacteria was high enough to supply for autotrophic growth. In addition, the amount of influent alkalinity into the bioreactor (7 mol-C/m^3) was sufficient to support the bioreactor operation, and the nitrification/denitrification process held the alkalinity level in the reactor to a range of 5.8-5.0 mol C/m^3. No significant change in alkalinity due to aeration was observed since the aeration tanks were maintained at an appropriate DO level (around 2 mg/L).

From a GHG mitigation perspective, it is important to consider energy recovery from waste sludge. The highest degree of GHG mitigation could be achieved where the highest possible fraction of the carbon found in the influent organic matter is converted to CH_4 and then used as an energy resource. Production of carbon dioxide or methane in the process depends upon the characteristics of wastewater and configuration of the process. Any changes to these characteristics and/or conditions will impact net GHG emissions. According to the results of the sensitivity analysis, CH_4 emission is most sensitive to the removal efficiency of COD in the primary settling tank. More COD removed from the primary settling tank (PST) results in more CH_4 emitted in exchange for CO_2. Improving removal efficiency in PST can provide an opportunity to reduce overall GHG emissions. However, influent COD is vital to supply carbon source for the denitrification process. In biological nitrogen removal processes, an external carbon dose is necessary if sufficient carbon source is not available from influent wastewater. Thus, there is a potential trade-off for carbon usage, which could be a subject of further study.

The potential beneficial effects of process control are highlighted in this study. Process control is an important part of the operation of modern wastewater treatment plants. As for the control in this study, one simple control loop (i.e. DO) was implemented to evaluate the effects of process control on the GHG prediction. The results of both sensitivity and uncertainty analyses showed that the control-loop system has different characteristics compared to the open-loop system, such as system stabilization, system behavior, and GHG emissions. Figure 3.13 and 3.14 illustrate dynamic GHG emissions in model runs without and with DO control in the aerobic reactors. The comparison in Figure 3.14 clearly shows a very large variation in N_2O emission corresponding to the dynamic load in the open-loop system. It can be seen that if control loops are employed properly, the control loops can lead to reduction in GHG emissions as well as better process performance. Consideration of other control loops for parameters such as internal recycle, return sludge flow rate, and waste sludge flow rate could be included in future investigations.

The ASMN_G model does not take into account all potential sources of GHG emissions from the wastewater treatment process. Dynamic mathematical models for anaerobic digestion that demonstrate biogas production are available in the literature (Siegrist et al., 2002; Batstone et al., 2002), whereas those for anaerobic wastewater treatment are scarce or not readily obtained, although various anaerobic processes, such as anaerobic contact, anaerobic filter, and A2O (Anaerobic /Anoxic /Aerobic) process may emit these gases. On the other hand, several researchers observed that biological nitrate reduction that results in the production of N_2O could be achieved with the methanogenic fermentation process in a single anaerobic bioreactor such as an anaerobic sludge digester (Garibay-Orijel et al., 2006; Huiliñir et al., 2009, 2011; Tugtas et al., 2009). Tugtas et al. (2009) attempted to incorporate the four-step denitrification process into the ADM1, however, its validity still needs to be experimentally supported under different nitrate feed conditions.

To explore the effects of variability in design and operational parameters on GHG estimates, an uncertainty analysis was carried out based on 14 input parameters. The other sources of uncertainty such as model structure, model parameters, and influent wastewater composition were not considered in this study and may produce some additional variations in the predicted emissions. Although the model was simulated mainly under steady-state conditions this study captured the variability of the potential

GHG emissions and the relative importance of input parameters in terms of their model output through both sensitivity and uncertainty analyses.

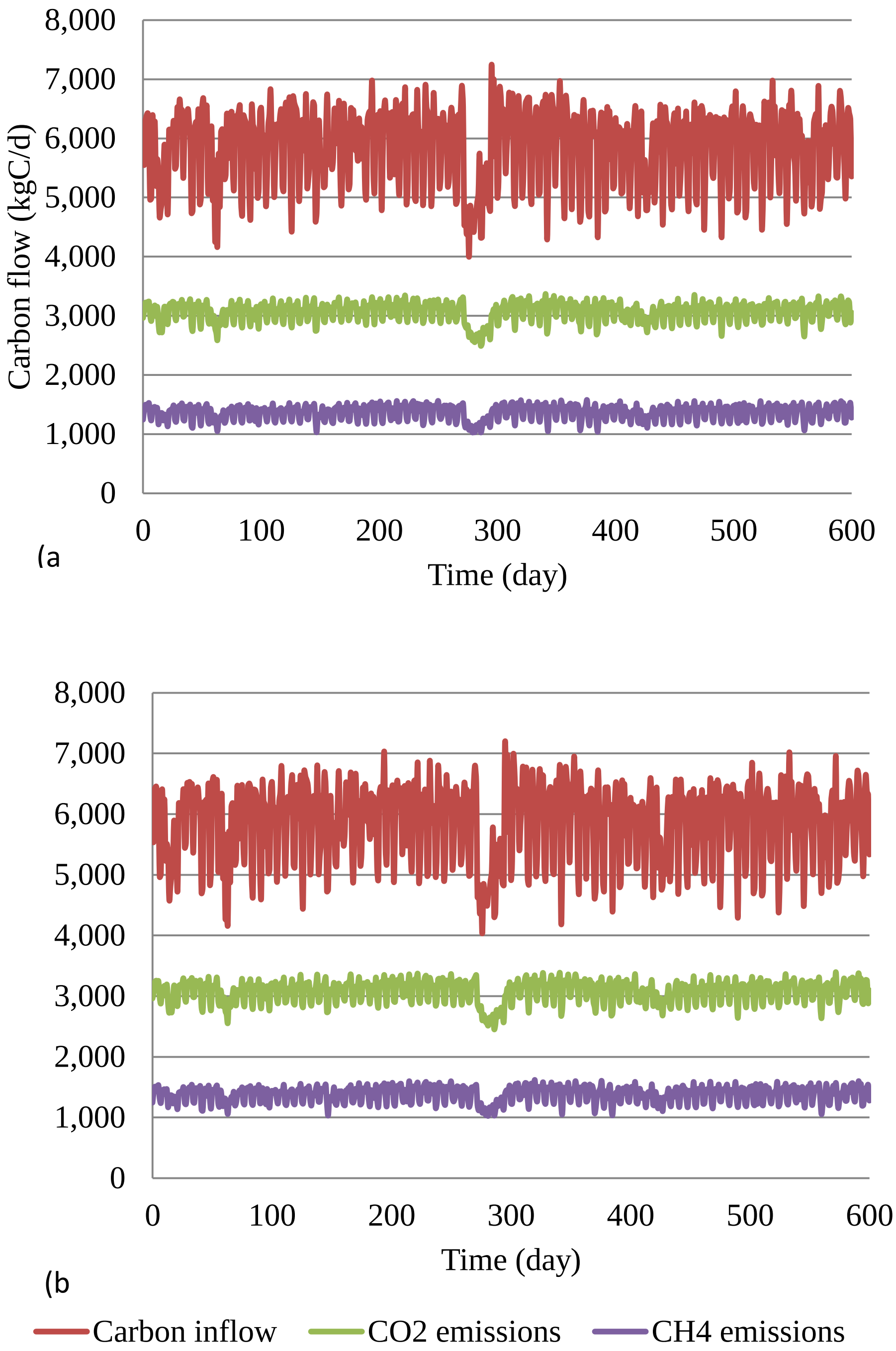

Figure 3.13: Dynamic CO_2 and CH_4 emissions: (a) open-loop system and (b) closed-loop (DO controlled) system.

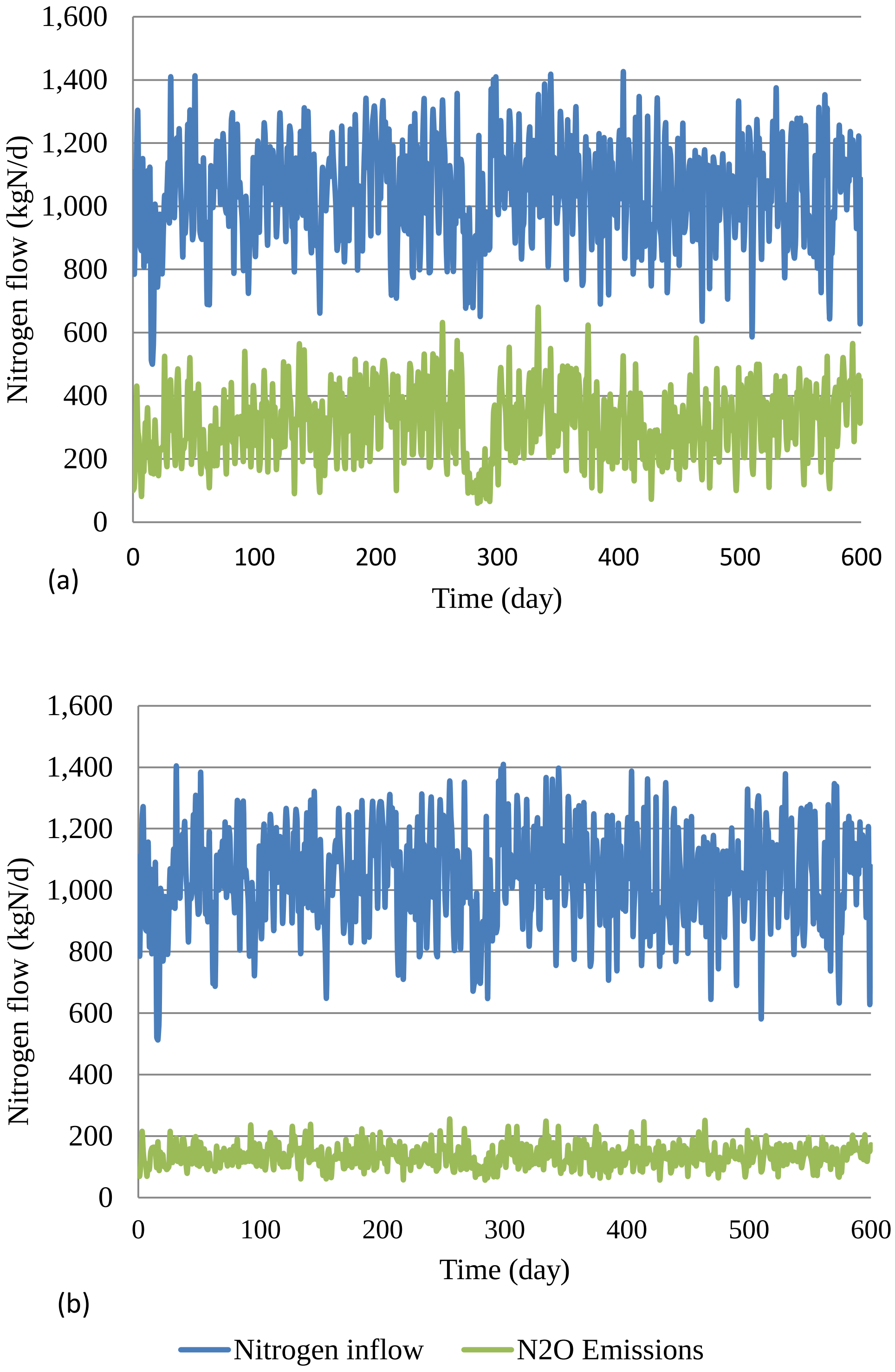

Figure 3.14: Dynamic N_2O emissions: (a) open-loop system and (b) closed-loop (DO controlled) system.

3.5 Conclusions

An elemental based wastewater treatment plant model (ASMN_G) was used to conduct GHG emissions estimation for WWTPs. The bioreactor portion of the model was the extension of ASMN model with inclusion of two main additional items: (1) nitrifier denitrification process that enabled the model to better describe N_2O production by AOB and (2) CO_2 state variable that allowed us to track the whole pathway of carbon cycle in the system. When comparing this model's results with previous studies in the literature, the estimated GHG emissions lie within an acceptable range.

In a wastewater treatment plant, GHG emissions may vary depending on influent wastewater characteristics, system configurations, and operating conditions. The sensitivity analysis identified that the two input parameters that have most significant influence on GHG estimation are aeration (or DO) and aerobic bioreactor volume. Of three GHGs considered by the model, N_2O emissions were the most sensitive to changes in input parameters. The results obtained from the sensitivity analysis provide significant insights into design and operational parameters which could be optimized to mitigate GHG emissions.

The uncertainty of the estimated GHG emissions was assessed using Monte Carlo simulations. The results indicate that the uncertainty of the estimation was fairly high, due to high degree of sensitivity to input parameters. It is important to highlight that significant variability was observed from N_2O emissions, which is strongly influential on overall uncertainty of the model. The results of the uncertainty analysis provide the possible range of prediction for GHG emissions, which show the potential to reduce the uncertainty.

