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# **FUGITIVE GREENHOUSE GAS EMISSIONS FROM WASTEWATER TREATMENT: UNDERSTANDING EMISSION GENERATION PROCESSES AND DEVELOPMENT OF APPROPRIATE SAMPLING METHODS**



**Michael Palandri**

**School of Environmental Systems Engineering  
The University of Western Australia**

**Supervisor: Dr Raj Kurup**

**Environmental Engineers International Pty Ltd**

**&**

**School of Environmental Systems Engineering**

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## ABSTRACT

Greenhouse gas (GHG) emissions resulting from wastewater treatment represent an area of great uncertainty for which the total global effects are currently unknown. Existing methodologies for estimating bulk emissions from wastewater treatment processes are heavily reliant on default correction and emission factors that are lacking in accuracy and scientific validation. Methane ( $\text{CH}_4$ ) and Nitrous Oxide ( $\text{N}_2\text{O}$ ) have been identified as the two most significant greenhouse gases (GHGs) released from wastewater treatment plants due to their significant global warming potential. There are many chemical and biological parameters, which influence the generation of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  from wastewater treatment, however the way in which these parameters interact is poorly understood. The lack of understanding stems from many countries having no regulatory requirements or managing protocols in place, and as such, there is insufficient full-scale process and emission data from the various treatment processes in use today.

By developing a comprehensive understanding of key factors leading to the generation of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  and improving on existing methods of sampling and monitoring, the waste management industry can improve the accuracy of existing emission quantification methodologies.

This study involved a comprehensive critical literature review to identify the key emission generation processes and influencing parameters in an effort to understand how they interact during various wastewater treatment processes. This was achieved by reviewing existing emission quantification methodologies published by the United Nations Framework Convention on Climate Change (UNFCCC), the Intergovernmental Panel for Climate Change (IPCC) and the National Greenhouse Energy Reporting Scheme (NGERS), as well as current relevant scientific literature. The study also investigated existing sampling and monitoring protocols and consequently developed sampling methods for measuring dissolved methane and biogas.

The study identified a significant deficiency in the understanding of dissolved methane formation in anaerobic effluent and its contribution to overall treatment plant emissions. Dissolved methane is not currently accounted for in existing methodologies. The understanding of  $\text{N}_2\text{O}$  emission from treatment plants is improving; however, current approved methodologies use incorrect and out-dated emission factors. The methods of sampling developed in this study were not completely successful but offer some potential for adoption if certain modifications are made. Further field studies should be undertaken to validate the use of such methods in the future.

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## CHAPTER 1. INTRODUCTION

In the past 200 years there has been a significant increase in atmospheric concentrations of greenhouse gases (GHGs) due to anthropogenic activities such as production and use of fossil fuels and other agricultural and industrial activities (El-Fadel and Massoud, 2001). We are living in a world in which we are becoming increasingly aware of the possible effects of human activities on climate change. One particular area of growing concern is the effect of emissions from wastewater treatment.

Wastewater treatment processes can contribute to GHGs through production of methane ( $\text{CH}_4$ ), nitrous oxide ( $\text{N}_2\text{O}$ ) and carbon dioxide ( $\text{CO}_2$ ) from treatment processes or resulting  $\text{CO}_2$  from energy required for treatment (Cakir and Stenstrom, 2005). The emission of GHG from post-consumer waste and wastewater treatment represents approximately 3% of total global anthropogenic GHG emissions, of which methane represents 90% of waste sector emissions (Bogner et al., 2008).

GHG emissions resulting from wastewater treatment processes are currently reported under the waste sector of the Inter-governmental Panel for Climate Change (IPCC). In most reported cases, emissions are not measured directly, rather estimated through use of approved methodologies that link emissions to measurable plant operation parameters (Foley and Lant, 2009). Due to the high variability of fugitive emissions associated with the different treatment processes in use today, it is difficult to estimate emissions accurately using these methodologies.

The methodologies used for estimating fugitive emissions vary depending on the regulatory requirements of the country in which the waste treatment is occurring. Generally, most countries employ methodologies and frameworks developed by the IPCC and the United Nations Framework for Climate Change (UNFCCC). More developed nations, such as Australia, have developed their own quantification methodologies. However, these are often derivatives of existing IPCC methodologies with the inclusion of certain location specific parameters and considerations. The National Greenhouse and Energy Reporting System (NGERS) was introduced in 2007 to provide data and accounting in relation to GHGs and energy consumption and production within Australia.

The development of existing methodologies has been an ongoing periodic process beginning with the formation of the IPCC in 1988. To some extent, the initial focus was on estimating indirect emissions from energy used for wastewater treatment rather than the direct fugitive emissions resultant from treatment processes. In addition to this, many of the earlier methodologies lacked comprehensive scientific validation. Until only recently, there was little known about how certain treatment processes contributed to N<sub>2</sub>O production. Due to the complexity involved in measuring N<sub>2</sub>O emissions from full scale WWTPs and the lack of standardised methods, N<sub>2</sub>O emissions from the waste sector have been estimated based on models and without the input of measured data (Law et al., 2012).

In a study undertaken by Guisasola et al. (2008), dissolved methane in discharged effluent was identified as a source of emissions currently not accounted for in any existing methodologies. In more recent times, significant independent scientific effort has been expended in gaining a better understanding of emission generation processes and the possible mitigation options that could be adopted. However, there still remains a scarcity of field data providing any significant insight on the quantity of GHG emitted and how the various chemical and microbial processes interact during treatment. This study aims to improve the understanding of complex treatment processes and how they influence CH<sub>4</sub> and N<sub>2</sub>O generation. In addition to this, methods of sampling and monitoring will be investigated to improve the collection of field data.



