

Quantification of Greenhouse Gas Emission from Wastewater Treatment Plants

By

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Abstract

Carbon dioxide, methane, and nitrous oxide are three types of greenhouse gases (GHGs) emitted from the wastewater treatment plants (WWTPs), which contribute to a significant carbon footprint. Therefore, the mitigation of GHG emission on the premise of ensuring standard effluent quality is a significant concern. In this study, GHGs emission from WWTPs can be divided into three categories: (1) energy and chemical consumption for wastewater treatment; (2) final disposal of biosolids; and (3) direct GHG emission from treatment processes. A model has been developed to quantify the greenhouse gases emission during wastewater treatment processes to help have a better understanding of the GHGs emission pathways. The estimation results of Guelph wastewater treatment show about 81% GHG is emitted from the final disposal field while 9% and 11% GHG is emitted from biological treatment and anaerobic digestion respectively. Based on estimation results, engineers could put forward suggestions on optimizing operation conditions to reduce GHG emission.

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Table of Contents

| | | |
|-------|--|----|
| 1. | Introduction | 9 |
| 1.1 | General | 9 |
| 1.2 | Scopes to estimate GHG emissions in a WWTP | 10 |
| 1.2.1 | Category 1. Direct emission from wastewater treatment processes | 10 |
| 1.2.2 | Category 2. Final disposal of biosolids | 12 |
| 1.2.3 | Category 3. Electricity and chemical consumption | 12 |
| 2 | Literature Review | 13 |
| 2.1 | Diverse types of GHGs emission during wastewater treatment process | 13 |
| 2.1.1 | Carbon dioxide (CO ₂) emission in WWTPs | 13 |
| 2.1.2 | Nitrous oxide (N ₂ O) emission in WWTPs | 15 |
| 2.1.3 | Methane (CH ₄) emission in WWTPs | 16 |
| 2.2 | Characteristics of Municipal Wastewater | 17 |
| 3. | Calculator Development | 17 |
| 3.1 | Aeration Tank/ Conventional Activated Sludge System. | 17 |
| 3.1.1 | Estimation of CO ₂ emitted from Aeration tank | 18 |
| 3.1.2 | Estimation of N ₂ O emission from activated sludge | 19 |
| 3.2 | Anaerobic Digestion | 21 |
| 3.2.1 | Estimation of biogas emitted from Anaerobic Digestion | 22 |
| 3.2.2 | Total CH ₄ and CO ₂ emission from anaerobic digestion | 23 |
| 3.3 | Final Biosolid disposal | 24 |
| 3.3.1 | GHGs emission from the final disposal of biosolids. | 24 |
| 4. | Sample Calculation | 25 |
| 4.1 | Sample calculation for GHGs emission from aeration tank/ activated sludge system | 25 |
| 4.2 | Sample calculation for GHGs emission from anaerobic digestion. | 26 |
| 4.3 | Sample calculation for GHGs emission from biosolids disposal. | 27 |
| 4.4 | Discussion | 28 |
| 5. | Summary & Outlook | 28 |
| | Appendix I- GHGs Calculation Summary of Guelph Wastewater Treatment Plant | 33 |

List of Figures

| | |
|---|----|
| Figure 1. Wastewater treatment levels, Canada, 1983 to 2009 (taken from the government of Canada)..... | 11 |
| Figure 2. a schematically layout of a WWTP with conventional activated sludge system. | 13 |
| Figure 3. Steps of anaerobic digestion process (adapted from Mustafa et al., 2013) | 14 |
| Figure 4. Biological and chemical pathways of N ₂ O production in the nitrification and denitrification processes. (Taken from the Campos et al., 2016)..... | 16 |
| Figure 5. Conventional Activated Sludge System | 19 |
| Figure 6. Anaerobic Digestion layout | 22 |

List of Tables

| | |
|--|----|
| Table 1. The GWP of GHGs on 100-year time Horizon..... | 10 |
| Table 2. Reported 2015 GHG emission by source (CO ₂ , CH ₄ , and N ₂ O included) (Adapted from the overview of 2015 reported emissions April 2017 Facility Greenhouse gas emission reporting) | 10 |
| Table 3. Unit processes of municipal wastewater treatment plant..... | 11 |
| Table 4. Typical numbers of parameters in raw influent (Adapted from Metcalf and Eddy et al. 4th ed. “Wastewater Engineering”). | 17 |
| Table 5. Nitrous oxide emissions (% of N-load) in full-scale and lab-scale measurement (adapted from Kampschreur et al., 2009a). | 20 |
| Table 6. Summary of N ₂ O Fluxes and Emission Factors Measured at Full-Scale WWTPs (adapted from AHN, 2010) | 21 |
| Table 7. Input parameters in activated sludge for the sample calculation (data from Guelph wastewater treatment plant). | 25 |
| Table 8. Assumed input parameters in anaerobic digester for the sample calculation. (data from Guelph wastewater treatment plant)..... | 26 |
| Table 9. Assumed input parameters of disposed biosolids for the sample calculation (data from Guelph wastewater treatment plant)..... | 27 |

1. Introduction

1.1 General

Recently, global warming caused by greenhouse gases has become one of the most critical issues in the environmental and climate change community. A greenhouse gas (often abbreviated as GHG) is a gas that traps the heat in the atmosphere, keeping the earth's surface warmer than it would be (EPA, 2018). Carbon dioxide, methane and nitrous oxide are three of the most abundant greenhouse gases in Earth's atmosphere. Different gases have a specific impact on the atmosphere in terms of their radiative efficiency and lifetime. Global warming potential (GWP) was developed to compare the global warming impacts of different gases. Generally, it represents the ratio between one kilogram of gas and one kilogram of carbon dioxide with a similar warming effect over the chosen time horizon, which is normally 100 years (EPA, 2018). Table 1 shows the global warming potentials measured on a 100-year horizon scale, relative to the emissions of carbon dioxide. In the past, managers in wastewater treatment plants have traditionally focused on minimizing operating cost on the basis of meeting effluent discharge limits. Municipal wastewater treatment plants (WWTPs) are known to be significant point sources of greenhouse gases emission including carbon dioxide, nitrous oxide, and methane. Therefore, there is an increasing need for mitigation of greenhouse gas emissions during wastewater treatment. Table 2 indicates the GHG emission from the wastewater treatment compared with other sources. It shows that 0.2% of GHGs

were emitted by wastewater treatment. However, GHGs emission from energy consumption for WWTP daily operation and sludge treatment, which could be a massive, are included in the different section. CO₂

Table 1. The GWP of GHGs on 100-year time Horizon

| Gas | Formula | Lifetime (years) | Radiative Efficiency $\left(\frac{W}{m^2 \cdot ppb}\right)$ | Global Warming Potential, 100-year |
|----------------|------------------|------------------|--|------------------------------------|
| Carbon Dioxide | CO ₂ | - | 1.4×10^{-5} | 1 |
| Nitrous Oxide | N ₂ O | 12 | 3.7×10^{-4} | 298 |
| Methane | CH ₄ | 114 | 3.03×10^{-3} | 25 |

Table 2. Reported 2015 GHG emission by source (CO₂, CH₄, and N₂O included) (Adapted from the overview of 2015 reported emissions April 2017 Facility Greenhouse gas emission reporting)

| | |
|---|---------------------------|
| Total CO ₂ N ₂ O & CH ₄ emission | 263 Mt CO ₂ eq |
| Stationary Fuel Combustion | 77% |
| Industrial Processes | 13% |
| Venting | 2% |
| Flaring | 2% |
| Fugitive Sources | 2% |
| On-site Transportation | 2% |
| Waste | 2% |
| Wastewater | 0.2% |

1.2 Scopes to estimate GHG emissions in a WWTP

There are three categories of GHG emission in wastewater treatment: 1. Electricity and chemical consumption, 2. Final disposal of biosolids and 3. Direct emission from wastewater treatment processes.