Further research is still needed to improve GHG estimations. The mechanisms for certain GHG emissions, especially in respect of N_2O emissions by AOB and in anaerobic sludge digestion remain unclear. Further research on the transformation of intermediate compounds in the nitrogen cycle such as NO and NH_2OH may be helpful to better estimate the emissions. In addition, for a better uncertainty analysis, investigating the influence of the choice of parameter distributions on the GHG distributions and determining the appropriate number of Monte Carlo shots for the model would be future topics to research.

CHAPTER 4: OPTIMIZATION OF WASTEWATER TREATMENT PLANT OPERATION FOR GREENHOUSE GAS MITIGATION

Abstract

This chapter deals with the determination of optimal operation of a wastewater treatment system for minimizing greenhouse gas emissions, operating costs, and pollution loads in the effluent. To do this, an integrated performance index (IPI) that includes three objectives was established to assess system performance. The ASMN_G model proposed in Chapter 3 was used to perform system optimization aimed at determining a set of operational parameters that can satisfy three different objectives. The complex nonlinear optimization problem was simulated using the Nelder-Mead Simplex optimization algorithm. A sensitivity analysis was performed to identify influential operational parameters on the system performance. The results obtained from the optimization simulations for six scenarios demonstrated that there are apparent trade-offs among the three conflicting objectives. In addition, the optimization simulation suggested an optimal range of operational parameters based on the proposed performance. The best optimized system simultaneously reduced greenhouse gas emissions by 37%, reduced operating cost by 15%, and improved effluent quality by 5% compared to the base case operation.

4.1 Introduction

The traditional management of wastewater treatment plants (WWTPs) has focused mainly on minimizing operating costs as well as satisfying the effluent discharge limits. The effluent quality and operating costs of the plants are primarily affected by operating conditions such as solids retention time (SRT), aeration, and internal recycle flow rate. Thus, optimal operation is an important part of successful management of modern wastewater treatment plants (Yoon et al., 2004; Ostace et al., 2011). In the near future, efforts must be made to extend system performance by minimizing greenhouse gas emissions because of the increasing attention on sustainable operation of infrastructure. Consequently, this makes the operation of WWTPs more complex and raises the possibility that a trade-off between the inherent tasks of wastewater treatment (i.e. aquatic pollutant removal at low costs) and the sustainable plant tasks (e.g. less global warming impact) may exist in wastewater treatment systems. Although all concerns may not reach their best practices simultaneously, trade-offs will have to be made in order to achieve a satisfactory overall performance.

To date, the quantification of environmental and economic performance has been a major interest of system analysis in evaluating activated sludge process control strategies (Copp, 2002; Benedetti et al., 2008; Quadros et. al, 2010). The most commonly used performance indices in the area of wastewater treatment systems, which have been used as measures to determine the impact of alternative operating scenarios, were proposed by Nopens et al. (2010). The main challenge in evaluating these criteria is that the quantity of each criterion has a different unit or scale, and thus their values may not necessarily be comparable. When system objectives can be assessed with a simple quantitative term, it is much easier for decision makers to analyze the results and find the most effective points of operational strategies. Therefore, an efficient approach is one that allows quantitative comparisons to evaluate management and control strategies of a plant with multiple decision criteria.

One approach to finding the best set of decisions for operating such a complex nonlinear system as wastewater treatment systems is using an optimization method with an integrated index. For wastewater treatment systems, optimal operating conditions can then be determined by means of optimization methods coupled with a predictive mathematical model of the wastewater treatment plant. A number of researchers have investigated optimization problems applied to the analysis and/or operational design of wastewater treatment plants. Most recent studies have focused either on model calibration (model parameters estimation) (Vanrolleghem et al., 2003; Fang et al., 2009; Wu and Liu, 2012) or on optimization of process design and control in different configurations (Kim et al., 2000; Balku and Berber, 2006; Holenda et al., 2008; Rivas et al., 2008; Maere et al., 2011; Cruz Bournazou et al., 2013). However, until now, there are only a few studies that have attempted to tackle wastewater treatment issues by conducting optimal operations with multi-objectives using optimization algorithms. In addition, no attempt has been made to evaluate plant-wide performance by means of optimization techniques. Finally, although a lot of attention has been paid to mitigate greenhouse gas emissions in wastewater treatment plants, the evaluation of system cost and water quality performance along with greenhouse gas emissions using optimization algorithms has not been accomplished.

In this context, the objective of the work presented in this chapter is to employ optimization techniques to determine how the operating conditions of WWTPs could be improved: by minimizing both the operating costs and greenhouse gas emissions as well as satisfying the effluent discharge limits. For this objective, an integrated performance index is proposed by combining multi-criteria into a single index. Namely the quantification of the environmental impacts caused by pollutants, such as effluent discharges and greenhouse gas emissions when introduced into the environment is implemented and then converted into normalized scores along with operating costs. The integrated index could facilitate evaluation of system performance and comparison of the impacts of operating conditions. This work relies on a numerical model that simulates plant operation, and predicts both direct and indirect emissions of CO_2, N_2O and CH_4. The numerical model was presented and explained in detail in Chapters 2 and 3.

4.2 Methods

4.2.1 Process Configuration

As previously used in Chapter 3, the configuration of the wastewater treatment plant used in this study was a modified closed-loop Ludzack-Ettinger (MLE) process, based on the benchmark layout as presented in Nopens et al. (2010) (Figure 4.1). The main process for the wastewater line comprises five bioreactors, of which the first two are anoxic and the next three are aerobic, one primary settler, and one secondary settler. Both primary and secondary sludge lines are fed to the anaerobic sludge digester. There are six operational parameters of interest in the system: (1) external carbon (i.e. methanol) dose rate into the first anoxic reactor (ECD), (2) dissolved oxygen (DO) concentration in the first aerobic reactor, (3) waste activated sludge flow rate (WS), (4) internal mixed-liquor recycle flow rate (IR), (5) return sludge flow rate (RS), and (6) operating temperature in the anaerobic sludge digester (ADT). For DO control, only the DO concentration in the first aerobic reactor was manipulated, and those in the following two aerobic reactors were fixed at the same concentration (i.e. 2.0 mg/L). This is because according to the results described in Chapter 3, the effects of DO concentration on GHG emissions were extremely significant in the first aerobic reactor due to its much more favorable environment for N_2O emission by ammonia-oxidizing bacteria (AOB).

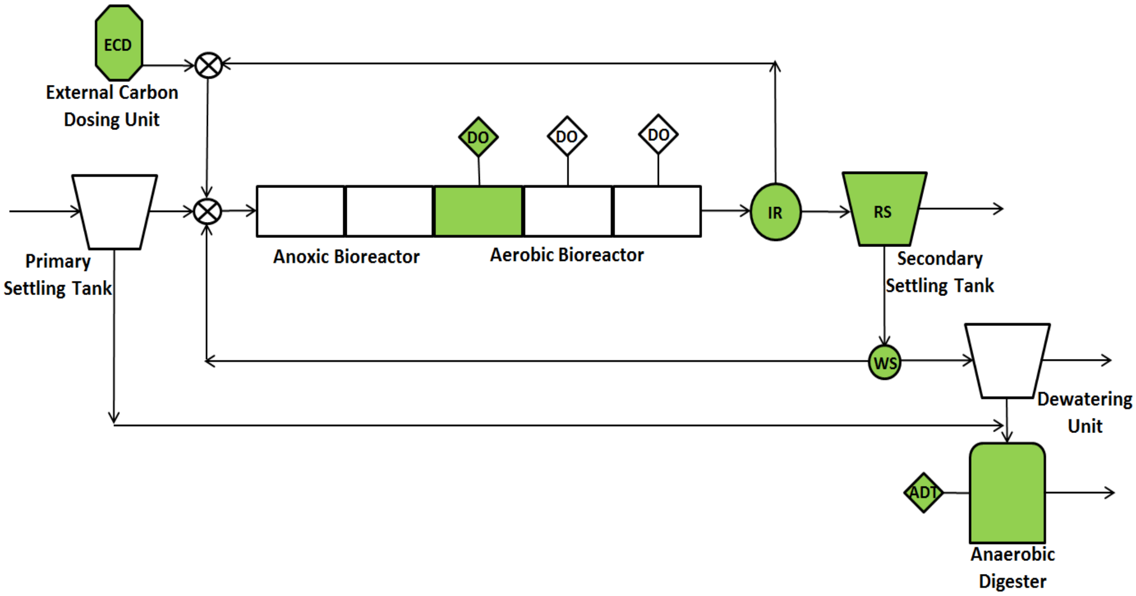

Figure 4.1: Schematic diagram of the Modified Ludzack-Ettinger (MLE) process under study. The unit processes to be optimized are shaded in green.

4.2.2 Process Models

For a plant-wide optimization, a sludge digestion model is generally connected to an activated sludge model. In this study, the Activated Sludge Model-Nitrogen for Greenhouse gases (ASMN_G) model was employed for activated process modeling. The ASMN_G model was proposed in Chapter 3 as an extension of the ASMN developed by

Hiatt and Grady (2008) in order to include further knowledge on greenhouse gas emissions. The merit of the ASMN is that the model describes denitrification as a four-step process and thus N_2O emissions are predictable. The ASMN_G model captured additional N_2O emissions through the autotrophic denitrification process. It also incorporated sources and sinks of CO_2 emissions by all biological processes in the model. The ADM1 model (Batstone et al., 2002) was used to simulate the sludge digestion process. This model is the most widely used model available to estimate biogas production from the sludge digestion process. The same values used in Chapter 2 were used for kinetic and stoichiometric parameters. The GHG model used in Chapter 2 needed to be modified in order to define the optimization problem (e.g. objective function, constraints, etc.) in it.

4.2.3 Performance Index

In order to evaluate system performance when optimizing the operation of the wastewater treatment system with multi-objectives, three performance indices were introduced: Effluent Quality Index (EQI), Operational Cost Index (OCI), and Greenhouse Gas Index (GGI). These indices were intended to facilitate the evaluation of the complex non-linear problem that involves trade-offs among economic and environmental goals. In the case of a multi-objective optimization problem, the objectives that are evaluated by different criteria of the system need to be integrated into a single objective. However, because these indices are measured in different scales or expressed in different units, they need to be appropriately combined, taking into account their complex characteristics and site-specific preferences. In the context of this study, a new index named the integrated performance index (IPI) was proposed. To do this, the magnitude of each index was first quantified and then normalized into a dimensionless value in order to numerically combine three different types of indices. Ultimately, a weighting factor was assigned to each index, and the weighted indices were combined into a single value. These weighting factors allow us to specify varying site-specific preferences between the indices under different economic, environmental, and social circumstances.

A composite index of effluent quality (i.e. EQI) was used to combine multiple indicators of effluent water quality. The EQI includes five major pollutants as indicators of the effluent quality: biochemical oxygen demand (BOD), chemical oxygen demand (COD), total nitrogen (TN), total Kjeldahl nitrogen (TKN), and total suspended solids (TSS). The EQI consists of two types of cost functions associated with effluent quality: the environmental costs (EC) and the violation costs (VC). First, the EC quantifies the environmental burden of effluent pollutants to a receiving water body. An example of environmental costs ($\mathrm{EC_{BOD}}$) is illustrated as:

$$\mathrm{EC_{BOD}} = \mathrm{BOD} \times \mathrm{Q_e} \times \left[\frac{\mathrm{BOD_L}}{10{,}000} + \frac{1 - \frac{\mathrm{BOD_L}}{10{,}000}}{1 + \left(\frac{\mathrm{BOD}}{\mathrm{BOD_L} \times 0.5} \right)^{-\mathrm{S}}} \right] \times \mathrm{W_{EQI}} \tag{4.1}$$

where BOD and $\mathrm{BOD_L}$ represent the concentration of effluent BOD and the BOD standard limit (mg/L), respectively, $\mathrm{Q_e}$ is the effluent flow rate ($\mathrm{m^3/d}$), the S denotes the slope of cost function, $\mathrm{W_{EQi}}$ is the weighting factor of EQI.

The EC is proportional to the amount of pollutants discharged into the environment and also proportional to a weighting factor of each pollutant. The weighting factor enables proper combining of different pollutants, and this can be determined based on the effluent limits by assuming that the limits would already reflect which criteria are more important in the water body. In this context, the weighting factor of each pollutant was calculated by its effluent limit divided by the effluent limit of COD, in which COD was used as the reference pollutant (see Table 4.1). The weighting factor may vary depending upon the relative importance of the pollutant to the overall water quality of the water body under study. In addition, the EC was designed to be permissive at such a low concentration as below background levels. In such case, there may not be any increase in the concentrations of pollutants in the receiving water body caused by the discharge. It was implemented by employing a logistic equation as described in the parenthesis part of Eq. (4.1), and its function is plotted in Figure 4.2. The slope of the function allows either an increase or decrease of the magnitude of the penalty function.