## CHAPTER 2. BACKGROUND

### 2.1 WASTEWATER TREATMENT PROCESSES

Waste generation is closely linked to population, urbanization and affluence, therefore resulting in significant challenges for collection, recycling, treatment and disposal of increasing quantities of solid waste and wastewater (Bogner et al., 2008). In the continued interest of protecting public health, preventing contamination of ground and surface water as well as preserving aquatic and terrestrial wildlife, it is essential to undertake appropriate wastewater treatment and disposal measures (Nemerow, 2009).

There are three main wastewater treatment stages:

- *Primary*: removal of larger solids;
- *Secondary*: biodegradation via microorganisms through promotion of biological processes; and
- *Tertiary*: purification of wastewater to remove pathogens and remaining contaminants.

Sludge is produced during all three stages of treatment, which can be treated further in the Secondary and Tertiary stages through aerobic and anaerobic stabilisation (digestion), composting and drying (IPCC, 2006).

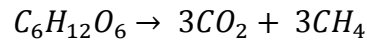
#### 2.1.1 Anaerobic Treatment

Anaerobic treatment processes are those in which bacteria breakdown complex organic substances in the absence of free dissolved oxygen (DO) (Massé and Masse, 2000). The treatment of wastewater through anaerobic processes involves the reduction of organic wastes via three main reactions:

- *Hydrolysis*;
- *Acetic Acid Formation*; and
- *Methane Production*:

(Lastella et al., 2002, De Mes et al., 2003)

The resulting proportions of methane and carbon dioxide from the breakdown of organic matter is represented in the following simplified reaction:



(Tchobanoglous et al., 2003)

Common anaerobic treatment infrastructure includes anaerobic lagoons, conventional digesters, filter bed reactors, fluidized bed reactors, two stage digesters and high rate digesters such as the Upflow Anaerobic Sludge Bucket (UASB) design (Kurup, 2011).

Anaerobic digestion (AD) is a highly effective process for the treatment of wastewater that results in the production of biogas: a mixture of 65-75% CH<sub>4</sub> by volume, 25-30% CO<sub>2</sub> and smaller amounts of N<sub>2</sub>O, H<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>S, water vapour and other gases (Tchobanoglous et al., 2003). Anaerobic wastewater treatments typically require post-treatment processes for polishing effluents to meet water quality standards for discharge (Matsuura et al., 2010). The post treatment processes following anaerobic treatment typically include aerated lagoons and activated sludge processes (Kurup, 2011).

### **2.1.2 Aerobic Treatment**

Aerobic treatment involves the conversion of organic matter to biomass and CO<sub>2</sub> by an aerobic bacterial culture and does not typically produce CH<sub>4</sub> unless the resulting biogas is treated anaerobically (Cakir and Stenstrom, 2005). Aerobic treatment processes demand significant oxygen, not all of which can be provided by surface diffusion. Therefore, in the absence of mechanical aeration, methanogenic bacteria become active resulting in methane emission from subsequent anaerobic digestion (Czepiel, 1993).

Aerobic treatment is often used as part of a treatment train where digestate and residual material (both liquid and sludge) discharged from anaerobic systems undergo mechanical aeration. For liquid streams, the typical treatment process consists of a suspended growth activated sludge system (Kurup, 2011).

### **2.1.3 Biological Nutrient Removal**

Biological nutrient removal (BNR) is a treatment process implemented to remove total nitrogen (TN) and total phosphorous (TP) from wastewater using targeted microorganisms under different environmental conditions in the treatment process (Masters and Ela, 2008). The need for nitrogen removal during wastewater treatment arises from water quality concerns over (i) The effect of ammonia on receiving water bodies with respect to dissolved oxygen (DO) concentrations; (ii) the need to provide nitrogen removal to control

eutrophication and (iii) the need to provide nitrogen control for water reuse applications (Nemerow, 2009).

BNR processes involve the conversion of influent nitrogen into harmless nitrogen gas, a process typically achieved via the following biological steps:

1. *Mineralisation/Ammonification* – complex organic nitrogen compounds converted to inorganic ammonium;
2. *Autotrophic nitrification* – microbially mediated oxidation of ammonium, primarily to nitrate and nitrite under aerobic conditions; and
3. *Heterotrophic denitrification* – microbially mediated reduction of nitrate and nitrite to nitrogen gas under anoxic conditions, and consumption of organic carbon.

(Foley and Lant, 2008)

Engineered BNR systems are considered to be highly effective in reducing aqueous nitrogen pollution from treated wastewater however such facilities do have the potential to emit a significant percentage of the influent nitrogen into the atmosphere as  $N_2O$  and  $NO$  (Kampschreur et al., 2008).

## 2.2 GREENHOUSE GAS EMISSIONS

Waste management activities typically generate  $CH_4$ ,  $N_2O$  and  $CO_2$ , however there is also potential for reduction of global impacts through materials recovery and energy production (Christensen et al., 2009).

### 2.2.1 Methane

Methane ( $CH_4$ ) is a colourless, odourless, combustible hydrocarbon which is considered to be the principal product resulting from anaerobic decomposition of organic matter in wastewater (Tchobanoglous et al., 2003). The global warming potential (GWP) of  $CH_4$  is 25 times that of  $CO_2$  over a 100 year horizon (Bogner et al., 2008). Methane resultant from wastewater treatment processes account for approximately 5% of total global methane emissions (Solomon et al., 2007) and 20% of the total radiative forcing from all of the long lived and globally mixed GHGs (Shindell et al., 2009).

### **2.2.2 Nitrous Oxide**

N<sub>2</sub>O has a GWP of 298 CO<sub>2</sub>-equivalents over a 100 year horizon (Solomon et al., 2007), therefore any small amount emitted to the atmosphere will contribute significantly to a treatment plants overall GHG footprint (Daelman et al., 2012).