1.2.1 Category 1. Direct emission from wastewater treatment processes

In category 1, the GHG emissions will be calculated from individual treatment processes in WWTPs. The wastewater treatment plants in Canada include the major unit processes are shown in table3. Some units are not indispensable, it

depends on the design and objective of the wastewater treatment. As shown in figure 1, in 2009, approximately 69% of the Canadian population had sewer systems with secondary treatment or better, which means most wastewater treatment plants include secondary treatment. Therefore, the GHGs emission from all processes will be taken into account.

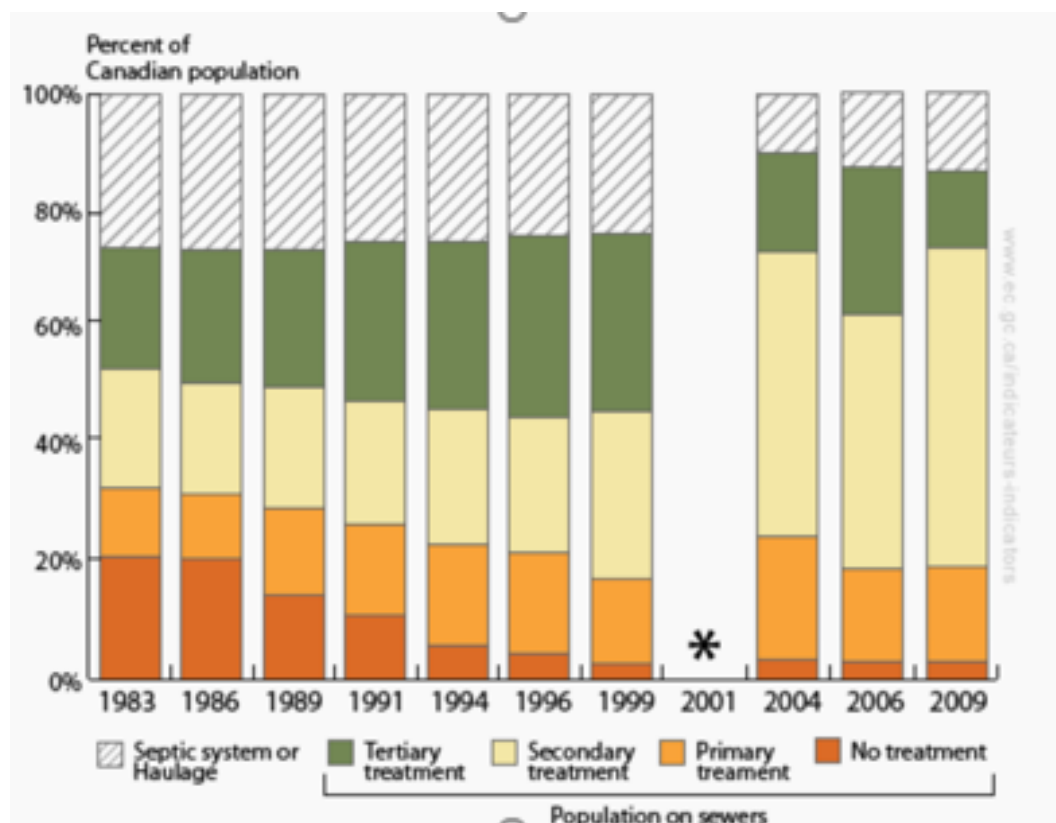


Figure 1. Wastewater treatment levels, Canada, 1983 to 2009 (taken from the government of Canada)

Table 3. Unit processes of municipal wastewater treatment plant.

| Treatment process | Serial number | Unit name | Function | GHGs emission |
|---------------------|---------------|-------------------|--|------------------------------------|
| Primary Treatment | 1 | Grit chamber | Removal of very large materials | Negligible |
| | 2 | Primary Clarifier | Removal of settleable organics | Negligible |
| Secondary Treatment | 3 | Bioreactor | Conversion of dissolved organics into bacteria cells and nutrients removal | CO ₂ & N ₂ O |
| | 4 | Secondary | Removal of bacteria | Negligible |

| | | | | |
|--------------------|---|---------------------|--|-----------------------------------|
| | | Clarifier | cells | |
| Tertiary Treatment | 5 | Tertiary Treatment | Further removal of specific substances | Negligible |
| Sludge Treatment | 6 | Aerobic digestion | Reduce sludge mass and nutrient | CO ₂ |
| | 7 | Thickening | Thickening sludge; increasing solids concentration | Negligible |
| | 8 | Anaerobic digestion | Reduce sludge mass | CO ₂ & CH ₄ |
| | 9 | Dewatering | Reduce water content by mechanical manners | Negligible |

1.2.2 Category 2. Final disposal of biosolids

This category includes the GHGs emission that occurs from the disposed biosolids. The GHGs composition in this category depends on the disposal method. For example, if the biosolids are incinerated, the total organic carbon (TOC) will convert to Carbon dioxide. For landfill, the emitted GHGs consists of methane and carbon dioxide

1.2.3 Category 3. Electricity and chemical consumption

In this category, the amount of greenhouse gases emission will be estimated in terms of electricity and chemicals consumption in WWTPs. Basically, it includes the electricity to maintain the daily operation of each treatment process will be counted. Chemicals consumption refers to metal salt for phosphorus removal, for example, ferric salt; lime, disinfection and dechlorinating. Besides, energy consumption of the sludge haulage is also a critical source of GHG emission. However, this category will not be included in this study.

2 Literature Review

2.1 Diverse types of GHGs emission during wastewater treatment process

Figure 2 schematically depicts a typical wastewater treatment plant with a conventional activated sludge system. Different boxes show the different treatment process and the GHGs gases emitted are illustrated beside each process. Carbon dioxide, methane and nitrous oxide are three major greenhouse gases released in a typical wastewater treatment plant.