Table 4.1: Weighing factors of water quality components

	COD	BOD	TN	TKN	TSS
Weighing factor	1	6	7.5	20	1.3
Effluent limits (mg/L)	60	10	8	3	45

Secondly, the violation cost (VC) was introduced as a constraint in order to prevent violations of the effluent limits for discharge into the environment and to force the optimization algorithm to explore only within the feasible region of the system. That is, if the concentration of any criteria pollutant in the effluent exceeds its maximum permissible limit, a penalty is imposed. By assigning a large number as the violation cost, this term can serve as a constraint and as a result, the objective function may not exceed the effluent limits. Finally, the overall effluent quality index was calculated as the sum of the environmental costs and the violation costs for each pollutant.

$$\mathrm{EQI} = \sum_{\mathrm{i}=1}^{5} (\mathrm{EC_i} + \mathrm{VC_i}) \tag{4.2}$$

where $\mathrm{EC_i}$ is the environmental costs for BOD, COD, TN, TKN, and TSS, $\mathrm{VC_i}$ is the violation costs for BOD, COD, TN, TKN, and TSS.

The functional form of Eq.(4.2) does not explicitly describe all the details of the cost function associated with effluent quality, but the logic of EQI is that the EC is applied only if effluent with same or lower BOD levels than the limit (≤ 10mg/L) is discharged; otherwise there is a switch to the VC in the function.

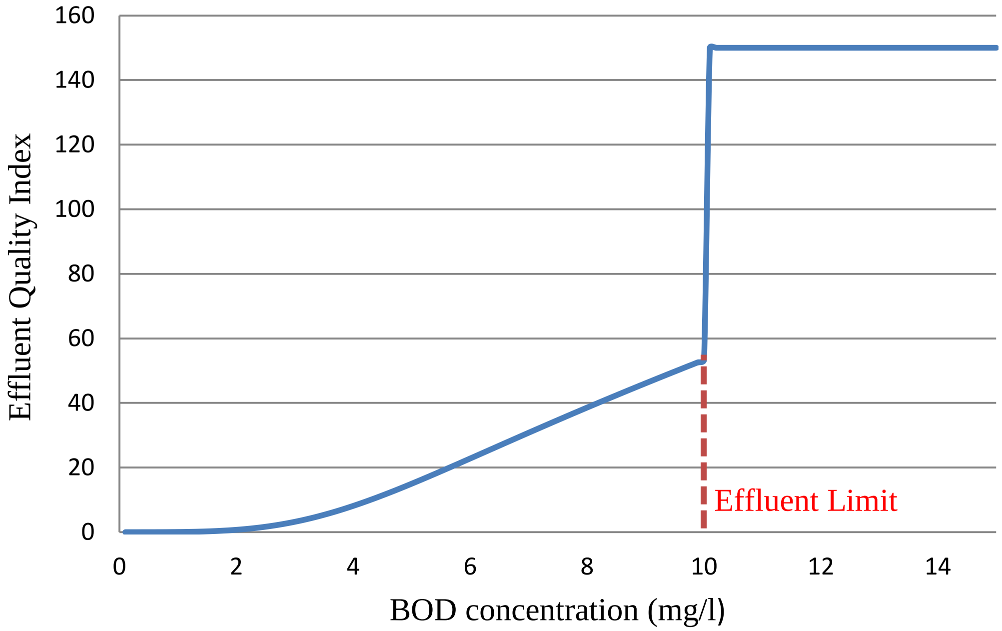

Figure 4.2: Example of a plot of effluent quality index of BOD effluent using Eq. (4.2)

The operating cost index (OCI) was primarily based on the approach proposed by Nopens et al., (2010). The OCI consists of major operating costs including (1) electricity use (for aeration (AE), pumping (PE), mixing (ME), heating for sludge digestion (HE), and revenues from biogas energy recovery (RE)), (2) external carbon dose (ECD), and (3) disposal of waste sludge produced (SP). The labor costs for maintenance and operation were not considered here. Heating energy required for digester operation was supplied by biogas collected from sludge digestion if available; otherwise electricity was used as the source of heating energy. It was assumed that excess biogas either earned revenue by being sold to other utilities or businesses, or was flared to avoid risks to human health and the environment. The operating cost index (OCI) was therefore calculated as:

$$\mathrm{OCI} = [(\mathrm{AE} + \mathrm{PE} + \mathrm{ME} + \mathrm{HE} - \mathrm{RE}) \times \mathrm{UC_{EE}} + \mathrm{ECD} \times \mathrm{UC_{ECD}} + SP \times \mathrm{UC_{SD}}] \qquad (4.3)$$

where the UC represents the unit costs for electric energy (EE), external carbon dose (ECD), and sludge disposal (SD).

The greenhouse gas index (GGI) took information from several sources of GHG emission from the plant, and both N_2O and CH_4 emissions were converted into CO_2-equivalents by using global warming potential (GWP). It was assumed that part of CH_4 produced from the sludge digester would be captured for energy recovery or would be flared, and as a result, there would be a small fraction of uncontrollable CH_4 leaks or inadvertent CH_4 venting in the system. In case of CH_4 capture, CH_4 was converted into CO_2 by chemical CO_2/CH_4 equivalent rather than GWP and then classified as a biogenic CO_2 emission. For this study, the methane capture rate (MCR) was set to a default factor of 90%. The greenhouse gas index (GGI) was therefore calculated as:

$$\mathrm{GGI} = \sum_{i=1}^{3} (\mathrm{G_i} \times \mathrm{GWP_i}) \tag{4.4}$$

where G_i is mass of CO_2, N_2O, and CH_4, GWP_i is global warming potential of CO_2, N_2O, and CH_4, UC_{cc} is unit cost of carbon credit, W_{GGI} is the weighting factor of GGI.

To provide a consistent basis for the comparison of system performance, all three indices were calculated as normalized values using expected maximum and minimum values of each index as:

$$x_n = \frac{x_{max} - x}{x_{max} - x_{min}} \tag{4.5}$$

Again, in order to integrate these three indices into a single index, a new weighing factor was assigned to each index on a scale of 0-1, in which the sum of the three weights was equal to 1. The weighing factor is typically assigned in order to discriminate between more important and less important indices according to the local and site-specific preferences. The Integrated performance index (IPI) is therefore defined as the weighted sum of three normalized and therefore non-dimensional criteria. As a default setting, each component in IPI had the same weight. The complete IPI was given by:

$$\mathrm{IPI} = \mathrm{EQI_n} \times \mathrm{W_{EQI}} + \mathrm{OCI_n} \times \mathrm{W_{OCI}} + \mathrm{GGI_n} \times \mathrm{W_{GGI}} \tag{4.6}$$

where W_i is weighting factor of each index (i).

The IPI was initially attempted to be defined as a single monetary term, but this approach was imperfect for several reasons, the most important of which was that the components were incomparable due to their different scales. Accordingly, each of the components was normalized by their range, which allowed large and small values of components to be compared.

4.2.4 Definition of Optimization Problem

The optimization problem dealt here was a multiple objective problem where trade-offs among three conflicting objectives should be made. There were three objectives to be minimized, namely (1) the amount of pollutants being discharged by the facility though effluent, (2) the operating costs, and (3) the amount of greenhouse gas emissions. These objectives conflict with one another. For example, the greenhouse gas minimization objective may adversely impact the effluent quality because pollutants present in the influent are removed in three different forms: sludge, effluent pollutants, and gases. Therefore, less carbon and nitrogen pollutions remain in the effluent if more pollutants are converted to GHGs or waste sludge. In addition, both greenhouse gas minimization and effluent discharge minimization objectives could be achieved at the expense of operating costs. A more detailed description of the interaction among the objectives is presented in Section 4.3.1.

There were a total of six decision variables (operational parameters) in the optimization problem: (1) DO level in the first aerobic reactor, (2) external carbon dose rate (ECD) (3) waste sludge flow rates (WS), (4) internal (nitrate) recycle flow rates (IR), (5) return sludge flow rates (RS), and (6) operating temperature of the anaerobic digestion (ADT). Initially, a sensitivity analysis was conducted in order to reduce the number of decision variables, but all six decision variables were sensitive to one of the three indices. The control strategy was derived by means of a mathematical optimization to achieve multiple objectives simultaneously. The ranges of variation of these decision variables were established within acceptable operational conditions as shown in Table 4.2.

Table 4.2 Bounds of Decision Variables

Decision variables	DO (mg/L)	ECD (m^3/d)	WS (m^3/d)	IR (m^3/d)	RS (m^3/d)	ADT (°C)
Upper bound	6	10	1200	150000	30000	40
Lower bound	1	0	300	30000	3000	30

The model imposed a number of constraints on both parameters and state variables that must be satisfied. They were included in the model by specifying lower and upper bounds on parameter values. In particular, the bounds of decision variables were determined within acceptable levels of operation as shown in Table 4.2. The effluent constraints were specified in the objective function (i.e. in EQI) by Eq. (4.2) to prevent any effluent violation.

There are different methods to deal with a multi-objective optimization problem (see e.g. Goicoechea et al., 1982). The aim of these methods is to identify a non-dominated solution also referred as the “Pareto” solution. Here, we have selected a well-known technique known as the weighted-sum method, which can be considered as a specific case of the more general compromise programming technique (Zeleny, 1973).

The complete optimization model is formulated as:

$$\text{Min IPI} = \mathrm{EQI_n} \times \mathrm{W_{EQI}} + \mathrm{OCI_n} \times \mathrm{W_{OCI}} + \mathrm{GGI_n} \times \mathrm{W_{GGI}} \tag{4.7}$$

subject to $X_{io} \leq X_i \leq X_{iu}$

$$EQ_j \leq EQ_{jl}$$

$$\text{Equations (4.2), (4.3), and (4.4)} \geq 0$$

where X_{io} and X_{iu} are lower and upper bounds of variables X_i, respectively. EQ_{jl} is the concentrations of effluent discharge limit for pollutant EQ_j (g/m^3). W_k is the weighting factor of index k, $\sum_{k=1}^{3} W_k = 1$.

4.2.5 Sensitivity Analysis

Prior to undertaking process optimization, a sensitivity analysis was performed on the model for six operational parameters and for each objective function and the integrated objective function. The sensitivity of the performance indices and their components to operational parameters was implemented not only to determine the important operational parameters for plant optimization, but also to investigate the relative effects of different operational options. Based on this information, optimization could be conducted with reduced number of parameters and the step size for solving the optimization problem could be determined. The relative sensitivity function was calculated from Eq. (3.9) by varying the parameters over feasible ranges and by calculating the relative percent changes in model objectives. The analysis was carried out using 80-day steady-state simulations. This simulation run time was determined by making preliminary simulations aimed at reducing the computation time while obtaining nearly the same sensitivity functions as the complete steady state condition.

4.2.6 Simulation Scenarios

In order to obtain a better understanding of the behavior of the model and to find the optimal operating conditions based on the proposed performance index, six scenarios of interest were simulated and evaluated as below and briefly summarized in Table 4.3.

Scenario 1: A baseline optimized operational setting was established as a reference scenario at normal operational set points in order to compare with other scenarios. Both biogenic and non-biogenic emissions were included. In all scenarios, 90% of the total amount of biogas generated from the anaerobic sludge digestion process was captured and the rest was released into the environment. All the captured biogas was used for energy recovery, and the excess energy after on-site use was sold for revenue. Equal weights were assigned for each of the three objectives.

Scenario 2: As mentioned in Chapter 3, there has been an ongoing debate regarding whether to include biogenic CO_2 emissions in the GHG estimations or not. To test the effects of these two classifications for the greenhouse gas estimation, only the non-biogenic CO_2 emissions generated from the bioreactor, digester, and biogas combustion were considered in the scenario.

Scenario 3: As presented in Chapter 3, the final disposal of biogas in WWTPs has a major impact on both the total GHG emission estimates and the operating costs. A decision has to be made regarding the final disposal of the biogas after being captured. Therefore, in this scenario, in contrast to Scenario 1, the captured biogas was flared on-site, converting the methane to less potent CO_2 rather than being used for energy recovery. Heating energy for operating the sludge digester was provided by external power supply.

Scenario 4-6: In a multi-objective optimization problem, the importance of each objective may vary depending on site-specific preferences. The proposed model expressed the importance by using weighting factors. In order to more clearly evaluate the impact of respective weights of each index, only one index was considered in each scenario without other index's interface. In other word, for a scenario one index is weighted 1 and the other two indices have a value of zero. These scenarios aim at showing how the model is able to find new operational settings corresponding to varying performance preferences. The scenarios also give insight as to the potential change in the optimal value for each of the indices when the other two indexes are not considered.