### **2.2.3 Carbon Dioxide**

Carbon dioxide is a product of energy used for powering plant processes such as pumping, aeration and transport. The breakdown of organic materials during wastewater treatment results in the production of biogenic CO<sub>2</sub>, however CO<sub>2</sub> production from biogenic sources is not considered as GHG emissions under current IPCC protocols (Bani Shahabadi et al., 2010).

## **2.3 SOURCES OF GREENHOUSE GAS EMISSIONS AT WWTP**

### **2.3.1 Methane**

The emission of CH<sub>4</sub> during wastewater treatment only occurs under anaerobic conditions and can therefore be expected from:

- Sewerage systems;
- Influent works;
- Anaerobic/anoxic tanks as part of activated sludge; and
- Sludge digestion and handling activities.

(Foley et al., 2011, Kurup, 2011)

CH<sub>4</sub> generation typically occurs in areas of high chemical oxygen demand (COD) and low oxygen concentration such as influent lines, primary settling tanks, secondary clarification tanks, sludge holding tanks and sludge transfer lines (Foley and Lant, 2008). CH<sub>4</sub> is also emitted to the atmosphere when effluent is physically aerated resulting in the stripping of gas from the effluent via diffusion (Czepiel, 1993).

Dissolved methane remaining in the discharged effluent from digesters, sludge thickeners and storage tanks is typically stripped during downstream processing, such as dewatering of sludge (Daelman et al., 2012). Some of the resulting methane may also remain in the reject water and be stripped during mechanical aggravation in aerated tanks. Studies by Guisasola et al. (2008) and Foley et al. (2009) identified rising mains and sewers as anaerobic environments that promote the production of methane downstream of the primary treatment

process. The discharge of methane from downstream sources is considered to be significant and is not currently recognised by any existing estimation methodologies (Foley et al., 2009).

### 2.3.2 Nitrous Oxide

The emission of  $N_2O$  occurs primarily in the activated sludge units of a WWTP as well as grit tanks, pre-sedimentation secondary clarifiers, sludge storage tanks and anaerobic sludge digesters (Kampschreur et al., 2009).  $N_2O$  is a known intermediate of both nitrification and denitrification processes and the net contribution of BNR  $N_2O$  emissions from wastewater treatment has only recently been acknowledged in GHG emission methodologies (Ahn et al., 2010). The processes of  $N_2O$  formation at these locations will be discussed in further detail in section 2.4.3.

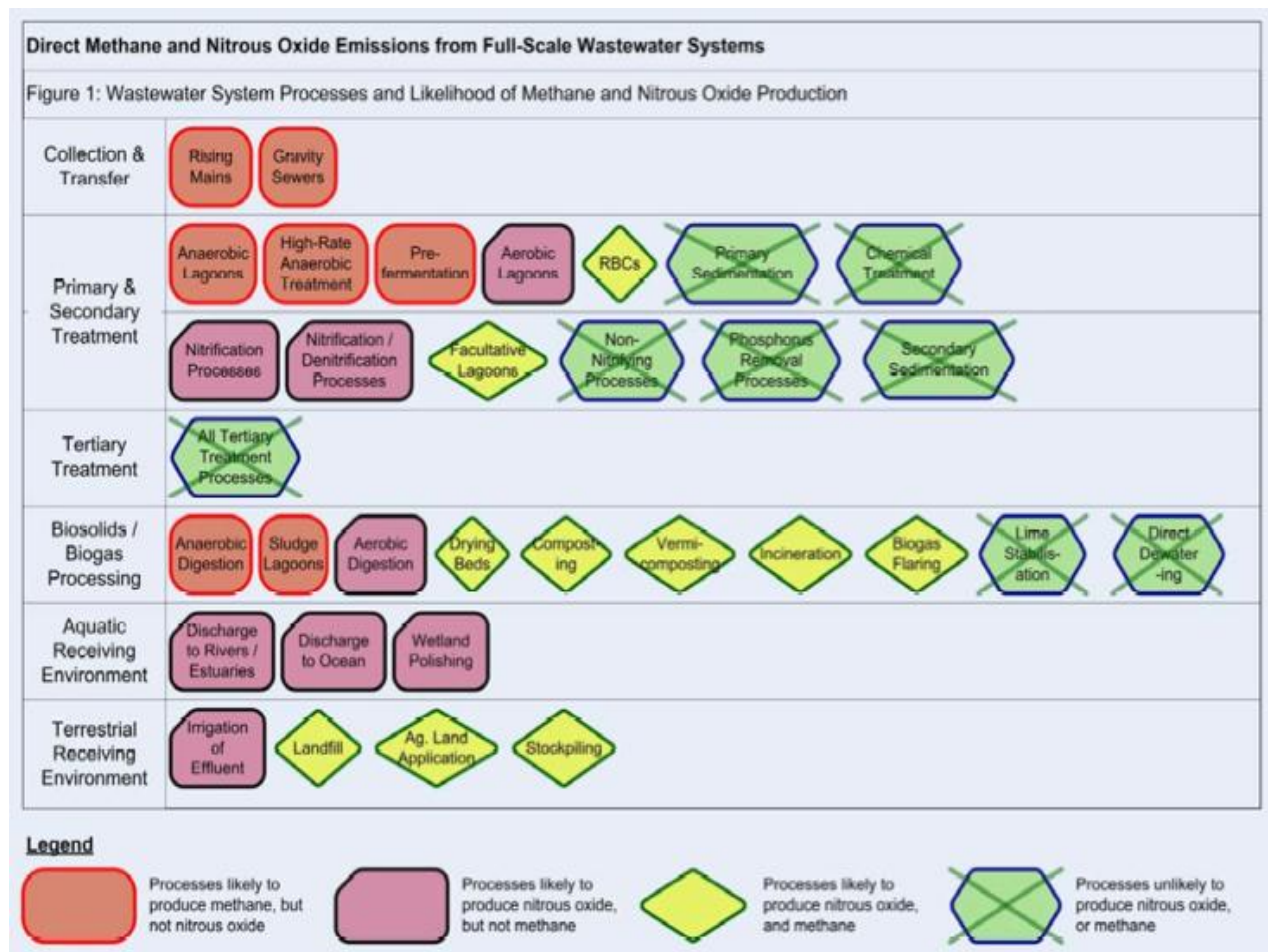


Figure 1: Direct  $CH_4$  and  $N_2O$  Emissions from Full-Scale Wastewater Treatment (Foley and Lant, 2009)