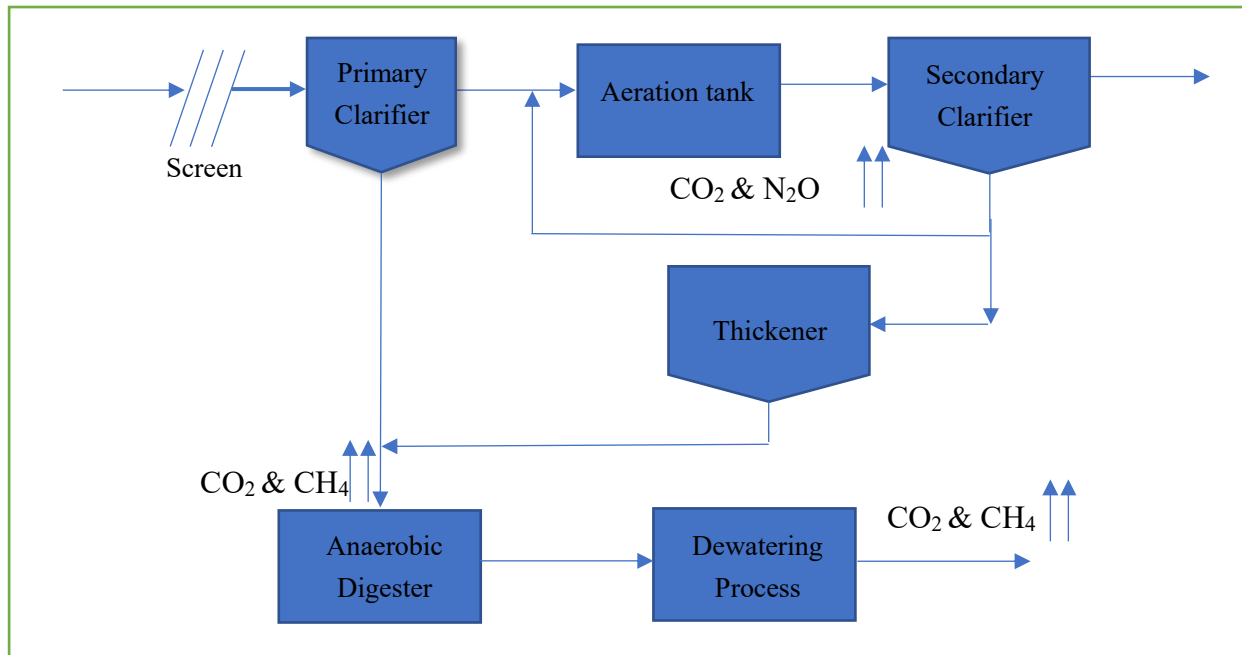
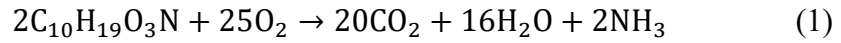


Figure 2. a schematically layout of a WWTP with conventional activated sludge system.

2.1.1 Carbon dioxide (CO_2) emission in WWTPs

Carbon dioxide is generated in both aerobic and anaerobic treatment processes. An aerobic wastewater treatment process is a biological process that takes place in the presence of oxygen. It has different kinds of techniques such as activated sludge process, trickling filters, aerated lagoons, etc. The activated sludge process is the

most widely used biological wastewater treatment in secondary treatment. Organic matter is oxidized in the aerobic treatment process in which oxygen acts as an electron acceptor, which is shown in equation (1) (The elemental composition of substrate is $C_{10}H_{19}O_3N$) (Metcalf & eddy, 2003):



Anaerobic wastewater treatment process is a biological process that occurs in the absence of oxygen. In municipal wastewater treatment plants, anaerobic treatment is generally applied for sludge treatment taking place in the anaerobic digester which is called anaerobic digestion (AD). It consists of various biological reactions, including hydrolysis, fermentation, acidogenesis, and methanogenesis. The reaction steps of AD are given in figure 3. As shown in the figure 3, carbon dioxide and methane are released during the process.

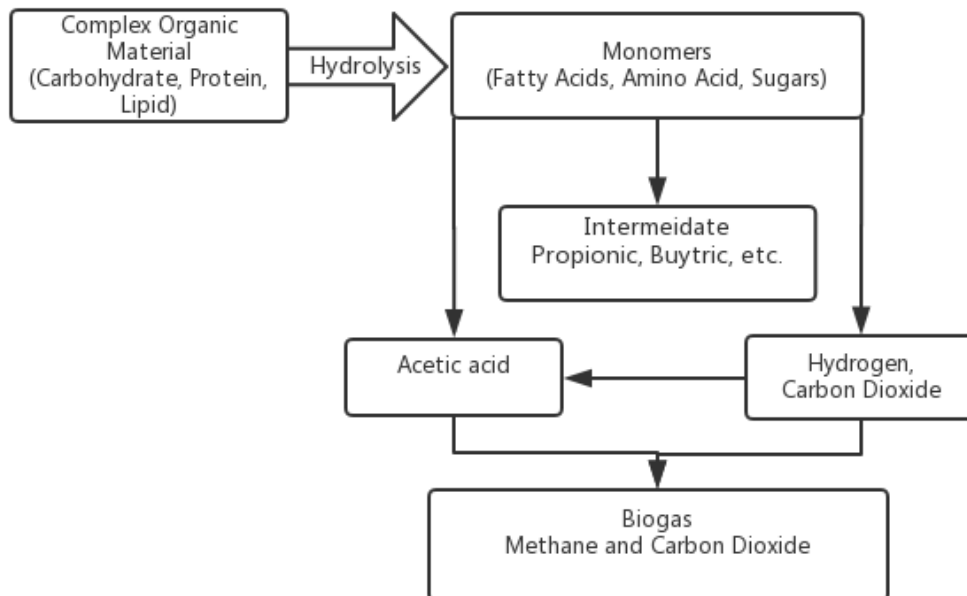


Figure 3. Steps of anaerobic digestion process (adapted from Mustafa et al., 2013)

2.1.2 Nitrous oxide (N₂O) emission in WWTPs

N₂O can be produced during biological nitrogen removal processes, which refer to both nitrification and denitrification (Wunderlin et al., 2011). Nitrification is a biological process that converts ammonia sequentially to nitrite (NO₂⁻) and nitrate (NO₃⁻). These reactions are performed by two different groups of bacteria: ammonium-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB). Nitrification could be divided into 2 sub-processes. The first sub-process is to produce NO₂⁻ by oxidation of ammonia which is carried out by AOB. In the second sub-process, nitrite is oxidized to NO₃⁻ by NOB. Denitrification is a biological process reducing nitrate or nitrite to nitrogen gas (N₂) via N₂O as an obligate intermediate (Wunderlin et al., 2012). According to Compos et al. (2017), there are three main pathways (figure 4) for N₂O production:

(a) Hydroxylamine (NH₂OH) oxidation

NH₂OH is produced as an intermediate during the first sub-process catalyzed by ammonia mono-oxygenase (Duan et al., 2017, Tallec et al., 2006). In the NH₂OH oxidation pathway, N₂O is formed if NH₂OH is not fully oxidized to NO₂⁻ (Massara et al., 2017).

(b) Heterotrophic denitrification

Wunderlin et al. state that incomplete denitrification can lead to N₂O emission because of the nitrite accumulation or oxygen inhibition (2012). Various enzymes are involved in denitrification, for example, nitrate reductases (NaR), nitrite reductases (NirR), nitric oxide reductases (NOR) and nitrous oxide reductases

(N₂OR) (Duan et al.,2017).

(c) Nitrifier denitrification

Nitrifier denitrification is a possible pathway of nitrification where AOB reduces NO₂⁻ to NO and N₂O. This is because respiratory enzymes in denitrification, which reduces NO₂⁻ to NO, and N₂O has been found in AOB species (Todt & Dörsch, 2016). Under the insufficient oxygen condition, NO₂⁻ starts to be reduced to NO by AOB instead of being oxidized to NO₃⁻ (Duan et al., 2017). A periplasmic copper-containing nitrite reductase (NirK) and/or unidentified nitrite reductase NO₂⁻ primarily perform the reduction of NO₂⁻ to NO. Then, NO is reduced to N₂O catalyzed by NOR (Massara et al., 2017). N₂O is the end product in the nitrifier denitrification process since nitrous oxide reductases (N₂OR), which reduces N₂O to N₂, have not been found in AOB (Duan et al., 2017).