Table 4.3: Summary of designed optimization scenarios

Scenario	Biogenic CO_2 included	Biogas energy recovery	Weighting factor		
			GGI	OCI	EQI
1	yes	yes	1/3	1/3	1/3
2	no	yes	1/3	1/3	1/3
3	yes	no	1/3	1/3	1/3
4	yes	yes	1	0	0
5	yes	yes	0	1	0
6	yes	yes	0	0	1

4.2.7 Optimization Methods

In general, activated sludge processes usually have highly non-linear behavior and therefore their optimizations are prone to converge to a local optimum. As the ASMN_G model was extended from ASMN to include GHG model, its complexity further increased. To ensure acceptable results from optimization simulations, two strategies were implemented in this study. First, optimization simulations were performed with five different sets of starting points for operational parameters, which are randomly chosen from knowledge on the process (Table 4.4). Although it was expected to obtain several local optima, output values of objective function close to the minimum value converged within a certain range. Secondly, two methods were implemented to solve the sixdimensional and multi-objective optimization problem. The first method was the Simplex optimization algorithm (Nelder and Mead, 1964), which is based on the sequential direct search method. Some applications of this method in the field of wastewater engineering can be found in the literature (Egea et al., 2007; Souza et al., 2008; Ludwig et al., 2011; Lust et al., 2012). The Simplex method was implemented using WEST simulation software. The Simplex method is an iterative method in which iterations proceed until the algorithm converges to an optimum. Due to the complexity of the optimization problem, the iterations averaged about 300 runs and went up to a maximum of 2,000 runs.

Table 4.4: Starting points for optimization simulation

No.	Parameters						IPI (Objective)	OCI	GGI	EQI
	DO (mg/L)	IR (m^3/d)	WS (m^3/d)	ECD (m^3/d)	RS (m^3/d)	ADT (^oC)				
1	2.0	86,000	400	3.5	23,000	35	47.262	15.046	14.365	17.851
2	4.0	120,000	600	5	8,000	37	52.062	15.041	19.868	17.153
3	5.0	140,000	500	2	10,000	33	43.709	12.273	14.839	16.598
4	1.0	100,000	310	2	15,000	39	48.972	14.150	17.986	16.836
5	3.0	90,000	800	1	12,000	35	46.501	9.673	21.277	15.551

The second method was the response surface methodology (RSM), which makes use of a set of statistical methods. The complete information of RSM can be found in Montgomery (2005). Several applications of RSM in wastewater treatment area can be found in the literature (Frigon et al., 2006; Akhbari et al., 2011; Mohapatra, et al., 2011). The RSM was implemented using Minitab software and the data was obtained by WEST simulation runs. Since the RSM was developed for the design and analysis of experiments, some modifications were needed to be made in cases, such as this study, where simulation data were used. For the same reason as the Simplex method, five different starting points were used. The 2^K full-factorial design was used in the first step to make a design around each starting point. A total of 65 simulations (64 for factorial design and 1 for center point) were needed for each 6-factors design. In the second step, the statistical analysis was performed using Analysis of Variance (ANOVA) for the evaluation of the effects of six factors (decision variables) on the response (objective) and for the information regarding the direction of steepest descent. Based on the result of the statistical analysis, a regression model that properly describes the relationship between the factors and the responses was derived. In the third step, assuming that it is likely that the starting points are located far from the actual optimum, the method of steepest descent was performed to rapidly move toward the optimum. The step size of the gradient vector was determined based on the regression coefficients of the second-order model because only a second-order model was fit to the simulation data. This line search started from the center point of the current design, and the process simulation was conducted at each step. The procedure continued along the path of steepest descent until no further decrease in response was observed at the next point. In the final step, another 2^K full-factorial design and its simulations were performed to check if an optimum would be reached. When no further improvement was observed around the currently best point, that point was regarded as the optimal setting of the decision variables; otherwise the sequence of steps was repeated with a new descent direction from the second step. In this study the steps were repeated 3 to 8 times under different starting points.

4.3. Results

4.3.1 Sensitivity Analysis

Based on the results of the sensitivity analysis, the sensitivity functions of the four indices (i.e. one integrated index and three individual indices) to the six influential parameters are ranked in Figure 4.3, and some additional information can be found in the appendix. The results showed that changes in the objective function significantly altered the ranking of the relative sensitivity. Each of the indices had different significant parameters. In Figure 4.3, the weight of each index was assumed to be equal. In general, insignificant parameters can be excluded for the model simulation based on the information obtained from a sensitivity analysis. However, considering the sensitivity analysis, it was decided to include all six operational parameters for the optimization simulation because they were all important to at least one of the four indices. For example, the sensitivity of both the integrated performance and the operating costs to ADT is significant, even though ADT has a negligible influence on both greenhouse gas emissions and effluent quality. In Figure 4.3, as the relative sensitivity functions are obtained by increasing the value of a specific parameter by 1%, direct proportion is indicated with a positive value while inverse proportion is indicated with a negative value. In a minimization problem, such as this study, a negative value describes a positive effect on the system performance. The sensitivity functions shown in Figure 4.3 revealed that a positive sensitivity caused by one parameter could be compensated by a negative sensitivity of the other parameters.

Among the considered parameters the most significant effects on the integrated performance originated from operating temperature in the digester, while the least significant effect was found at the waste sludge flow rate. The importance of the internal (nitrate) recycle to the effluent quality is not surprising, due to the fact that the effluent nitrogen criterion is very strict and the internal recycle is the most important parameter influencing the nitrogen removal efficiency. Contrary to common knowledge on the operation of an activated sludge process, it was shown that both operating costs and effluent quality were less sensitive to DO level. This could be explained by the fact that the DO level in the first aerobic reactor is the only parameter to be optimized and the DO levels of the two other aerobic reactors are controlled at a fixed value (2.0 mg/L). Thus, this might cause relatively small contribution to the two objectives.

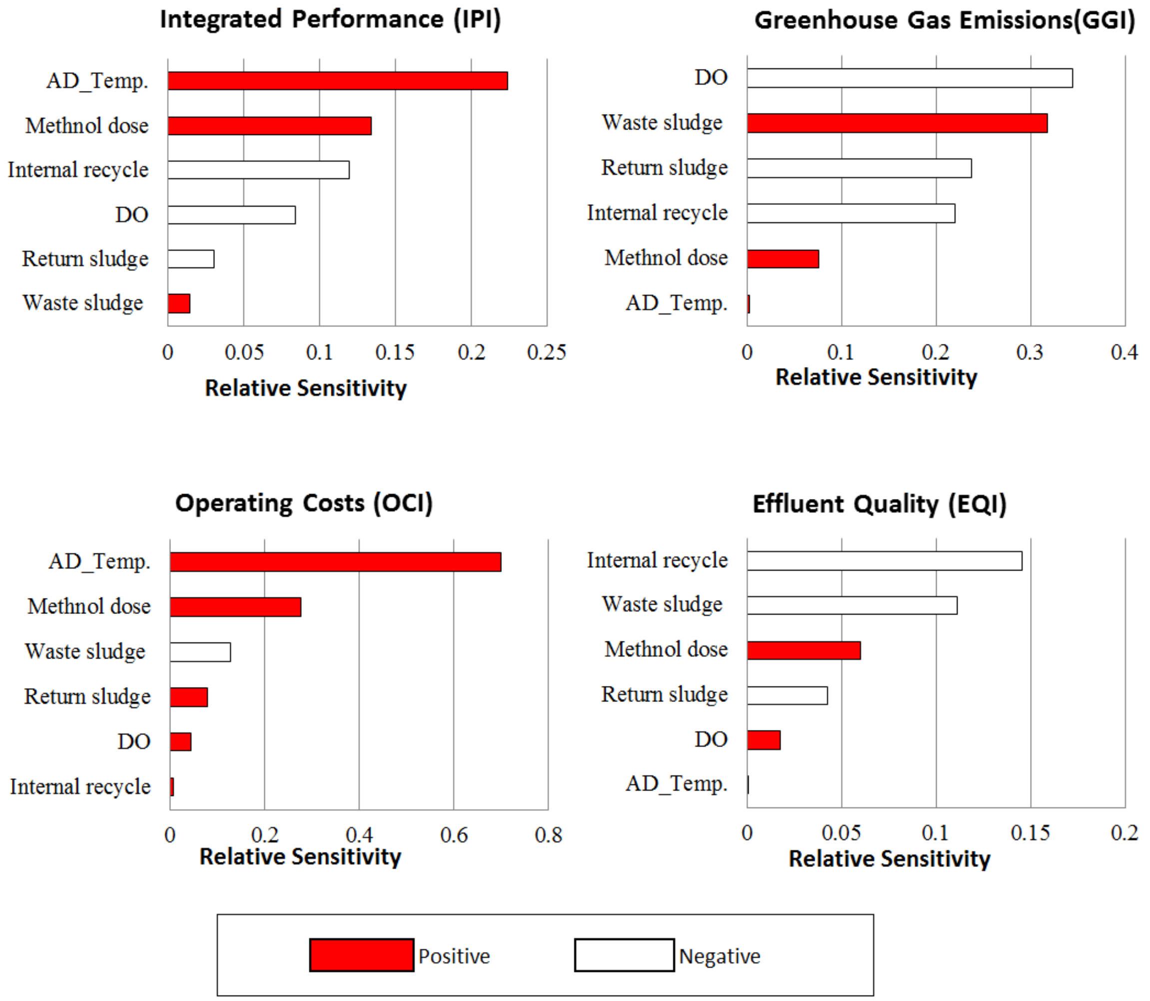

Figure 4.3: Graphical ranking of the relative sensitivity of operational parameters based on 1% perturbation of the operational parameter

4.3.2 Results of Response Surface Methodology

The system optimization on system performance was carried out using the response surface methodology (RSM). As defined in section 4.2.4, six factors (operational parameters) were chosen for a two level full factorial design, resulting in 64 design points for each center point to be simulated. A statistical analysis (i.e. ANOVA) was carried out on the simulation results, and the main effects and interaction effects were estimated. The coefficient of determination (R^2) and the adjusted determination coefficient (adjusted R^2) for the final optimal point after conducting the method of steepest decent was calculated as 91.40% and 89.65%, respectively. The second-order regression equation was established on the basis of the statistical analysis in coded units as shown in Eq. (4.8):

$$\begin{aligned} IPI = {} & 39.590-0.324DO+2.130IR+1.123WS+1.176ECD+0.110RS+0.689ADT \\ & -0.316IRxECD-0.686IRxWSxECD-0.707IRxWSxRS+0.644WSxECDxRS \end{aligned} \tag{4.8}$$

Table 4.5 reports the optimized operational parameters of the minimum objective function. The optimized parameters obtained from five different starting points converged into a certain range. It was noticed that the variation of return sludge (RS) was large due to its insignificant effect on the objective function. The results also showed that an increase of dissolved oxygen and of the internal recycle flow rate from the reference case would lead to an improvement of system performance. It was noted that the operating temperature of the anaerobic digester had more impact on the system performance in comparison to the dissolved oxygen level of the first aerobic reactor. Initially both methods were used to perform the optimization. It was found that both response surface and Simplex methods yielded similar optimal values, but the Simplex method was a more efficient way in terms of simulation time and ease of use. Therefore the Simplex method was used through the remainder of the study.

Table 4.5: Ranges of optimized operational parameters obtained from the response surface method

Parameters						Objective function	
DO (mg/L)	IR (m^3/d)	WS (m^3/d)	ECD (m^3/d)	RS (m^3/d)	ADT (°C)	IPI	% Improvement
3.12 – 3.52	93,980 – 10,9500	300 – 460	0.72 – 0.94	11,500 – 23,000	30.0 – 31.4	40,333 – 40,857	13.8

4.3.3 Optimization of Baseline Scenario

As has been in previous research on optimization of wastewater treatment processes (e.g. Jiang et al., 2008; Fang et al., 2009) in all scenarios, the optimization simulations converged to several local optima, due to the complexity of the response surface and a limitation of the search algorithm there was not a common optimal solution regardless of the starting points used. Rather each starting point produced an optimal solution that had a slightly different vector of operating parameter values and a slightly different optimal value. For this reason, both the objective function and the optimized parameters were described by a range, which gave more information, rather than a single value. The optima, that were much higher than average of the other trials, were likely caused by being trapped in a local optimum and therefore were excluded.

The effects of the system optimization under different scenarios can clearly be seen in Figure 4.4 - 4.7. Figure 4.4 depicts improvements in overall performance that are possible through optimization of operational parameters. The magnitude of system improvements that were achieved through system optimization is expressed in terms of the integrated performance index, which tells us how much system performance is improved as a percentage of the initial level when the system is operated at the optimized operational conditions found. In Scenario 1, by performing the operation optimization, the overall system performance (IPI) was improved by approximately 15% compared to the initial performance. This value was derived from the performance improvement of the individual components of the index (i.e. OCI improved 11%, GGI improved 31%, and EQI improved 2%). There were clear trade-offs amongst the conflicting three objectives (i.e. OCI, GGI, and EQI), although this particular result is not shown in Figure 4.4. For example, the simulation results showed that decreased GHG emissions (GGI) and improved effluent quality (EQI) resulted in improved overall system performance (IPI), but these improvements came at the expenses of increased operational costs (OCI). Figure 4.5 – 4.7 present a detailed description of the simulation results with unnormalized values of each index. Scenario 1 (reference case) achieved a high GHG reduction, but relatively low improvements in cost and effluent quality.