### 2.3.3 Principles of Methane Generation from Full-Scale WWTP

Methane ( $\text{CH}_4$ ) is resultant from the biodegradation of biomass by microorganisms under anaerobic conditions (Scheehle and Doorn, 2003). Anaerobic digestion is a very complex process that relies on several groups of microorganisms acting symbiotically to reduce organic wastes into  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  through three basic steps in the absence of oxygen (Chan et al., 2009). The three steps are:

#### 1. *Hydrolysis*

Hydrolysis is the rate-limiting step in the formation of methane which involves extracellular enzymes de-polymerising organic macromolecules (i.e. carbohydrates proteins and fats) into simple sugars, amino acids, long chain fatty acids and  $\text{CO}_2$  (Lastella et al., 2002).

#### 2. *Acidogenesis*

Acid forming microorganisms (acetogens) degrade long chain fatty acids producing acetic acid, molecular hydrogen and  $\text{CO}_2$  (Lastella et al., 2002).

#### 3. *Methanogenesis*

During this stage, methane forming microorganisms (methanogens) work in a syntrophic relationship with acetogens to maintain relatively neutral pH conditions and low dissolved hydrogen concentrations (Foley and Lant, 2008). Therefore, methane generation occurs within the liquid phase of the anaerobic digester.

The methane produced in the liquid phase of an anaerobic reactor can subsequently:

- Remain dissolved in the liquid phase (possibly at super-saturated concentrations);
- Be stripped to the gas phase by natural mass transfer and/or aggravation (mechanical aeration);
- Undergo continued oxidation to  $\text{CO}_2$  by methanotrophic bacteria in aerobic environments; or
- Be further utilised as the carbon and energy source for heterotrophic denitrification in anoxic zones.

(Foley and Lant, 2008)

#### *Aerobic Methanotrophic Oxidation*

Methanotrophic bacteria typically occur in aerobic surface environments where methane is present and reach growth optimum under mesophilic conditions (Jewell et al., 1992). Under

micro-aerated surface conditions, methanotrophic bacteria consume methane as their primary carbon and energy source to produce organic products (Miguez et al., 1999, Costa et al., 2000, Gavazza dos Santos et al., 2004). Aerobic methane oxidation is important in the context of fugitive emissions as many of the existing treatment processes operate in a quasi-anaerobic-aerobic state. Therefore it is important to understand the syntrophic relationship that exists between microorganisms in anaerobic-aerobic zones in order to estimate the potential for CH<sub>4</sub> emissions (Foley and Lant, 2008).

Depending on the conditions within anaerobic digesters, the resulting methane will preferentially transfer to the gas phase via mechanical stripping or by natural mass transfer (Pauss et al., 1990). If the atmospheric conditions within the anaerobic digester are super-saturated then some of the methane will remain dissolved in the effluent (Foley and Lant, 2008).

#### **2.3.4 Methane Mass Transfer Kinetics**

Mass transfer is defined as the movement of molecules from a phase with higher chemical potential (concentration or partial pressure) to the lower chemical potential until equilibrium is reached (Kashid et al., 2011). CH<sub>4</sub> is generated in relatively high concentrations in the liquid phase of a reactor and as such there is a strong driving force for CH<sub>4</sub> to be emitted to the atmosphere from reactors as ambient concentrations of CH<sub>4</sub> in the atmosphere are very low (Kurup, 2011).

In the past, biological treatment processes have been successfully described by the theory of continuous cultivation of microorganisms and the mathematical application of process kinetics has been used to describe aerobic and anaerobic biological treatment processes (Tchobanoglous et al., 2003, Lawrence and McCarty, 1969). Process kinetics plays a pivotal role in the development and operation of anaerobic treatment systems. In addition to the quantitative description of the rates of waste utilisation, process kinetics also deals with operational and environmental factors affecting these rates. A sound knowledge of kinetics allows for the optimisation of performance and better process control (Pavlostathis and Giraldo-Gomez, 1991) as well as greater accuracy in quantifying emissions.

The thermodynamic equilibrium between gas phase and liquid phase concentrations of methane can be described by Henry's Law at low pressures (Tchobanoglous et al., 2003):

$$p_{CH_4} = K_H \times [CH_4]_{liq}^* \quad (1)$$

Where:

$p_{CH_4}$	=	Partial pressure of CH <sub>4</sub> (atm)
$K_H$	=	Henry's Law constant for CH <sub>4</sub>
$[CH_4]_{liq}^*$	=	Equilibrium concentration of CH <sub>4</sub> in water

The solubility of CH<sub>4</sub> does not remain constant rather it varies with temperature and partial pressure (Judd, 2002). The solubility of methane in water is essentially zero therefore any exposure of wastewater effluent to the ambient atmosphere will likely force the release of dissolved CH<sub>4</sub> under natural mass transfer. Furthermore, any form of mechanical aeration or perturbation will increase the stripping rate of dissolved methane (Czepiel, 1993).

In order to understand the solubility of gases in wastewater, it is necessary to consider the mass transfer between the liquid phase and the gas phase. There are two key controlling mechanisms:

1. *Thermodynamic equilibrium* - at steady state, methane concentration in the gas phase (partial pressure) is equal to methane concentration in the liquid phase (solubility).
2. *Mass transfer kinetics* - the rate at which methane achieves thermodynamic equilibrium varies depending on the mass transfer coefficient ( $k_L a$ ).