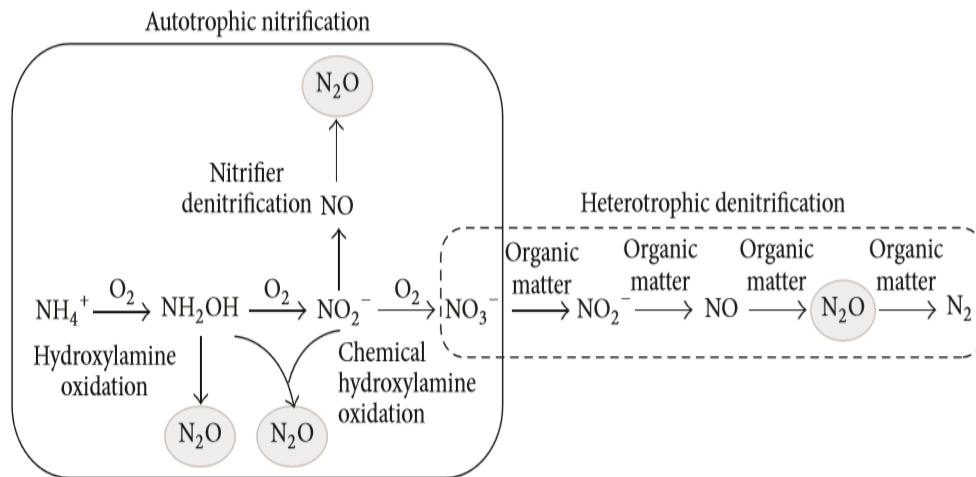


Figure 4. Biological and chemical pathways of N₂O production in the nitrification and denitrification processes. (Taken from the Campos et al., 2016)

2.1.3 Methane (CH₄) emission in WWTPs

Methane gas is generally produced in anaerobic digestion and potentially in final

biosolids disposal due to the decomposition of the organic matters in the absence of oxygen.

2.2 Characteristics of Municipal Wastewater

Domestic wastewater comes mainly from households, offices, commercial and urban utilities. It is mainly excrement and washing sewage, which centralized into the municipal sewage pipe network system and is transferred to the sewage treatment plant for treatment. The water quality obviously has the characteristics of day and night periodicity and seasonal cycle. Typical numbers of domestic wastewater are shown in table 4.

Table 4. Typical numbers of parameters in raw influent (Adapted from Metcalf and Eddy et al. 4th ed. "Wastewater Engineering").

| Compounds | Typical (mg/L) | Range (mg/L) |
|---------------------------------------|----------------|--------------|
| Total Solids (TS) | 720 | 390-1230 |
| Total Suspended Solids(TSS) | 210 | 120-400 |
| Volatile Suspended Solids (VSS) | 160 | 95-315 |
| Settleable Solids | 10 | 5-20 |
| BOD ₅ (as O ₂) | 190 | 110-350 |
| COD (as O ₂) | 430 | 250-800 |
| Total Nitrogen (as N) | 40 | 20-70 |
| Organic Nitrogen(as N) | 15 | 8-25 |
| Free Ammonia (as N) | 25 | 12-45 |
| Nitrate, nitrite (as N) | 0 | 0 |
| Total Phosphorus (as P) | 7 | 4-12 |
| Organic Phosphorus (as P) | 2 | 1-4 |
| Inorganic Phosphorus(as N) | 5 | 3-10 |

3. Calculator Development

3.1 Aeration Tank/ Conventional Activated Sludge System.

A typical flow scheme of activated sludge process is shown in figure 5. Effluent

from the primary clarifier flows into an aeration tank for further removal of organic matters and nutrients. During this process, carbon dioxide and nitrous oxide will be emitted.

3.1.1 Estimation of CO₂ emitted from Aeration tank.

i. COD Balance for Substrate

A COD balance of biomass in biological treatment can be expressed as follows:

$$\Delta\text{COD}_{\text{as}} = Q_{\text{in,as}} * \text{COD}_{\text{in,as}} - (Q_{\text{e}} * \text{COD}_{\text{eff,as}} + Q_{\text{w}} * \text{COD}_{\text{was}})$$

Where $\Delta\text{COD}_{\text{as}}$ = the COD change after aerobic treatment [mg/L]

$Q_{\text{in,as}}$ = aerobic tank influent flow rate [m³/d]

Q_{e} = secondary Clarifier flow rate [m³/d];

Q_{w} = waste activated sludge flow rate [m³/d];

$\text{COD}_{\text{in,as}}$ = influent COD of active sludge [mg/L];

$\text{COD}_{\text{eff,as}}$ = effluent COD of active sludge [mg/L];

COD_{was} = COD of waste activated sludge [mg/L];

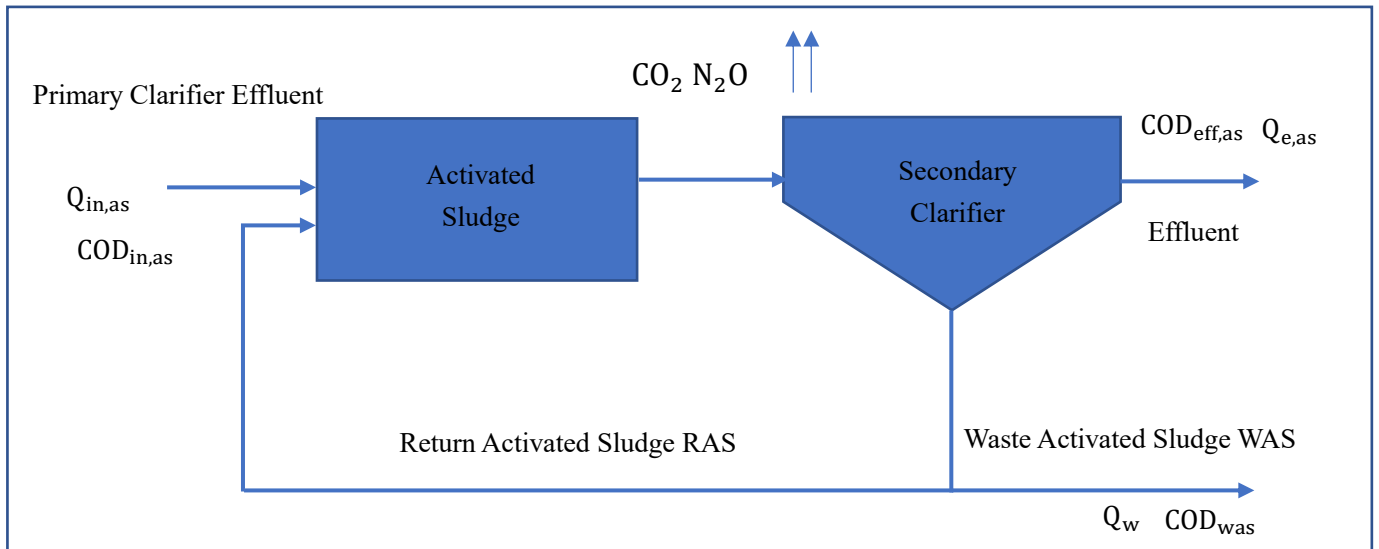
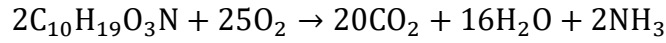


Figure 5. Conventional Activated Sludge System

ii. Derivation of COD/TOC ratio.