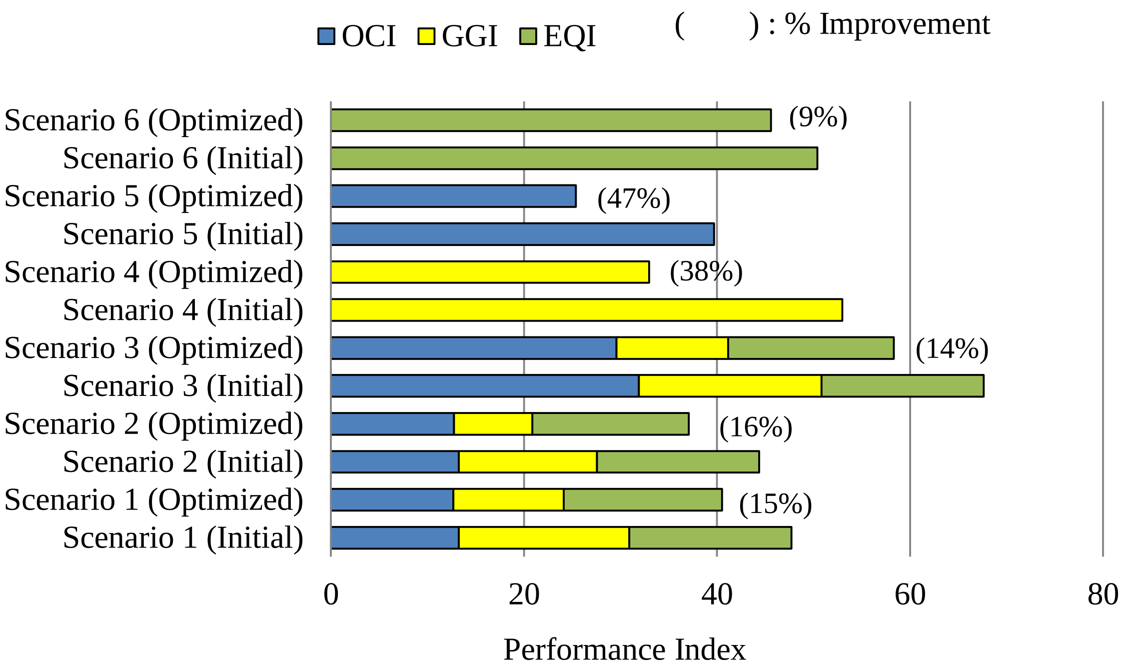

Figure 4.4: Comparison of performance index under six scenarios

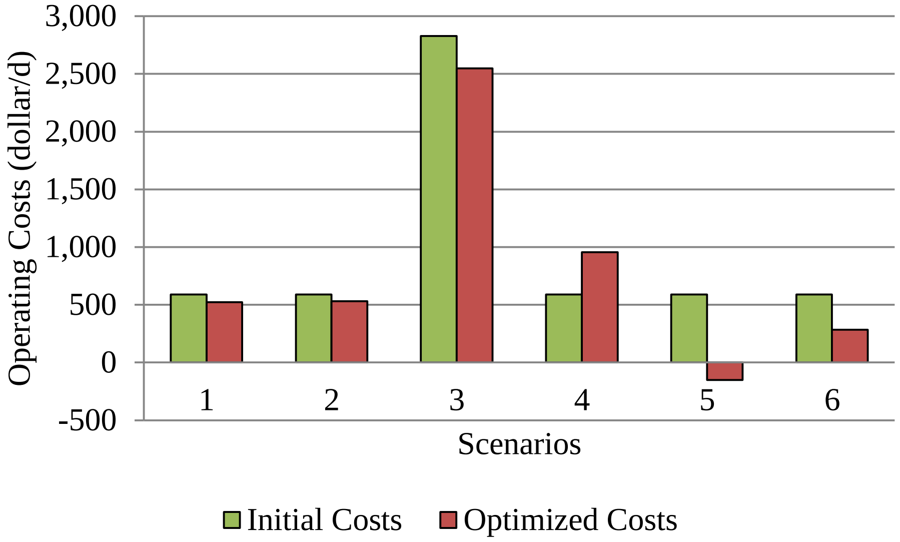

Figure 4.5: Comparison of operating costs under six scenarios

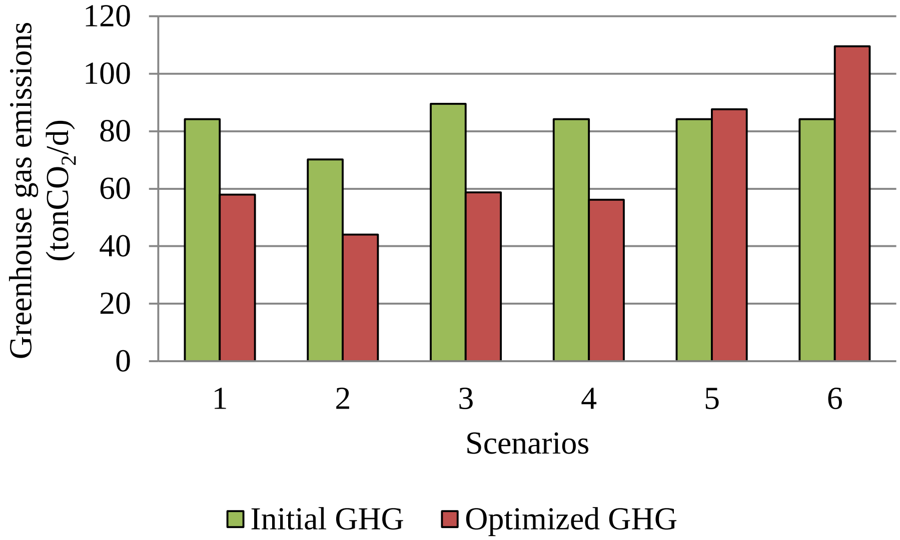

Figure 4.6: Comparison of greenhouse gas emissions under six scenarios

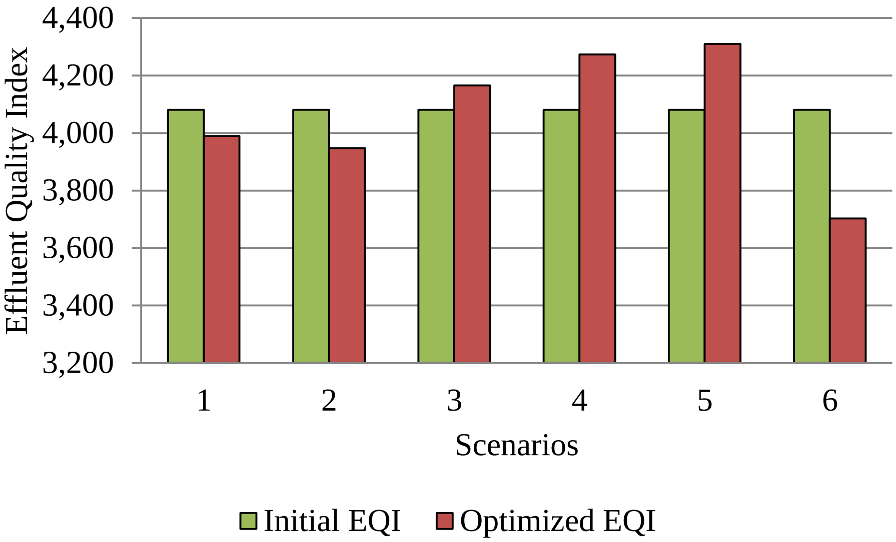

Figure 4.7: Comparison of effluent quality under six scenarios

The results of optimal operational parameters from five starting points under six scenarios are presented in Appendix E. Each of these values represents a set of operational parameters and corresponds with its objective function value. Some outliers are observed from the results of the optimization runs. To get a better view of the optimal operating conditions in terms of the system performance, the values are summarized in Figure 4.8 after discarding the extreme outliers. The operational parameters converged to a certain range of optimal operational conditions. It could be noticed that the variation of more sensitive parameters such as the digester operating temperature and the methanol dose rate were much lower than those of other less sensitive parameters.

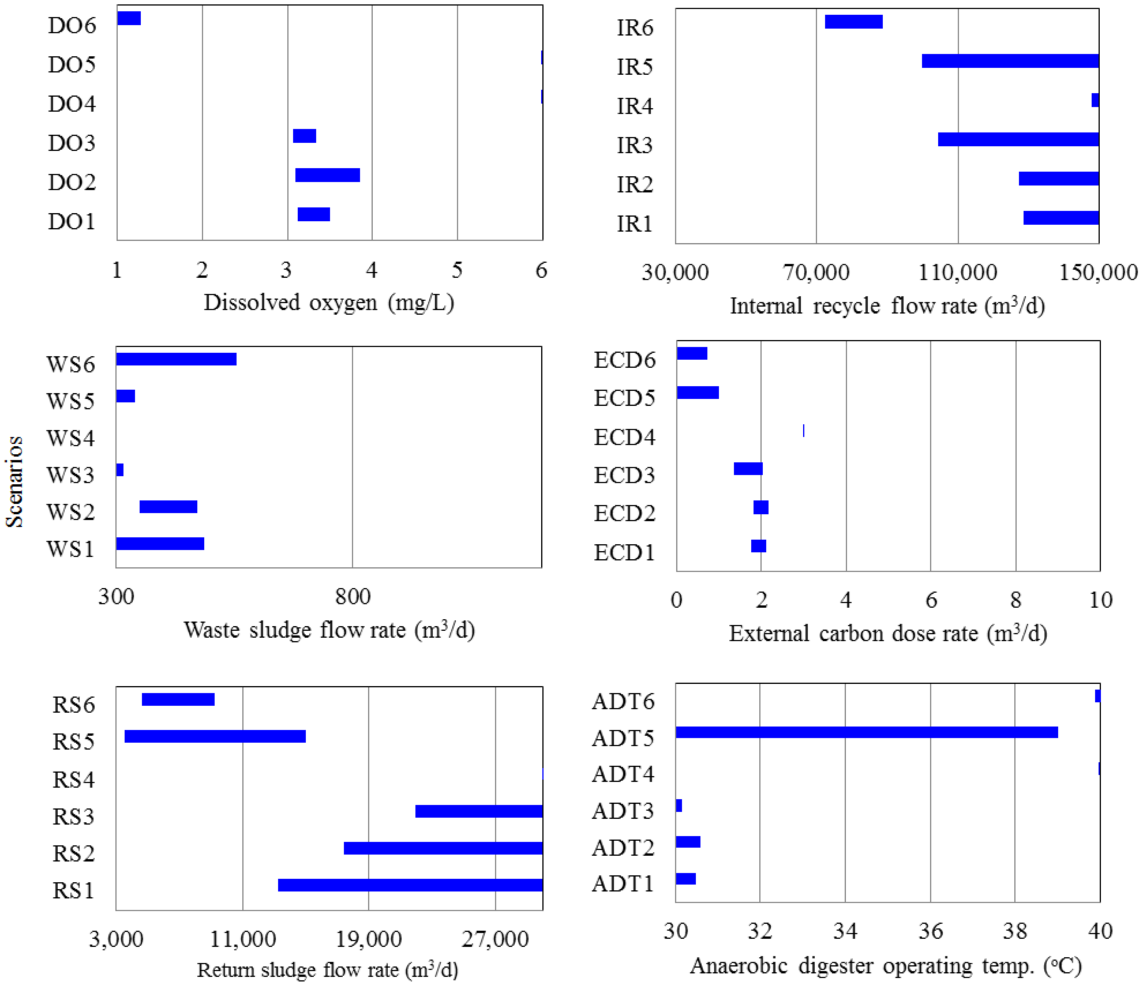

Figure 4.8: Optimized operational parameters to each scenario. The ranges of the parameters in the x-axis show the operating range.

4.3.4 Effects of Exclusion of Biogenic CO_2 Emissions

The amount of biogenic CO_2 emissions can vary depending on several factors such as influent characteristics and operational conditions. Biogenic CO_2 emissions in this work accounted for 20 - 30 % of total greenhouse gas emissions under different operational conditions or scenarios. When comparing the cases with and without biogenic CO_2 emissions (Scenario 2), quite similar optimal values of operational parameters were obtained as depicted in Figure 4.8.

4.3.5 Effects of Biogas Energy Recovery

The biogas generated from the anaerobic digester is generally combusted for energy recovery or flared to prevent any possible hazards. There is no doubt that biogas energy recovery may be beneficial when reducing both operating costs and greenhouse gas emissions. As expected, in the case of no energy recovery (Scenario 3), the minimum operating costs were dramatically increased by four times due to energy purchase for digester heating. Meanwhile, the other two objectives, greenhouse gas emissions and effluent quality, were not significantly affected, but there was an implicit trade-off among the sub-objectives. For example, the total amounts of greenhouse gas emissions were almost the same for both optima because of a trade-off between direct and indirect emissions. Energy recovery led to a slightly better effluent quality (approximately 5%) on EQI basis by allowing more carbon and nitrogen pollution present in the wastewater to be converted to gaseous pollution. Similar ranges of optimized parameters were obtained, compared to Scenario 1. However, as an exception, slightly lower ranges of waste sludge flow rate (higher solids retention time (SRT)) were observed in the case of energy recovery because the waste sludge flow rate was the least sensitive parameter for both scenarios and thereby converged to a wider range of optimal values.