(Boyadjiev and Babak, 2000)

The value of  $k_L a$  is a reflection of how well a gas diffuses through a liquid as well as representing interfacial surface area available for mass transfer (Abbassi-Guendouz et al., 2012). The interfacial surface area is dependent on physical parameters such as reactor geometry, reactor turbulence and degree of mixing (Kashid et al., 2011). Based on these principles, each methanogenic reactor will be governed by different mass transfer kinetics.

Liquid to gas mass transfer in wastewater treatment processes requires knowledge of the volumetric mass transfer coefficient of resultant gases (Pauss et al., 1990). For anaerobic processes where homogeneous gas and liquid phases are considered, mass balances for metabolites can be established for both liquid and gas phases.

Mass balance for the liquid phase:



$$\frac{d[gas]_L}{dt} = D([gas]_{L,in} - [gas]_{L,ef}) - k_l a([gas]_L - [gas]_L^*) \quad (2)$$

Mass balance for the gas phase:

$$\frac{d[gas]_g}{dt} = \frac{V_L}{V_g} k_l a([gas]_L - [gas]_L^*) - \frac{Q_g p_{gas}}{V_g R T} \quad (3)$$

Where:

$D$	=	The dilution rate (hour <sup>-1</sup> )
$[gas]_{L,in}$	=	The concentration of dissolved gas in the influent (moles litre <sup>-1</sup> )
$[gas]_{L,ef}$	=	The concentration of dissolved gas in the effluent (moles litre <sup>-1</sup> )
$k_l a$	=	The global volumetric mass transfer coefficient for a bioreactor (hour <sup>-1</sup> )
$[gas]_L$	=	The concentration of the dissolved species in the reactor (moles litre <sup>-1</sup> )
$[gas]_L^*$	=	The concentration of the dissolved species in the reactor at thermodynamic equilibrium (moles litre <sup>-1</sup> )
$V_L$	=	The volume of the liquid phase (litres)
$V_g$	=	The volume of the gas phase (litres)
$Q_g$	=	The gas flow rate (litres)
$p_{gas}$	=	The partial pressure of the gas species (pascals)
$R$	=	The ideal gas constant (8.314 Pa mole <sup>-1</sup> K <sup>-1</sup> )
$T$	=	Temperature (K)

In equations (2) and (3), the driving force for the transfer from the liquid phase to the gas phase is expressed as the difference between the actual concentration of dissolved gas and the concentration that would be in equilibrium with the partial pressure of the given species in the gas phase (Pauss et al., 1990).

When assuming ideal gas behaviour where  $\frac{d[gas]_g}{dt} = 0$ , Equation (1) and (3) can be combined and rearranged to show:

$$\frac{[gas]_L}{[gas]_L^*} = \frac{Q_v}{k_L a \cdot K_H \cdot R \cdot T} + 1 \quad (4)$$

Equation (4) demonstrates that it is possible for the concentration of dissolved methane to exceed thermodynamic concentration, resulting in supersaturated conditions for closed systems. Methane super-saturation is proportional to the volumetric gas production rate, therefore a faster rate of methane generation will more likely result in a supersaturated solution. Super-saturation is inversely proportional to solubility, therefore poorly soluble gases such as methane are more likely to be saturated. There also exists an inverse relationship with mass transfer, with stagnant reactors more likely to result in supersaturated conditions than well-mixed reactors (Pauss et al., 1990, Pavlostathis and Giraldo-Gomez, 1991).

### 2.3.5 Principles of Nitrous Oxide Generation from Full-Scale WWTP

Tighter regulation on total nitrogen removal from wastewater has encouraged a global effort to develop and implement cost-effective engineered BNR strategies for use at WWTPs. Engineered BNR facilities are effective in reducing aqueous nitrogen loading however a percentage of the total effluent load is emitted to the environment as gaseous nitrous oxide ( $N_2O$ ) and nitric acid ( $NO$ ) (Ahn et al., 2010).

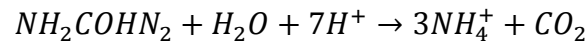
It is generally recognised that  $N_2O$  can be emitted either as a by-product of aerobic nitrification and/or as an intermediate in the anoxic denitrification process (Hanaki et al., 1992, Kampschreur et al., 2009).

The process of biological nutrient removal (BNR) removes total nitrogen (TN) and total phosphorous (TP) from wastewater through the use of specific micro-organisms under different environmental conditions (Tchobanoglous, 2003). The aim of BNR is the conversion of influent nitrogen into harmless nitrogen gas, a process typically achieved via the following biological steps:

#### *Mineralisation/Ammonification*

Ammonification is the conversion of soluble nitrogen into ammonia-N, which typically occurs when microorganisms consume soluble organic matter containing nitrogen

(Federation, 2005). Ammonification occurs under anaerobic conditions and is represented in the following simplified equation:



Because ammonification occurs as heterotrophic biomass destroys nitrogen-containing soluble organic matter, it is likely that the depletion rate is proportional to the rate of soluble substrate removal (Nemerow, 2009).

### Nitrification

Nitrification refers to the two-step biological process where, firstly, ammonia is oxidized to nitrite and, secondly, nitrite is oxidized to nitrate (Tchobanoglous, 2003). The process of nitrification is performed by three different groups of autotrophic microbes: ammonium oxidizing bacteria (AOB) and ammonium oxidizing archaea (AOA) which convert ammonia into nitrite, and nitrite oxidizing bacteria (NOB) which convert nitrite into nitrate (Kampschreur et al., 2008). Under oxygen-limiting and anoxic conditions, AOB including *Nitrosomonas europaea* and *N.eutropha*, have the potential to utilise nitrite ( $NO_2^-$ ), dimeric nitrogen dioxide ( $N_2O_4$ ) and ammonium ( $NH_4^+$ ) as electron acceptors to produce  $N_2O$  and  $NO$  (Yu et al., 2010).