In this study, $C_{10}H_{19}O_3N$, and $C_5H_7O_2N$ are used to represent the substrate and biomass (Leslie Grady, 2011). According to the chemical equation of oxidation of the substrate, the stoichiometric relationship between oxygen and carbon can be calculated. Then, the COD/TOC ratio could be derived. The stoichiometric relationship of substrate oxidation can be expressed as the following equation.



Based on the equation above, the COD/TOC ratio could be calculated as:

$$\begin{aligned} \frac{25\text{mol} - O_2}{2\text{mol} - VSS} \times \frac{32\text{g} - O_2}{1\text{mol} - O_2} \times \frac{1\text{mol} - VSS}{201\text{g} - VSS} &= 1.99 \frac{\text{g} - O_2}{\text{g} - VSS}; \\ 1.99 \frac{\text{g} - O_2}{\text{g} - VSS} \times \frac{201\text{g} - VSS}{120\text{g} - C} &= 3.33 \frac{\text{g} - O_2}{\text{g} - C}; \\ \text{TOC, as} &= \frac{\Delta\text{COD}}{3.33 \frac{\text{g} - O_2}{\text{g} - C}} \left[\frac{\text{mg}}{\text{L}} \right]; \end{aligned}$$

iii. Total CO₂ emission from activated sludge

The assumption has been made that all the removed carbon in the aerobic reaction is converted to CO₂ and emitted into the atmosphere. Therefore, the total CO₂ emission from activated sludge could be calculated as:

$$\text{CO}_2 \text{ emission, as} = \text{TOC, as} \times \frac{44 \text{ g} - \text{CO}_2}{12\text{g} - C} \left[\frac{\text{g}}{\text{d}} \right];$$

3.1.2 Estimation of N₂O emission from activated sludge

Most wastewater treatment plants in Ontario achieved nitrification with long sludge retention time, so N₂O emission is included in this GHG estimation calculator.

i. Total Kjeldahl Nitrogen (TKN) Balance for Substrate

$$\Delta \text{TKN}_{\text{as}} = Q_{\text{in,as}} \times \text{TKN}_{\text{in,as}} - (Q_{\text{e}} \times \text{TKN}_{\text{eff,as}} + Q_{\text{w}} \times \text{TKN}_{\text{was}});$$

Where $\Delta \text{TKN}_{\text{as}}$ = the TKN change after aerobic treatment [mg/L]

$Q_{\text{in,as}}$ = aerobic tank influent flow rate [m^3/d]

Q_{e} = secondary Clarifier effluent flow rate [m^3/d];

Q_{w} = waste activated sludge flow rate [m^3/d];

$\text{TKN}_{\text{in,as}}$ = influent TKN of active sludge [mg/L];

$\text{TKN}_{\text{eff,as}}$ = effluent TKN of active sludge [mg/L];

TKN_{was} = TKN of waste activated sludge [mg/L]

ii. Interpretation of % removed TKN emitted as N_2O .

In this study, data was collected from previous research papers (see table 5 and table 6).

Table 5. Nitrous oxide emissions (% of N-load) in full-scale and lab-scale measurement (adapted from Kampschreur et al., 2009a).

| Reference | N_2O emission (% of N-load) | Remarks |
|------------------------------|---|--|
| Full-scale | | |
| Czepiel et al. (1995) | 0.035 | |
| Wicht and Beier (1995) | 0.6 | N_2O emission increased with increasing nitrogen load |
| Sommer et al. (1998) | 0.02 | |
| Kimochi et al. (1998) | 0.05 | |
| Lab-scale | | |
| Thoern and Soerensson (1996) | 1.2 | N_2O emission increased with decrease of pH |
| Chung and Chung (2000) | 0.25 | N_2O emission increased with decrease of COD/N |
| Tsuneda et al. (2005) | 0.3 | N_2O emission ratio increased with increasing salt concentration |
| Tsuneda et al. (2006a) | 0.1-0.4 | N_2O emission independent of salt concentration |

| | | |
|-----------------------|-----------------------|---|
| Tallec et al. (2006b) | 0.2–1 (0.4 average) | N ₂ O emission ratio increased with decreasing oxygen concentration |
| Tallec et al. (2006b) | 0.1–1.3 (0.2 average) | N ₂ O emission ratio increased with decreasing methanol addition |
| Tallec et al. (2008) | 0.4 | N ₂ O emission is largest at 0.3mg – O ₂ /L and lower above and below this oxygen concentration |

Table 6. Summary of N₂O Fluxes and Emission Factors Measured at Full-Scale WWTPs (adapted from AHN, 2010)

| Plant Configuration | Temp (°C) | % Influent TKN emitted as N ₂ O | % Influent TN emitted as N ₂ O |
|----------------------|------------|--|---|
| Separate-stage BNR | 15 ± 0.48 | 0.03 ± 0.00 | 0.03 ± 0.00 |
| | 23 ± 0.28 | 0.01 ± 0.00 | 0.01 ± 0.00 |
| | 14 ± 0.248 | 0.16 ± 0.10 | 0.19 ± 0.12 |
| Four-stage Bardenpho | 23 ± 0.20 | 0.60 ± 0.29 | 0.66 ± 0.32 |
| Step-feed BNR 1 | 25 ± 0.28 | 0.62 ± 0.27 | 0.90 ± 0.39 |
| | 17 ± 0.12 | 0.18 ± 0.18 | 0.37 ± 0.36 |
| Step-feed non-BNR | 30 ± 2.3 | 0.24 ± 0.02 | 0.63 ± 0.06 |
| Separate centrate | 34 ± 0.32 | 0.54 ± 0.16 | 0.96 ± 0.32 |
| | 11 ± 0.20 | 0.40 ± 0.14 | 0.92 ± 0.32 |
| Plug-flow 1 | 23 ± 0.46 | 0.41 ± 0.14 | 0.70 ± 0.24 |
| | 11 ± 0.41 | 0.62 ± 0.15 | 1.7 ± 0.41 |
| Plug-flow 2 | 22 ± 0.58 | 0.09 ± 0.03 | 0.22 ± 0.06 |
| MLE 1 | 26 ± 1.8 | 0.07 ± 0.04 | 0.09 ± 0.05 |
| MLE 2 | 26 ± 0.27 | 0.06 ± 0.02 | 0.07 ± 0.03 |
| Oxidation ditch | 19 ± 0.58 | 0.03 ± 0.01 | 0.03 ± 0.01 |
| Step-feed BNR 3 | 24 ± 0.78 | 0.05 ± 0.03 | 0.06 ± 0.03 |

iii. Total N₂O emission from activated sludge

$$\text{N}_2\text{O emission, as} = \Delta\text{TKN}_{\text{as}} \times \% \text{ removed TKN as N}_2\text{O}$$