4.3.6 Effects of Weights

Based on the weight assigned to each index, the objective will be oriented towards a different optimal point. Regarding the comparison of different weights (Scenario 4 - 6), the results of optimization simulations with five different starting points showed that Scenario 4 (weight of GGI, OCI, and EQI = 1:0:0) and Scenario 5 (weight of GGI, OCI, and EQI = 0:1:0) were significantly improved in terms of IPI (about 38 and 44%, respectively). This seemed to be due to high degree of flexibility in GGI and OCI. Scenario 6 (weight of GGI, OCI, and EQI = 0:0:1) showed the least performance improvement (9%) compared to the other two. Removal capacity of the process used was supposed to be one of the main reasons for this limited improvement.

The effluent quality of the plant was compared for the three scenarios. Table 4.6 shows that despite the only purpose of Scenario 6, not all criteria of effluent quality were improved. The total nitrogen (TN) concentration of Scenario 6 was actually worse than the other two scenarios. The most practical effluent improvement was accomplished by TKN removal. TKN concentration is the most strictly regulated under the given effluent limits. Although effluent quality was not a goal of Scenario 4 and 5, effluent quality was stable throughout the simulations due to the violation cost function.

Table 4.6: Comparison of effluent quality (mg/L) for Scenario 4 - 6

EQI Criteria	Effluent Limit	Scenario 4 (GGI)	Scenario 5 (OCI)	Scenario 6 (EQI)
COD	60.00	34.28	29.77	29.83
BOD	10.00	8.47	7.44	7.46
TN	8.00	6.60	6.31	7.12
TKN	3.00	2.29	2.98	2.00
TSS	45.00	13.00	9.20	9.30

4.4. Discussion

With increasing objectives and complexity of wastewater treatment processes, advanced operational strategies are highly demanded. Regarding the optimum operating conditions found, it seems that it would be possible to obtain very satisfactory system performance, i.e. minimizing operating costs and greenhouse gas emission, and at the same time treating the wastewater at better levels. Direct methane emission to the environment is thought be to be unusual at most WWTPs, and thus the contribution of methane to the total greenhouse gas emissions may be minor (less than 10%) if it is converted to carbon dioxide. Since this is the case for methane emissions at most plants, N_2O emission control is essential for the objective of minimizing greenhouse gas emissions. According to the plant-wide nitrogen balance analysis in Chapter 2, N_2 and N_2O are the main end gaseous products of the nitrogen removal process. Considering environmental aspects, efforts should be made to promote N_2 emissions rather than N_2O emissions. As seen in the results of sensitivity analysis and scenario analysis in this chapter, the GGI, in particular N_2O emissions, is significantly affected by DO levels. In the case of equal weights (Scenario 1-3), as seen in Figure 4.8 the optimal dissolved oxygen levels in the first aerobic reactor exist between 3 and 4 mg/L, at which N_2O production by ammonia-oxidizing bacteria (AOB) is prevented and complete nitrification is promoted. It is therefore suggested that the DO level in the first aerobic reactor should be maintained in this range, which is 50 - 100 % higher than the other aerobic reactors, to minimize greenhouse gas emissions. In this case, the GHG emission reduction that occurs by controlling N_2O emission is much greater than the indirect emission caused by intensive aeration.

In order to satisfy the effluent quality, it is important that the effluent TKN and TN should be properly controlled because these two water criteria are problematic due to their sensitivity and thereby often exceeded the limits. As seen in the sensitivity analysis (Figure 4.3), it is noticed that the effluent quality is significantly affected by three operational parameters: internal recycle, waste sludge (SRT), and external carbon dose (methanol). High internal recycle (400 - 500 % of the influent flow) is recommended for complete denitrification. In addition, long SRT controlled by waste sludge is required for nitrification, however it caused an increase in the effluent TKN and TN concentrations. The optimum waste sludge was between 300 and 480m^3/d, corresponding to the total system SRT range from 15 to 22 days. It is shown that a methanol dose of about 2m^3/d would be enough to promote complete denitrification, which is approximately 40 % less than the reference values.

Energy recovery from biogas is considered a worthwhile strategy because its advantage lies not only in the cost savings, but also in mitigating the environmental concerns posed by greenhouse gas emissions. The amount of biogas production is directly proportional to that of sludge production. Sludge production could be maximized by either decreased SRT or decreased biodegradation of organic substrate, resulting in an increase of organic substrate fed to the anaerobic digester. However, these strategies do not always give benefits. The well-intentioned practice of maximizing biogas production to minimize greenhouse gas emissions and operating cost may inadvertently be contributing large amounts of carbon and nitrogen loads to the environment. The denitrification process requires a carbon source, and thus external carbon would have to be added if more organic substrate is removed from the primary clarifier than is needed for the denitrification process. This can also lead to an unbalanced COD/N ratio for the denitrification process, causing increased N_2O production. Moreover, only the biodegradable part (i.e. volatile suspended solids (VSS)) of sludge is converted to biogas, and the remaining part is transported off-site for disposal. The present model does not consider sludge transportation costs for offsite disposal, but it could give somewhat different results. A suggestion for further study here is to include these costs as well. No significant changes of the biogas production were observed within the assigned operating temperature range of the digester (30-40 ^{o}C). As presented in Chapter 2, biogas is often oversaturated with the digester effluent. A technology to economically recover dissolved CH_4 from the effluent could make anaerobic treatment more favorable in reducing greenhouse gas emissions and operating costs.

An important issue that is often encountered when solving a nonlinear optimization problem is local optimum. In fact, as the model became more complex with the inclusion of a new model, both optimization algorithms (i.e. RSM and Simplex) tended to end their search at different local optima. This is a clear indication of the nonlinear nature of the system. Since this problem was already encountered by other researchers, the optimization algorithm was implemented with some countermeasures. It is important to note that the quality of optimization simulation is significantly affected by starting points of the parameters to be optimized and their step size. For a better solution, it was attempted to run the optimization simulations with different starting points. Due to the complexity of the model and the resulting substantial computational load (i.e. large amount of computational time required), only five sets of starting points of the parameters were used for each scenario. When using the WEST simulator, about 10 to 15 minutes of computational time were required per iteration in each scenario, and about two hundred to two thousand iterations were required to find an optimum solution for each scenario. Accordingly, the solution of this optimization simulation may not guarantee to be a global optimum. Further research is therefore needed in order to reduce computational time while ensuring convergence to a proper solution. In addition, in both optimization algorithms, the step size of parameters was determined based on the information from regression coefficients or sensitivity analysis. From the preliminary runs by the Simplex method, it was observed that a smaller step size generally increased the number of iteration; however this did not guarantee a best solution. A correct choice of step size is crucial for obtaining correct results. Further research on these problems is needed; however it is beyond the time scope of this study. Nevertheless, this optimization work provided a useful means for finding optimal operating conditions in WWTPs.

4.5. Conclusions

Due to increasing attention towards sustainable infrastructure, some recent studies have dealt with wastewater treatment systems by considering the reduction of greenhouse gas emissions as well as operating costs and effluent quality. However, few attempts have been made to satisfy all three objectives simultaneously. In this study, with the aid of an optimization algorithm, multi-objectives of WWTPs could be achieved simultaneously. To do this, an integrated index that combined the three objectives was proposed, which was necessary for the optimization simulation and could cover all the major concerns in the wastewater treatment system. To the author’s knowledge, it was the first time that optimization simulation using activated sludge models along with these three criteria was implemented. The model developed in Chapter 3 was used to determine optimum operating conditions of the nonlinear system. From the comprehensive implementation of system optimization, it can be concluded that more sustainable system will be achieved even in existing facilities by improving inadequate operating strategies. It is hoped that the proposed model could help inform decisions for evaluating the success of sustainable practices for wastewater treatment plants. In order to improve this work for practical applications, further research is needed to reduce the computational time and identify a proper step size used by the Simplex method.

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APPENDIX A: STOICHOMETRY OF PROCESS REACTIONS IN ASMN DERIVED BY ELEMENTAL BALANCE

Chemical composition:

$S_S - C_{c1}H_{h1}O_{o1}$, $X_{BH} - C_{c2}H_{h2}O_{o2}N_{n2}$, $X_P - C_{c3}H_{h3}O_{o3}N_{n3}$, $X_S - C_{c4}H_{h4}O_{o4}$

1. Aerobic Growth of heterotrophs

$$\frac{1}{Y_\mathrm{H}}C_{c1}H_{h1}O_{o1}+\frac{-4c1-h1+2o1+(4c2+h2-3n2-2o2)Y_\mathrm{H}}{4Y_\mathrm{H}}O_2+n2NH_4^+$$

$$\rightarrow C_{c2}H_{h2}N_{n2}O_{o2}+\frac{-h1+h2Y_\mathrm{H}-3n2Y_\mathrm{H}}{2Y_\mathrm{H}}H_2O+\frac{-c1+c2Y_H}{Y_H}CO_2+n2H^+$$

2. Anoxic Growth of heterotrophs ($NO_3^- \rightarrow NO_2^-$)

$$\frac{1}{Y_\mathrm{H}}C_{c1}H_{h1}O_{o1}+\frac{-4c1-h1+2o1+(4c2+h2-3n2-2o2)Y_\mathrm{H}}{2Y_\mathrm{H}}NO_3^-+n2NH_4^+$$

$$\rightarrow C_{c2}H_{h2}N_{n2}O_{o2}+\frac{-4c1-h1+2o1+(4c2+h2-3n2-2o2)Y_\mathrm{H}}{2Y_\mathrm{H}}NO_2^-$$

$$+\frac{-h1+(h2+3n2)Y_\mathrm{H}}{2Y_\mathrm{H}}H_2O+\frac{-c1+c2Y_H}{Y_H}CO_2+n2H^+$$

3. Anoxic Growth of heterotrophs (NO_2^- → NO)

$$\frac{1}{Y_{\mathrm{H}}}C_{c1}H_{h1}O_{o1}+\frac{\text{-}4c1\text{-}h1+2o1+(4c2+h2\text{-}3n2\text{-}2o2)Y_{\mathrm{H}}}{2Y_{\mathrm{H}}}NO_2^-$$

$$+n2NH_4^+ +\frac{\text{-}4c1\text{-}h1+2o1+(4c2+h2\text{-}2n2\text{-}2o2)Y_{\mathrm{H}}}{2Y_{\mathrm{H}}}H^+$$

$$\rightarrow C_{c2}H_{h2}N_{n2}O_{o2}+\frac{\text{-}4c1\text{-}h1+2o1+(4c2+h2\text{-}\ 3n2\text{-}\ 2o2)Y_{\mathrm{H}}}{2Y_{\mathrm{H}}}NO$$

$$+\frac{-2c2+(h2\text{-}\ 3n2)Y_{\mathrm{H}}+2c1+h1-o1}{2Y_{\mathrm{H}}}H_2O+\frac{-c1+c2Y_H}{Y_H}CO_2$$

4. Anoxic Growth of heterotrophs (NO → N_2O)

$$\frac{1}{Y_{\mathrm{H}}}C_{c1}H_{h1}O_{o1}+\frac{\text{-}4c1\text{-}h1+2o1+(4c2+h2\text{-}3n2\text{-}2o2)Y_{\mathrm{H}}}{2Y_{\mathrm{H}}}NO+n2NH_4^+$$

$$\rightarrow C_{c2}H_{h2}N_{n2}O_{o2}+\frac{\text{-}4c1\text{-}h1+2o1+(4c2+h2\text{-}\ 3n2\text{-}\ 2o2)Y_{\mathrm{H}}}{2Y_{\mathrm{H}}}N_2O$$

$$+\frac{-h1+(h2\text{-}3n2)Y_{\mathrm{H}}}{2Y_{\mathrm{H}}}H_2O+\frac{-c1+c2Y_H}{Y_H}CO_2+n2H^+$$

5. Anoxic Growth of heterotrophs ($N_2O \rightarrow N_2$)

$$\frac{1}{Y_\mathrm{H}} C_{c1}H_{h1}O_{o1} + \frac{-4c1-h1+2o1+(4c2+h2-3n2-2o2)Y_\mathrm{H}}{2Y_\mathrm{H}} N_2O + n2NH_4^+$$

$$\rightarrow C_{c2}H_{h2}N_{n2}O_{o2} + \frac{-4c1-h1+2o1+(4c2+h2-3n2-2o2)Y_\mathrm{H}}{2Y_\mathrm{H}} N_2$$

$$+\frac{-h1+(h2-3n2)Y_\mathrm{H}}{2Y_\mathrm{H}} H_2O + \frac{-c1+c2Y_H}{Y_H} CO_2 + n2H^+$$