**Figure 2: AOB/AOA Reactions**

Oxidation of ammonia to nitrite

Step	Reaction
1	$NH_3 + O_2 + 2H^+ + 2e^- \rightarrow NH_2OH + H_2O$ Ammonia mono-oxygenase
2	$NH_2OH + H_2O \rightarrow NO_2^- + 5H^+ + 4e^-$ Hydroxyl amine oxidoreductase
3	$0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Total	$NH_3 + 1.5O_2 \rightarrow NO_2^- + H^+ + H_2O$

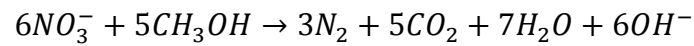
**Figure 3: NOB Reactions**

Oxidation of nitrite to nitrate

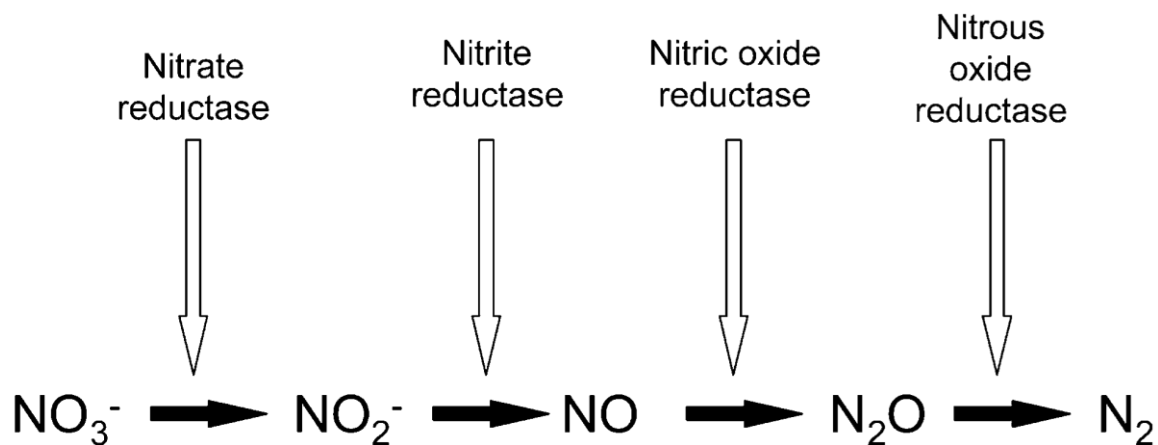
Step	Reaction
1	$HONO + H_2O \rightarrow HONO_2 + 2H^+ + 2e^-$ Nitrite oxidoreductase
2	$0.5O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Total	$HONO + 0.5O_2 \rightarrow HONO_2$

### Denitrification

Denitrification is the reduction of nitrogen oxides, primarily nitrate, to gaseous nitrogen compounds such as molecular di-nitrogen (Kampschreur et al., 2008). The denitrification reaction is shown in the following stoichiometric equation:



This microbiological process is coupled to the respiration (oxidation) of organic matter (Schulthess and Gujer, 1996). The dominant denitrification process is anoxic heterotrophic denitrification, which is considered to be more dominant in wastewater treatment than aerobic nitrifier-denitrification (Kampschreur et al., 2009).



**Figure 4: Denitrification pathway and enzymes involved (after Wrage et al. (2001))**

Biological nitrogen removal processes via nitrification and denitrification have been applied in many wastewater treatment plants due to the increasing demand for higher effluent quality (Itokawa et al., 2001). However, it is understood that the conditions favourable to efficient removal of nitrogen, such as low DO, are also favourable to the generation of  $\text{N}_2\text{O}$  emissions (Yang et al., 2009).

## **2.4 INTERNATIONAL GREENHOUSE GAS REPORTING**

When studying the different GHG reporting and accounting mechanisms available, the procedures can be easily confusing. The different accounting and reporting procedures originate from the work of a large number of individuals and organisations producing methodologies, standards and protocols of varying complexities and technicalities for a range of different scopes (Gentil et al., 2009). The following is a succinct overview of some of the major existing methodologies.

### **2.4.1 IPCC**

The Intergovernmental Panel on Climate Change (IPCC) was established in 1988 to assess the ongoing human impacts on climate change through the comprehensive, objective, and transparent attainment of global scientific, technical and socio-economic information. The IPCC includes a Task Force on national GHG inventories and three working groups, which provide regular assessment reports (IPCC, 2012). The IPCC prepares periodic reports on special topics relating to climate change and through the Task Force, provides support to the United Nations Framework Convention on Climate Change (UNFCCC) on the methodologies for national GHG inventories (Gentil et al., 2009).

The 2006 IPCC guidelines provide a methodology for annual accounting of GHG emissions for the IPCC waste sector (Bogner et al., 2008). The methodology is used to compile national inventory reports and is based on a three-tiered accounting method. Tier 1 provides IPCC default data to countries with little data available. Tier 2 includes first order decay (FOD) equations with some defined IPCC default factors and finally Tier 3 includes FOD equations coupled with nationally developed parameters (Gentil et al., 2009).

### **2.4.2 UNFCCC**

The United Nations Framework Convention on Climate Change (UNFCCC) was formed in 1992 in order for countries to “work cooperatively to limit the rise in average global temperatures and the resulting climate change and to cope with whatever impacts were by then inevitable” (UNFCCC 2012). The compilation of an annual national GHG inventory covering the four key sectors of energy, industrial processes, agriculture and forestry, land use and waste is one of the key obligations for participating countries. The reporting is undertaken

by a national agency and transferred to the intergovernmental level, which is supervised by the UNFCCC (Gentil et al., 2009).