3.2 Anaerobic Digestion

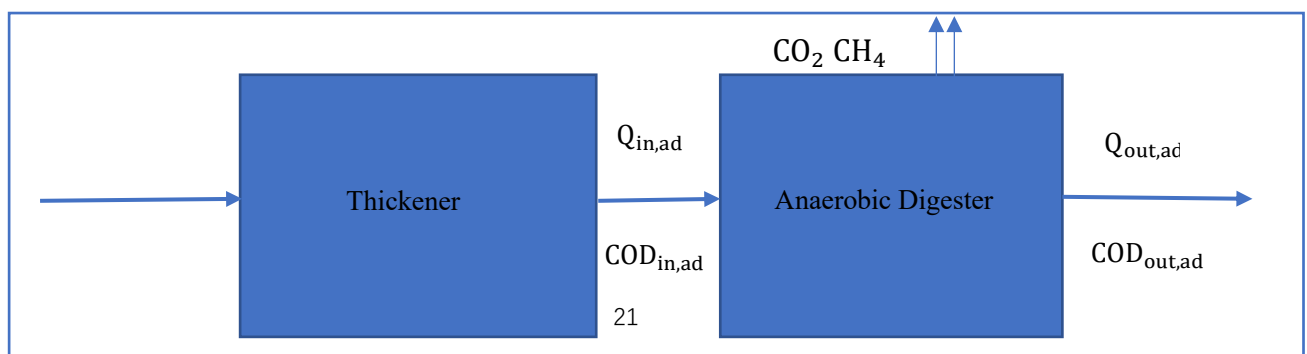


Figure 6. Anaerobic Digestion layout

Figure 6 presents a layout of an anaerobic digester. Thickened sludge flows into the anaerobic tank to break down the biodegradable materials in the absence of oxygen. Methane and carbon dioxide are released because of biosolids decomposition by various biological reactions: hydrolysis, fermentation, acidogenesis, and methanogenesis. The amount of methane production could be calculated by balancing the COD between the influent sludge and effluent sludge of the anaerobic digester. The carbon dioxide and methane emission could be estimated based on the biosolid composition. Typically, the biogas from anaerobic digestion consists of 2/3 CH₄ and 1/3 CO₂.

3.2.1 Estimation of biogas emitted from Anaerobic Digestion.

i. COD Balance for Sludge

A COD balance of biomass in anaerobic digestion can be expressed as follows:

$$\Delta\text{COD}_{\text{as}} = Q_{\text{in,ad}} * \text{COD}_{\text{in,ad}} - Q_{\text{out,ad}} * \text{COD}_{\text{eff,ad}}$$

Where $\Delta\text{COD}_{\text{as}}$ = the COD change after anaerobic treatment [mg/L]

$Q_{\text{in,ad}}$ = the amount of sludge flow into the anaerobic digester [m³/d]

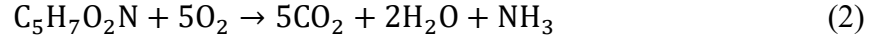
$Q_{\text{out,ad}}$ = the amount of sludge flow out from anaerobic digester [m³/d];

$\text{COD}_{\text{in,ad}}$ = COD of influent sludge in anaerobic digestion [mg/L];

$\text{COD}_{\text{eff,as}}$ = Effluent COD of digested sludge [mg/L];

ii. Derivation of COD/TOC ratio.

According to the chemical equation of oxidation of substrate, the stoichiometric relationship between oxygen and carbon could be calculated. Then the COD/TOC ratio could be derived. The stoichiometric relationship of sludge oxidation can be expressed as equation (2):



Based on the equation above, the COD/TOC ratio could be calculated as:

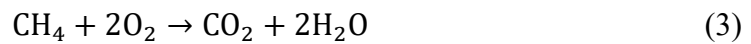
$$\begin{aligned} \frac{5\text{mol} - O_2}{1\text{mol} - \text{VSS}} \times \frac{32\text{g} - O_2}{1\text{mol} - O_2} &= 160 \frac{\text{g} - O_2}{1\text{mol} - \text{VSS}} \\ 160 \frac{\text{g} - O_2}{\text{mol} - \text{VSS}} \times \frac{1\text{mol} - \text{VSS}}{5\text{mol} - C} &= 32 \frac{\text{g} - O_2}{\text{mol} - C} \\ \text{TOC, ad} &= \frac{\Delta\text{COD}}{32 \frac{\text{g} - O_2}{\text{mol} - C}} \left[\frac{\text{mol}}{\text{L}} \right]; \end{aligned}$$

3.2.2 Total CH₄ and CO₂ emission from anaerobic digestion

As illustrated before, approximately one-third of biogas is CO₂ while the remaining two-thirds are CH₄. Thus, the total CH₄ and CO₂ emission from anaerobic digestion could be calculated respectively as:

$$\begin{aligned} \text{CH}_4 \text{ emission, as} &= \text{TOC, ad} \times \frac{2}{3} \times \frac{16\text{g} - \text{CH}_4}{1\text{mol} - C} \left[\frac{\text{g}}{\text{d}} \right]; \\ \text{CO}_2 \text{ emission, as} &= \text{TOC, as} \times \frac{1}{3} \times \frac{44\text{g} - \text{CO}_2}{1\text{mol} - C} \left[\frac{\text{g}}{\text{d}} \right]; \end{aligned}$$

In some wastewater treatment plants, CH₄ produced in anaerobic digestion will be burned for reducing the global warming impact or energy recovery. In that case, all the amount of CH₄ will convert to CO₂ (equation 3):



3.3 Final Biosolid disposal

After the dewatering process, the concentrated sludge cakes are needed to be disposed. The amount of GHGs emission by disposed biosolids depends on the disposal method. For landfill disposal, TOC of the disposed biosolids will be distributed into CO₂ and CH₄. Based on the landfill composition, the fraction between CO₂ and CH₄ could be determined as 45% and 55% (Bove & Lunghi, 2006).

3.3.1 GHGs emission from the final disposal of biosolids.

i. COD balance for the final biosolids

$$\Delta\text{COD}_{fb} = Q_{\text{out,ds}} * \text{COD}_{\text{out,ds}};$$

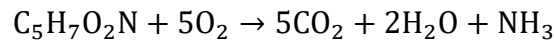
Where ΔCOD_{fb} = the COD change after aerobic treatment [mg/L]

$Q_{\text{out,ds}}$ = the amount of concentrated sludge come out from dewatering systems [m³/d]

$\text{COD}_{\text{eff,as}}$ = Effluent COD of dewatered sludge [mg/L]

ii. Derivation of COD/TOC factor ratio.

The stoichiometric relationship of biosolids oxidation can be expressed as the following equation.



Based on the equation above, the COD/TOC ratio could be calculated as:

$$\frac{5\text{mol} - \text{O}_2}{1\text{mol} - \text{VSS}} \times \frac{32\text{g} - \text{O}_2}{1\text{mol} - \text{O}_2} = 160 \frac{\text{g} - \text{O}_2}{1\text{mol} - \text{VSS}}$$
$$160 \frac{\text{g} - \text{O}_2}{\text{mol} - \text{VSS}} \times \frac{1\text{mol} - \text{VSS}}{5\text{mol} - \text{C}} = 32 \frac{\text{g} - \text{O}_2}{\text{mol} - \text{C}}$$

$$\text{TOC, ad} = \frac{\Delta \text{COD}}{32 \frac{\text{g} - \text{O}_2}{\text{mol} - \text{C}}} \left[\frac{\text{mol}}{\text{L}} \right].$$

iii. Total CH₄ and CO₂ emission from final disposal biosolids.