6. Decay of Biomass

$$C_{c2}H_{h2}N_{n2}O_{o2} + \frac{-c3n2+c2n3f_p}{c3} H^+$$

$$+[\frac{c3(2c4h2-2c2h4-h4o2-h2o4-n2(6c4-h4-3o4))}{c3(4c4+h4-2o4)}$$

$$+\frac{-c2f_p(2c4h3-c3h4-6c4n3+h4o3-h3o4+3n3o4)}{c3(4c4+h4-2o4)}]H_2O$$

$$\rightarrow \frac{-4c2c3-c3h2+3c3n2+2c3o2+c2f_p(4c2+h3-3n2-2o3)}{c3(4c4+h4-2o4)} C_{c3}H_{h3}N_{n3}O_{o3}$$

$$+\frac{c2f_p}{c3} C_{c4}H_{h4}N_{n4}O_{o4} + \frac{-c3n2+c2n3f_p}{c3} NH_4^+$$

$$+[\frac{c3(c4h2-c2h4-2c4o2-2c2o4-3n2c4)}{c3(4c4+h4-2o4)}$$

$$-\frac{c2f_p(c4h3-c3h4-3c4n3+2c4o3-2c3o4)}{c3(4c4+h4-2o4)}] CO_2$$

7. Aerobic Growth of AOB

$$c2CO_2 + \frac{Y_{A1}n2+1}{Y_{\mathrm{A1}}}NH_4^+ + (c2 + \frac{h2-3n2-2o2}{4} - \frac{3}{2Y_{A1}})O_2$$

$$\rightarrow C_{c2}H_{h2}N_{n2}O_{o2} + \frac{h2Y_{\mathrm{A1}}\ -3n2Y_A - 2}{2\ Y_{A1}}H_2O + \frac{1}{Y_{A1}}NO_2 + (n2 + \frac{2}{Y_{A1}})H^+$$

8. Aerobic Growth of NOB

$$c2CO_2 + n2NH_4^+ + (c2 + \frac{h2-3n2-2o2}{4} - \frac{1}{2Y_{A2}})O_2 + \frac{1}{Y_{A2}}NO_2^-$$

$$\rightarrow C_{c2}H_{h2}N_{n2}O_{o2} + \frac{h2-3n2}{2}H_2O + \frac{1}{Y_{A2}}NO_3 + n2H^+$$

9. Autotrophic Denitrification (NO$_2$ →NO, added for ASMN_G)

$$c2CO_2 + (1 + \frac{1}{Y_{A1}})NH_4^+ + \frac{-f_o(-3+10Y_{A1})}{2Y_{A1}}O_2 + (5 - 4c2 + 20f_o - h2 - 2n2 + 2o2$$

$$+ \frac{5}{Y_{A1}} - \frac{6f_o}{Y_{A1}})NO_2 + \left(4 - 4c2 + 20f_o - h2 - 2n2 + 2o2 + \frac{4}{Y_{A1}} - \frac{6f_o}{Y_{A1}}\right)H^+$$

$$\rightarrow C_{c2}H_{h2}N_{n2}O_{o2} + (4 - 2c2 + 10f_o - h2 - n2 + o2 + \frac{4-3f_o}{Y_{A1}})H_2O$$

$$+ (6 - 4c2 + 20f_o - h2 - 3n2 + 2o2 + \frac{6(1-f_o)}{Y_{A1}})NO$$

10. Autotrophic Denitrification (NO →N$_2$O, added for ASMN_G)

$$c2CO_2 + (n2 + \frac{1}{Y_{A1}})NH_4^+ + \left(\frac{3f_o - 10f_oY_{A1}}{2Y_{A1}}\right)O_2 + (-4c2 + 20f_o - h2 + 3n2 + 2o2 + \frac{6(1-f_o)}{Y_{A1}}NO$$

$$\rightarrow C_{c2}H_{h2}N_{n2}O_{o2} + (\frac{1}{Y_{A1}} - \frac{h_2 - 3n_2}{2})H_2O + \frac{1}{Y_{A1}}NO_2^- + (n_2 + \frac{2}{Y_{A1}})H^+ + (-2c2 + 10f_o + o2 - \frac{(h2 - 3n2)}{2} + \frac{3(1-f_o)}{Y_{A1}})N_2O$$

APPENDIX B: PLANT-WIDE CARBON, NITROGEN, AND COD MASS BALANCES

Carbon mass balance (%)

Items		Total	Inflow		Outflow			
			Influent	External Carbon	Bioreactor	Digester	Effluent	Sludge disposal
Model components	S_{CO2}	-	0	0	0	0	1.0	0
	S_I	-	0.2	0	0	0	2.5	0
	S_S	-	10.0	10.0	0	0	0.2	0
	X_{BA1}	-	0	0	0	0	0.1	0
	X_{BA2}	-	0	0	0	0	0	0
	X_{BH}	-	3.4	0	0	0	1.5	0
	X_I	-	14.4	0	0	0	0.9	22.7
	X_P	-	0	0	0	0	0.4	0.8
	X_S	-	59.8	0	0	0	0.1	3.6
	Alk	-	-	-	0	2.8	-	-
Gas Stripping	CO_2	44.4	0	0	34.2	10.2	0	0
	CH_4	19.1	0	0	0	19.1	0	0
Inflow		100	90.0	10.0	0	0	0	0
Outflow		100	0	0	34.2	32.1	6.5	27.2
Total			100		100			

Nitrogen mass balance (%)

Items		Total	Inflow	Outflow			
			Influent	Bioreactor	Digester	Effluent	Sludge disposal
Model components	S_{N2}	-	0	0	0	37.5	0
	S_{N2O}	-	0	0	0	0.2	0
	S_{ND}	-	12.0	0	0	0.6	0
	S_{NH}	-	48.1	0	0	1.5	0.9
	S_{NO}	-	0	0	0	0.1	0
	S_{NO2}	-	0	0	0	0.5	0
	S_{NO3}	-	0	0	0	12.0	0
	X_{BA1}	-	0	0	0	0.1	0
	X_{BA2}	-	0	0	0	0	0
	X_{BH}	-	4.2	0	0	1.8	0
	X_I	-	11.6	0	0	0.7	18.2
	X_{ND}	-	24.1	0	0	0.1	2.3
	X_P	-	-	0	0	0.4	0.9
Gas Stripping	N_2O	7.9	0	7.9	0	0	0
	N_2	13.4	0	13.3	0.1	0	0
	NO	1.0	0	1.0	0	0	0
Inflow		100	100	0	0	0	0
Outflow		100	0	22.2	0.1	55.4	22.3
Total			100	100			

COD mass balance (%)

Items		Total	Inflow		Outflow			
			Influent	External Carbon	Bioreactor	Digester	Effluent	Sludge disposal
Model components	S_I	-	2.2	0	0	0	2.3	0
	S_S	-	10.4	10.4	20.9	0	0.2	0
	X_{BA1}	-	0	0	-0.4	0	0	0
	X_{BA2}	-	0	0	-0.1	0	0.1	0
	X_{BH}	-	3.0	0	-10.2	0	0	0
	X_I	-	11.9	0	0	0	1.5	18.7
	X_P	-	0	0	-3.8	0	1.1	0.9
	X_S	-	62.2	0	32.4	0	0.5	3.8
Gas Stripping	CO_2	39.5	0	0	0	0	0	0
	CH_4	18.6	0	0	0	32.9	0	0
Inflow		100	89.6	10.4	0	0	0	0
Outflow		100	0	0	38.8	32.9	5.0	23.4
Total			100		100			

APPENDIX C: STOICHIOMETRY OF NITRIFIER DENITRIFICATION DERIVED BY REDOX REACTIONS

1. The nitrite reduction reaction was constructed first:

---

fe·(1-fo)·Ra : $fe\cdot(1\text{-}fo)\cdot(NO_2^- + 2H^+ + e^- \rightarrow NO + H_2O)$

fe·fo·Ra : $fe\cdot(1\text{-}fo)\cdot(0.25O_2 + 2H^+ + e^- \rightarrow H_2O)$

fs·Rc : $fs(0.05NH_4^+ + 0.2CO_2 + 0.05HCO_3^- + H^+ + e^- \rightarrow 0.05C_5H_7NO_2 + 0.45H_2O)$

-Rd : $0.167NH_4^+ + 0.33H_2O \rightarrow 0.167NO_2^- + 1.333\ H^+ + e^-$

R: $(0.513\text{-}0.68fo)NO_2^- + (0.347\text{-}0.68fo)H^+ + 0.183NH_4^+ + 0.17foO_2 + 0.064CO_2 + 0.016HCO_3^-$

$\rightarrow 0.016C_5H_7NO_2 + 0.68(1\text{-}fo)NO + (0.34fo - 0.494)H_2O$

---

2. The nitric oxide reduction reaction is determined:

---

fe·(1-fo)·Ra : $fe\cdot(1\text{-}fo)\cdot(NO + H^+ + e^- \rightarrow 0.5N_2O + 0.5H_2O)$

fe·fo·Ra : $fe\cdot(1\text{-}fo)\cdot(0.25O_2 + 2H^+ + e^- \rightarrow H_2O)$

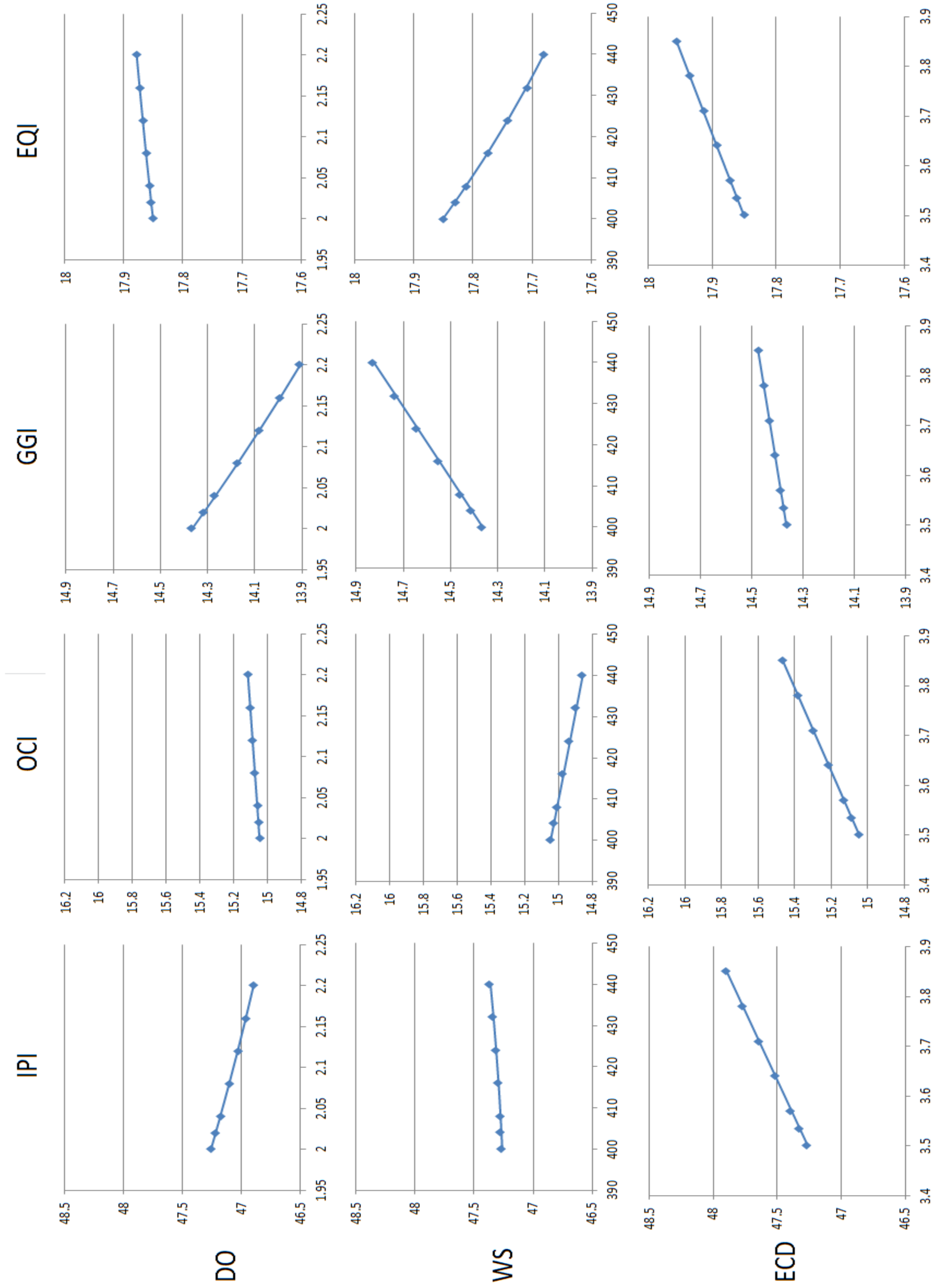
fs·Rc : $fs(0.05NH_4^+ + 0.2CO_2 + 0.05HCO_3^- + H^+ + e^- \rightarrow 0.05C_5H_7NO_2 + 0.45H_2O)$