In 1995, many countries realised the inadequacy of climate change reduction strategies and subsequently adopted the Kyoto Protocol. The Kyoto Protocol legally binds developed countries to emission reduction targets. There are currently 37 developed nations bound to the protocol, which in principle applies a heavier burden on developed nations to achieve “common differential responsibilities” (UNFCC, 2012).

The Kyoto Protocol offers participating countries an additional means of meeting targets by employing three market-based mechanisms. They are as follows:

- Emissions Trading;
- Clean Development Mechanisms (CDM); and
- Joint Implementation (JI).

CDM projects allow emission reduction projects in developing countries to earn certified emission reduction (CER) credits each equivalent to one tonne of CO<sub>2</sub>. CER's can be traded or sold and used by industrialised countries to meet part of their emission reduction targets under the Kyoto Protocol (UNFCC, 2012).

In late 2011, the UNFCCC prepared a technical report to research and evaluate the most appropriate calculation methods and options for emissions quantification. Contained in the report are several methodologies relevant to emissions reduction for wastewater treatment. The relevant methodologies were:

- ACM0014: “Mitigation of GHG from treatment of industrial wastewater”;
- ACM0010: “Consolidated baseline methodology for GHG emission reductions from manure”; and
- AM0025: “Avoided emissions from organic waste through alternative waste treatment processes”.

The evaluation of methodologies is discussed in further detail in section 4.1.5.

### **2.4.3 National Greenhouse Reporting and Energy Reporting Scheme (Australia)**

The National Greenhouse and Energy Reporting Scheme (NGERS) was introduced in 2007 to provide data and accounting in relation to greenhouse gas emissions and energy

consumption/production within Australia. The NGERs regulations provide detailed requirements for reporting, including definitions of operational control, facilities, the requirement for registration and the types of GHG emissions and consumption/production that have to be reported (Foley et al., 2011).

#### 2.4.4 Mass Balance Approach

A commonly used approach for quantifying total emissions is the formation of mass balances for individual treatment process. These mass balances draw upon the analytical field data as well as observable plant data (i.e. flow rates, reactor volumes, solids capture efficiencies, biosolids tonnages and composition, biogas production and composition).

The purpose of mass balance analysis is to characterise WWTP operations such that both COD and TN balances over the WWTP generally achieve greater than 90% closure and to determine the volumetric mass transfer of CH<sub>4</sub> and N<sub>2</sub>O released to the atmosphere (Foley and Lant, 2009).

The IPCC and NGERs prescribe the following generalised approaches for estimating methane emissions generated from domestic wastewater treatment systems. These methodologies provide a holistic approach for determining total emissions based on observable plant data and default emission and correction factors.

*IPCC: Total CH<sub>4</sub> Emissions from Domestic Wastewater*

$$CH_4Emissions = [\sum_{i,j}(U_i \cdot T_{i,j} \cdot EF_j)](TOW - S) - R \quad (5)$$

Where:

$CH_4Emissions$	=	CH <sub>4</sub> emissions in inventory year, kg CH <sub>4</sub> /yr.
TOW	=	Total organics in wastewater in inventory year, kg BOD/yr.
S	=	Organic component removed as sludge in inventory year, kg BOD/yr.
$U_i$	=	Fraction of population in income group $i$ in inventory year
$T_{i,j}$	=	Degree of utilisation of treatment/discharge pathway

or system,  $j$ , for each income group fraction  $i$  in inventory year.

- I = Income group: rural, urban high income and urban low income.
- J = Each treatment/discharge pathway or system.
- R = Amount of CH<sub>4</sub> recovered in inventory year, kg CH<sub>4</sub>/yr.

*NGERS: Total CH<sub>4</sub> Emissions from Domestic Wastewater Treatment*

$$CH_{4gen} = [(COD_w - COD_{sl} - COD_{eff}) \times F_{wan} \times EF_{wij}] + [(COD_{sl} - COD_{trl} - COD_{tro}) \times F_{slan} \times EF_{slij}] \quad (6)$$

Where:

- $COD_w$  =  $P \times DC_w$ , where  $P$  is the population served by the operation of the facility during the year and measured in numbers of persons.  
 $DC_w$  = the quantity in tonnes of COD per capita of wastewater for a year using a default of 0.0585 tonnes/pp.

- $CH_{4gen}$  = Generated methane from commercial wastewater and sludge treatment by the facility during the year measured in CO<sub>2</sub>-e tonnes.

- $COD_w$  = Chemical oxygen of wastewater entering the plant during the year measured in tonnes.

- $COD_{sl}$  = Quantity of COD removed as sludge from wastewater and treated in the plant measured in tonnes of COD.

- $COD_{eff}$  = Quantity of COD in effluent leaving the facility during the year measured in tonnes.

- $F_{wan}$  = Fraction of COD anaerobically treated by the plant



during the year.

$EF_{wij}$	=	Default methane emission factor for wastewater with a value of CO <sub>2</sub> -e tonnes per tonne COD.
$COD_{trl}$	=	Quantity of COD in sludge transferred out of the plant and removed to landfill measured in tonnes of COD.
$COD_{tro}$	=	Quantity of COD in sludge transferred out of plant and removed to a site other than landfill measured in tonnes of COD.
$F_{slan}$	=	The fraction of COD in sludge anaerobically treated by the plant during the year.
$EF_{slij}$	=	Default methane emission factor for sludge: 5.3 CO <sub>2</sub> -e tonnes per tonne COD (sludge).

*IPCC: Total N<sub>2</sub>O Emission from Domestic Wastewater Treatment*

$$N_2O \text{ Emissions} = N_{Effluent} \cdot EF_{Effluent} \cdot \frac{44}{28} \quad (7)$$

Where:

$N_2O \text{ Emissions}$	=	N <sub>2</sub> O emissions in an inventory year, kg N <sub>2</sub> O/yr.
$N_{Effluent}$	=	Nitrogen in the effluent discharged to aquatic environments, kg N/yr.
$EF_{Effluent}$	=	Emission factor for N <sub>2</sub> O emissions from discharged wastewater, kg N <sub>2</sub> O-N/kg

The factor 44/28 is applied to convert kg N<sub>2</sub>O-N into kg N<sub>2</sub>O.