For CH₄ emission:

$$\text{CH}_4 \text{ emission, as} = \text{TOC, ad} \times 0.55 \times \frac{16 \text{ g} - \text{CH}_4}{1 \text{ mol} - \text{C}} \left[\frac{\text{g}}{\text{d}} \right];$$

For CO₂ emission:

$$\text{CO}_2 \text{ emission, as} = \text{TOC, as} \times 0.45 \times \frac{44 \text{ g} - \text{CO}_2}{1 \text{ mol} - \text{C}} \left[\frac{\text{g}}{\text{d}} \right];$$

4. Sample Calculation

4.1 Sample calculation for GHGs emission from aeration tank/ activated sludge system

Table 7. Input parameters in activated sludge for the sample calculation (data from Guelph wastewater treatment plant).

| Input Parameters | Entered Value | Unit |
|--|---------------|----------------------|
| Inflow rate ($Q_{\text{in,as}}$) | 50217 | (m ³ /d) |
| Inflow COD concentration ($\text{COD}_{\text{in,as}}$) | 295.5 | (mg/L) |
| Inflow Kjeldahl nitrogen ($\text{TKN}_{\text{in,as}}$) | 42.3 | (mg/L) |
| Outflow rate ($Q_{\text{out,as}}$) | 49636 | (m ³ /d) |
| Outflow COD concentration ($\text{COD}_{\text{out,as}}$) | 2.30 | (mg/L) |
| Outflow kjeldahl nitrogen ($\text{TKN}_{\text{out,as}}$) | 1.7 | (mg/L) |
| Was rate (Q_{was}) | 581 | (m ³ /d) |
| Was COD concentration (COD_{was}) | 14800 | (mg/L) |
| Was kjeldahl nitrogen (TKN_{was}) | 800 | (mg/L) |

For CO₂ emission:

$$\begin{aligned}
& \text{CO}_2 \text{ eq. } \left(\frac{\text{kg}}{\text{d}} \right) \\
&= \frac{\left[50217 \left[\frac{\text{m}^3}{\text{d}} \right] \times 295.5 \left[\frac{\text{mg}}{\text{L}} \right] - 49636 \left[\frac{\text{m}^3}{\text{d}} \right] \times 2.30 \left[\frac{\text{mg}}{\text{L}} \right] - 581 \left[\frac{\text{m}^3}{\text{d}} \right] \times 14800 \left[\frac{\text{mg}}{\text{L}} \right] \right]}{3.33 \frac{\text{g} - \text{O}_2}{\text{g} - \text{C}}} \\
&\times \frac{44 \text{g/mol}}{12 \text{g/mol}} \times \frac{1 \text{kg}}{1000 \text{g}} = 6743.8 \text{ CO}_2 \text{ eq. } \left(\frac{\text{kg}}{\text{d}} \right);
\end{aligned}$$

For N₂O emission:

$$\begin{aligned}
\text{N}_2\text{O} \left(\frac{\text{kg}}{\text{d}} \right) &= \left(50217 \left[\frac{\text{m}^3}{\text{d}} \right] \times 42.3 \left[\frac{\text{mg}}{\text{L}} \right] - 49636 \left[\frac{\text{m}^3}{\text{d}} \right] \times 1.7 \left[\frac{\text{mg}}{\text{L}} \right] \right. \\
&\quad \left. - 581 \left[\frac{\text{m}^3}{\text{d}} \right] \times 800 \left[\frac{\text{mg}}{\text{L}} \right] \right) \times 0.41\% \frac{\text{g} - \text{N}_2\text{O} - \text{N}}{\text{g} - \text{TKN} - \text{N}} \times \frac{1 \text{kg}}{1000 \text{g}} \\
&= 6.458 \left(\frac{\text{kg}}{\text{d}} \right) = 1924.48 \text{ CO}_2 \text{ eq. } \left(\frac{\text{kg}}{\text{d}} \right)
\end{aligned}$$

4.2 Sample calculation for GHGs emission from anaerobic digestion.

Table 8. Assumed input parameters in anaerobic digester for the sample calculation. (data from Guelph wastewater treatment plant).

| Input Patameters | Entered Value | Unit |
|--|---------------|----------------------|
| Inflow rate (Q _{in,ad}) | 658 | (m ³ /d) |
| Inflow COD concentration (COD _{in,ad}) | 30000 | (mg/L) |
| Outflow rate (Q _{out,as}) | 658 | (m ³ /d) |
| Outflow COD concentration (COD _{out,as}) | 18300 | (mg/L) |

For CH₄ emission:

$$\begin{aligned}
\text{CH}_4 \left(\frac{\text{kg}}{\text{d}} \right) &= \frac{\left[658 \frac{\text{m}^3}{\text{d}} \times 30000 \frac{\text{mg}}{\text{L}} - 658 \frac{\text{m}^3}{\text{d}} \times 18300 \frac{\text{mg}}{\text{L}} \right]}{32 \frac{\text{g} - \text{O}_2}{\text{mol} - \text{C}}} \times 0.67 \frac{\text{kg} - \text{CH}_4}{\text{kg} - \text{biogas}} \\
&\times \frac{16 \frac{\text{g}}{\text{mol}}}{1000 \frac{\text{g}}{\text{kg}}} = 2566.20 \frac{\text{kg}}{\text{d}} = 59022.6 \text{ CO}_2 \text{ eq. } \left(\frac{\text{kg}}{\text{d}} \right)
\end{aligned}$$

For CO₂ emission:

$$\text{CO}_2 \left(\frac{\text{kg}}{\text{d}} \right) = \frac{\left[658 \frac{\text{m}^3}{\text{d}} \times 30000 \frac{\text{mg}}{\text{L}} - 658 \frac{\text{m}^3}{\text{d}} \times 18300 \frac{\text{mg}}{\text{L}} \right]}{32 \frac{\text{g} - \text{O}_2}{\text{mol} - \text{C}}} \times 0.33 \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{biogas}} \\ \times \frac{44 \frac{\text{g}}{\text{mol}}}{1000 \frac{\text{g}}{\text{kg}}} = 3493.24 \text{ CO}_2 \text{eq.} \left(\frac{\text{kg}}{\text{d}} \right)$$

If the methane is captured and burn for energy regeneration, then it will convert to CO_2 ,
the new CH_4 emission (which is emitted as CO_2):

$$\text{CH}_4 \left(\frac{\text{kg}}{\text{d}} \right) = \frac{\left[658 \frac{\text{m}^3}{\text{d}} \times 30000 \frac{\text{mg}}{\text{L}} - 658 \frac{\text{m}^3}{\text{d}} \times 18300 \frac{\text{mg}}{\text{L}} \right]}{32 \frac{\text{g} - \text{O}_2}{\text{mol} - \text{C}}} \times 0.67 \frac{\text{kg} - \text{CH}_4}{\text{kg} - \text{biogas}} \\ \times \frac{16 \frac{\text{g}}{\text{mol}}}{1000 \frac{\text{g}}{\text{kg}}} \times \frac{44 \text{g/mol}}{12 \text{g/mol}} = 12937.9 \text{ CO}_2 \text{eq.} \left(\frac{\text{kg}}{\text{d}} \right);$$