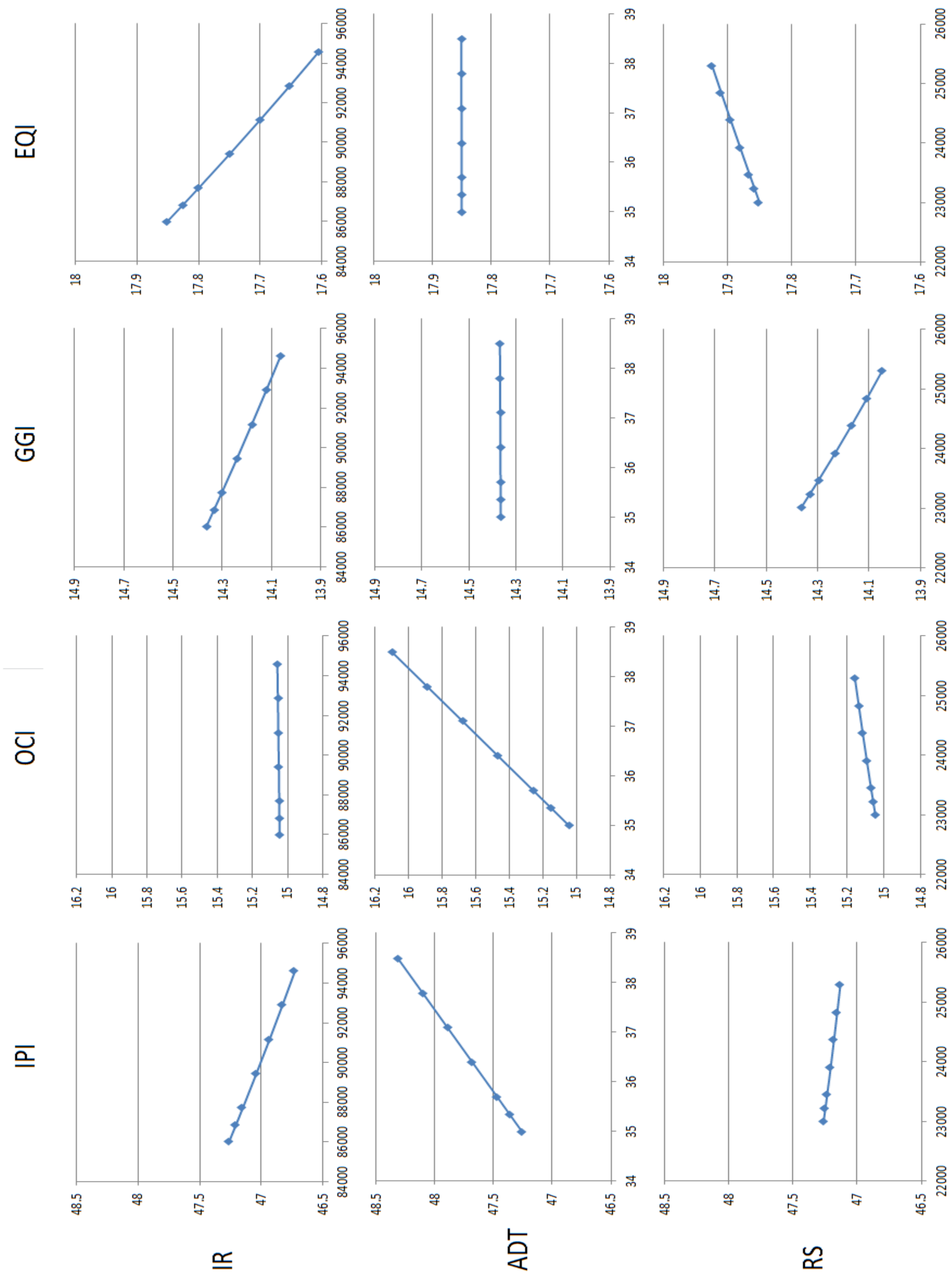
-Rd : $0.167NH_4^+ + 0.33H_2O \rightarrow 0.167NO_2^- + 1.333\ H^+ + e^-$

R: $0.68(1\text{-}fo)NO + 0.183NH_4^+ + 0.17foO_2 + 0.064CO_2 + 0.016HCO_3^-$

$\rightarrow 0.016C_5H_7NO_2 + 0.34(1\text{-}fo)N_2O + 0.167NO_2^- + 0.15H_2O + 0.33H^+$

APPENDIX D: BREAKDOWN OF SENSITIVITY ANALYSIS RESULTS WITH EQUAL WEIGHT




IPI
OCI
GGI
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RS
48.5
48
47.5
47
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16.2
16
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APPENDIX E: RESULTS OF THE OPTIMAL OPERATION SOLUTION OBTAINED FROM THE SIMPLEX METHOD

Scenario 1

Starting point	Case	Parameters						Objective function	Total cost (dollar/d)	Total GHG emissions (ton CO_2 /d)	Effluent Quality
		DO (g/m^3)	IR (m^3/d)	WS (m^3/d)	ECD (m^3/d)	RS (m^3/d)	ADT (°C)				
1	Initial	2.0	86,000	400	3.5	23,000	35.0	43.7	806	55.3	4,331
	Optimized	3.3	148,823	471	2.1	29,954	30.0	36.8	505	44.2	3,930
2	Initial	4.0	120,000	600	5.0	8,000	37.0	48.6	805	78.8	4,165
	Optimized	3.1	146,054	349	1.9	17,430	30.1	36.7	454	45.5	3,925
3	Initial	5.0	140,000	500	2.0	10,000	33.0	40.5	473	58.8	4,034
	Optimized	3.4	149,981	471	2.2	29,981	30.0	36.8	511	44.0	3,928
4	Initial	1.0	100,000	310	2.0	15,000	39.0	45.6	698	71.3	4,090
	Optimized	6.0	130,580	305	1.7	12,317	30.1	38.0	669	42.8	3,965
5	Initial	3.0	90,000	800	1.0	12,000	35.0	43.5	161	86.7	3,786
	Optimized	3.9	127,487	455	1.8	28,207	30.6	37.0	510	43.7	3,989

Scenario 2

Starting point	Case	Parameters						Objective function	Total cost (dollar/d)	Total GHG emissions (ton CO_2 /d)	Effluent Quality
		DO (g/m^3)	IR (m^3/d)	WS (m^3/d)	ECD (m^3/d)	RS (m^3/d)	ADT (ºC)				
1	Initial	2.0	86,000	400	3.5	23,000	35.0	43.7	806	55.3	4,331
	Optimized	3.3	148,823	471	2.1	29,954	30.0	36.8	505	44.2	3,930
2	Initial	4.0	120,000	600	5.0	8,000	37.0	48.6	805	78.8	4,165
	Optimized	3.1	146,054	349	1.9	17,430	30.1	36.7	454	45.5	3,925
3	Initial	5.0	140,000	500	2.0	10,000	33.0	40.5	473	58.8	4,034
	Optimized	3.4	149,981	471	2.2	29,981	30.0	36.8	511	44.0	3,928
4	Initial	1.0	100,000	310	2.0	15,000	39.0	45.6	698	71.3	4,090
	Optimized	6.0	130,580	305	1.7	12,317	30.1	38.0	669	42.8	3,965
5	Initial	3.0	90,000	800	1.0	12,000	35.0	43.5	161	86.7	3,786
	Optimized	3.9	127,487	455	1.8	28,207	30.6	37.0	510	43.7	3,989

Scenario 3

Starting point	Case	Parameters						Objective function	Total cost (dollar/d)	Total GHG emissions (ton CO_2 /d)	Effluent Quality
		DO (g/m^3)	IR (m^3/d)	WS (m^3/d)	ECD (m^3/d)	RS (m^3/d)	ADT (°C)				
1	Initial	2.0	86,000	400	3.5	23,000	35.0	65.8	2,881	75.4	4,331
	Optimized	5.4	112,008	368	1.7	29,347	30.8	59.0	2,674	57.2	4,155
2	Initial	4.0	120,000	600	5.0	8,000	37.0	74.2	3,298	99.1	4,165
	Optimized	3.4	104,297	314	1.4	29,927	30.2	57.7	2,396	59.5	4,277
3	Initial	5.0	140,000	500	2.0	10,000	33.0	63.7	2,735	76.9	4,034
	Optimized	3.1	149,981	300	2.1	29,991	30.0	57.8	2,499	58.8	4,146
4	Initial	1.0	100,000	310	2.0	15,000	39.0	67.5	2,744	91.7	4,090
	Optimized	6.0	107,948	335	1.5	24,410	30.3	59.4	2,709	57.2	4,181
5	Initial	3.0	90,000	800	1.0	12,000	35.0	67.1	2,490	104.5	3,786
	Optimized	3.3	132,511	313	1.7	21,929	30.1	57.6	2,467	60.6	4,066

Scenario 4

Starting point	Case	Parameters						Objective function	Total cost (dollar/d)	Total GHG emissions (ton CO_2 /d)	Effluent Quality
		DO (g/m^3)	IR (m^3/d)	WS (m^3/d)	ECD (m^3/d)	RS (m^3/d)	ADT (°C)				
1	Initial	2.0	86,000	400	3.5	23,000	35.0	43.1	806	70.3	4,331
	Optimized	6.0	147,918	300	3.0	29,981	40.0	28.6	1,375	50.0	4,206
2	Initial	4.0	120,000	600	5.0	8,000	37.0	59.6	805	93.4	4,165
	Optimized	5.2	77,437	319	1.2	27,434	39.9	30.1	939	52.2	4,455
3	Initial	5.0	140,000	500	2.0	10,000	33.0	44.4	473	72.3	4,034
	Optimized	6.0	149,937	300	3.0	29,997	40.0	28.6	1,382	50.0	4,199
4	Initial	1.0	100,000	310	2.0	15,000	39.0	54.0	698	85.5	4,090
	Optimized	6.0	146,161	300	3.0	29,968	30.1	28.6	1,015	50.0	4,209
5	Initial	3.0	90,000	800	1.0	12,000	35.0	63.8	161	99.4	3,786
	Optimized	5.6	146,259	333	0.6	3,503	30.1	49.0	68	78.5	4,296

Scenario 5

Starting point	Case	Parameters						Objective function	Total cost (dollar/d)	Total GHG emissions (ton CO_2 /d)	Effluent Quality
		DO (g/m^3)	IR (m^3/d)	WS (m^3/d)	ECD (m^3/d)	RS (m^3/d)	ADT (^oC)				
1	Initial	2.0	86,000	400	3.5	23,000	35.0	45.1	806	70.3	4,331
	Optimized	1.0	150,000	1,200	0.0	30,000	30.0	21.9	-124	86.8	4,162
2	Initial	4.0	120,000	600	5.0	8,000	37.0	45.1	805	93.4	4,165
	Optimized	1.3	149,974	300	0.0	3,544	30.0	20.3	-190	88.1	4,261
3	Initial	5.0	140,000	500	2.0	10,000	33.0	36.8	473	72.3	4,034
	Optimized	1.0	149,979	338	0.0	4,395	30.1	20.7	-172	88.8	4,655
4	Initial	1.0	100,000	310	2.0	15,000	39.0	42.4	698	85.5	4,090
	Optimized	2.0	100,000	330	1.0	15,000	39.0	42.1	611	87.4	3,921
5	Initial	3.0	90,000	800	1.0	12,000	35.0	29.0	161	99.4	3,786
	Optimized	1.0	149,999	1,200	0.0	30,000	30.0	21.9	-123	86.8	4,162

Scenario 6

Starting point	Case	Parameters						Objective function	Total cost (dollar/d)	Total GHG emissions (ton CO_2 /d)	Effluent Quality
		DO (g/m^3)	IR (m^3/d)	WS (m^3/d)	ECD (m^3/d)	RS (m^3/d)	ADT (^oC)				
1	Initial	2.0	86,000	400	3.5	23,000	35.0	53.6	806	70.3	4,331
	Optimized	1.0	88,634	300	0.0	4,625	40.0	43.9	219	118.5	3,566
2	Initial	4.0	120,000	600	5.0	8,000	37.0	51.5	805	93.4	4,165
	Optimized	4.6	59,997	1,197	0.5	21,582	30.0	46.6	-5	93.4	3,780
3	Initial	5.0	140,000	500	2.0	10,000	33.0	49.8	473	72.3	4,034
	Optimized	1.3	72,481	553	0.7	9,121	39.9	44.9	296	120.4	3,644
4	Initial	1.0	100,000	310	2.0	15,000	39.0	50.5	698	85.5	4,090
	Optimized	6.0	99,907	907	2.0	14,956	39.0	48.3	694	89.4	3,918
5	Initial	3.0	90,000	800	1.0	12,000	35.0	46.7	161	99.4	3,786
	Optimized	1.1	79,465	533	0.1	9,253	40.0	44.4	217	118.0	3,604