4.3 Sample calculation for GHGs emission from biosolids disposal.

Table 9. Assumed input parameters of disposed biosolids for the sample calculation (data from Guelph wastewater treatment plant).

| Input Parameters | Entered Value | Unit |
|---|---------------|---------------------------|
| Dewater Sludge ($Q_{\text{in,ad}}$) | 54.7 | (m^3/d) |
| Outflow COD concentration ($\text{COD}_{\text{in,ad}}$) | 214400 | (mg/L) |

For CH_4 emission:

$$\text{CH}_4 \left(\frac{\text{kg}}{\text{d}} \right) = \frac{54.7 \left(\frac{\text{m}^3}{\text{d}} \right) \times 214400 \frac{\text{mg}}{\text{L}}}{32 \left(\frac{\text{g} - \text{O}_2}{\text{mol} - \text{C}} \right)} \times 0.55 \frac{\text{kg} - \text{CH}_4}{\text{kg} - \text{landfill gas}} \times \frac{16 \frac{\text{g}}{\text{mol}}}{1000 \frac{\text{g}}{\text{kg}}} \\ = 3225.11 \frac{\text{kg}}{\text{d}} = 74177.58 \text{ CO}_2 \text{eq.} \left(\frac{\text{kg}}{\text{d}} \right);$$

For CO_2 emission:

$$\text{CO}_2 \left(\frac{\text{kg}}{\text{d}} \right) = \frac{54.7 \left(\frac{\text{m}^3}{\text{d}} \right) \times 214400 \frac{\text{mg}}{\text{L}}}{32 \left(\frac{\text{g} - \text{O}_2}{\text{mol} - \text{C}} \right)} \times 0.45 \frac{\text{kg} - \text{CO}_2}{\text{kg} - \text{landfill gas}} \times \frac{44 \frac{\text{g}}{\text{mol}}}{1000 \frac{\text{g}}{\text{kg}}} \\ = 7259.5 \text{ CO}_2 \text{eq.} \left(\frac{\text{kg}}{\text{d}} \right);$$

4.4 Discussion

As shown from the sample calculation of Guelph wastewater treatment plant, total GHG emission from category 1 and 2 are 152354.6 kg-CO₂eq/d. If the methane is captured and burnt for energy regeneration, the total emission is 100389 kg-CO₂eq/d. The result shows 53% GHG is emitted from final disposal while 5% and 41% GHG emitted from biological treatment and anaerobic digestion respectively. However, if the methane is combusted for energy reuse, most GHG (about 81%) is emitted from final disposal field. 9% and 11% GHG is emitted from biological treatment and anaerobic digestion respectively.

5. Summary & Outlook

The calculator developed in this study is providing an accurate estimation of greenhouse gas emission in terms of carbon dioxide and methane emission during wastewater treatment process. However, the estimation of nitrous oxide needs to be improved as there are inadequate published paper about nitrous oxide emission. In addition, the existing results of nitrous oxide emission estimation in both lab scale and plant scale are various due to weak correlations between N₂O emission and various operation conditions, such as dissolved oxygen, temperature, pH, sludge retention time, and ammonia concentration. Moreover, C/N ratio, a carbon-to-nitrogen ratio of the mass of carbon to the mass of nitrogen of the wastewater, is worthy of attention in terms of nitrous oxide emission in the future study. There are two pathways of nitrogen removal: 1. nitrification, 2. cell growth. Low C/N ratio, which means there is sufficient

nitrogen but limited carbon, will result in more nitrous oxide emission during treatment process. The reason behind this is because low C/N ratio makes the nitrification is dominated in the nitrogen removal. As one of the pathways of nitrous oxide emission is nitrification, there is more N_2O emitted with low C/N ratio condition.

In this study, all calculations are based on the unit COD. However, the unit that wastewater treatment plants normally report is biological oxygen demand (BOD) and volatile suspended solids (VSS). There are typical conversion coefficients for VSS, BOD and COD, i.e., $COD/VSS=1.42$, $COD/BOD_5=2.1$ (Metcalf & eddy, 2003). Therefore, the relationship developed in the study is consistent if use the BOD or VSS as units.

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Appendix I- GHGs Calculation Summary of Guelph Wastewater Treatment Plant

| | | | |
|---|-----------------------|-----------|---------------------------|
| Final disposal (Landfill) | | | |
| Input parameter | | | |
| COD of Disposal sewage sludge | COD _{ss} | 214.4 | g/L |
| Sludge Volume out from Wastewater plant | Q _{eff,wwtp} | 54.7 | m ³ /d |
| Calculation results | | | |
| Mass of GHG | | 81463.9 | kg of CO ₂ e/d |
| CO₂ Emission | | | |
| Input parameters | | | |
| Flow rate in Active sludge | Q _{in,as} | 50217 | m ³ /d |
| Flow rate out from Active sludge | Q _{eff,as} | 49636 | m ³ /d |
| Flow rate of Waste Activated Sludge effluent | Q _{w,as} | 581 | m ³ /d |
| Influent COD of Active sludge | COD _{in,as} | 0.295 | g/L |
| Effluent COD of Active sludge | COD _{eff,as} | 0.0023 | g/L |
| COD of waste active sludge | COD _{was} | 14.8 | g/L |
| Calculation results | | | |
| Equivalent GHG | | 6743.80 | kg of CO ₂ e/d |
| N₂O Emission | | | |
| Input parameters | | | |
| Flow rate in Active sludge | Q _{in,as} | 50217 | m ³ /d |
| Flow rate out from Active sludge | Q _{eff,as} | 49636 | m ³ /d |
| Flow rate of Waste Activated Sludge effluent | Q _{w,as} | 581 | m ³ /d |
| Influent total kjeldahl nitrogen, TKN _{in,as} | | 0.0423 | g-N/L |
| Effluent total Kjeldahl nitrogen, TKN _{eff,as} | | 0.0017 | g-N/L |
| Total kjeldahl nitrogen of waste active sludge | | | |
| TKN _{was,as} | | 0.8 | g/L |
| Calculation results | | | |
| Equivalent GHG | | 1924.33 | kg of CO ₂ e/d |
| Anaerobic Digestion | | | |
| Input parameters | | | |
| Flow rate in Anaerobic Digestion | Q _{in,ad} | 658 | m ³ /d |
| Flow rate out from Anaerobic Digestion | Q _{eff,ad} | 658.0 | m ³ /d |
| Influent COD of Anaerobic Digestion | COD _{in,ad} | 30 | g/L |
| Effluent COD of Anaerobic Digestion | COD _{eff,ad} | 18.3 | g/L |
| Calculation results | | | |
| Equivalent GHG (without CH ₄ combustion) | | 62551.1 | kg of CO ₂ e/d |
| Equivalent GHG (with CH ₄ combustion) | | 12937.9 | kg of CO ₂ e/d |
| Total Equivalent GHG emission (Without AD-CH₄ combustion) | | | |
| | | 152683.12 | kg of CO ₂ e/d |
| Total Equivalent GHG emission (With AD-CH₄ combustion) | | | |
| | | 103069.92 | kg of CO ₂ e/d |