*NGERS: Total N<sub>2</sub>O Emission from Domestic Wastewater Treatment*

$$E_j = (N_{in} - N_{trl} - N_{tro} - N_{out}) \times EF_{secij} + N_{out} \times EF_{disij} \quad (8)$$

Where:

$E_j$	=	Emissions of $N_2O$ released from human sewage treated by the plant during the year measured in tonnes of $N_2O$ and expressed in $CO_2$ -e tonnes.
$N_{in}$	=	The quantity of nitrogen entering the plant during the year measured in tonnes of nitrogen.
$N_{trl}$	=	The quantity of nitrogen in sludge transferred out of the plant and removed to landfill during the year measured in tonnes of nitrogen.
$N_{tro}$	=	The quantity of nitrogen in sludge transferred out of the plant and removed to a site other than landfill during the year measured in tonnes of nitrogen.
$N_{out}$	=	Quantity of nitrogen leaving the plant in effluent during the year measured in tonnes of nitrogen
$EF_{secij}$	=	The emission factor for wastewater treatment: 4.9 tonnes of $N_2O$ measured $CO_2$ -e per tonne of nitrogen produced.
$EF_{disij}$	=	The emission factor for nitrogen discharge differentiated by the discharge environment: 4.9 tonnes of $N_2O$ measured $CO_2$ -e per tonne of nitrogen produced.

The generalised equations used in the estimation of emissions are heavily dependent on the various plant specific inputs and the default parameters provided by the authors of the methodologies. The default parameters provided by the authors are often based on best estimates or expert opinion rather than valid scientific research. Over the last decade there has been significant research undertaken in the area of GHG emission from wastewater treatment. Some of the key findings of the published research have been adopted for existing methodologies, however it remains an ongoing process.

#### *UNFCCC Methodologies (as outlined in Kurup (2011))*

The following methodologies have been developed by the UNFCCC to estimate emissions from secondary wastewater treatment processes.

### **1. Estimation of $CH_4$ emissions from wastewater (AM0025, 2011)**

If wastewater is treated anaerobically or released untreated, resulting CH<sub>4</sub> emissions are estimated as follows:

$$PE_{CH_4,w,y} = Q_{COD,y} \cdot P_{COD,y} \cdot B_0 \cdot MCF_p \quad (9)$$

Where:

- PE<sub>CH<sub>4</sub>,w,y</sub> = Methane emissions from the wastewater treatment in year y (tCH<sub>4</sub>/y)
- Q<sub>COD,y</sub> = Amount of wastewater treated anaerobically or released untreated from the project activity in year y (m<sup>3</sup>/yr.), which shall be measured monthly and aggregately annually
- P<sub>COD,y</sub> = Chemical Oxygen Demand (COD) of wastewater (tCOD/m<sup>3</sup>), which will be measured monthly and averaged annually
- B<sub>0</sub> = Maximum methane producing capacity (tCH<sub>4</sub>/tCOD)
- MCF<sub>p</sub> = Methane conversion factor (fraction), preferably local specific value should be used. In absence of local values, MCF<sub>p</sub> default values can be obtained from table 6.3, chapter 6, volume 4 from IPCC 2006 guidelines

In the case of all CH<sub>4</sub> being emitted into air directly, then:

$$PE_{w,y} = PE_{CH_4,w,y} \cdot GWP_{CH_4} \quad (10)$$

## 2. CH<sub>4</sub> emission calculation in “Mitigation of greenhouse gas emissions from treatment of industrial wastewater”, (ACM0014, 2011)

The methodology proposes two alternative methods for the estimation of methane emissions from treatment lagoons:

- (a) The Methane Conversion Factor Method (described in Step (a)); and
- (b) The Organic Removal Ratio Method (described in Step (b)).

### (a)Methane conversion factor method

Project methane emissions from treatment of the effluent from the digester are estimated as follows:

$$PE_{CH_4,effluent,y} = GWP_{CH_4} \times MCF_{PJ,y} \times B_o \times (COD_{PJ,effl,dig,y} - COD_{PJ,effl,lag,y}) \quad (11)$$

with

$$COD_{PJ,effl,dig,y} = \sum_{m=1}^{12} F_{PJ,effl,dig,m} \times w_{COD,effl,dig,m} \quad (12)$$

and

$$COD_{PJ,effl,lag,y} = \sum_{m=1}^{12} F_{PJ,effl,lag,m} \times w_{COD,effl,lag,m} \quad (13)$$

Where:

- $PE_{CH_4,effluent,y}$  = Project emissions from treatment of wastewater effluent from the anaerobic digester in year  $y$  (tCO<sub>2</sub>e/yr.)
- $GWP_{CH_4}$  = Global Warming Potential of methane valid for the commitment period (tCO<sub>2</sub>e/tCH<sub>4</sub>)
- $MCF_{PJ,y}$  = Project methane conversion factor (fraction) in year  $y$ , representing the fraction of ( $COD_{PJ,effluent,y} \times B_o$ ) that degrades to CH<sub>4</sub>.
- $B_o$  = Maximum methane producing capacity, expressing the maximum amount of CH<sub>4</sub> that can be produced from a given quantity of chemical oxygen demand (tCH<sub>4</sub>/tCOD). Taking into account the uncertainty of this estimate, use a value of 0.21 kg CH<sub>4</sub>/kg COD as a conservative assumption for  $B_o$
- $COD_{PJ,effl,dig,y}$  = Quantity of chemical oxygen demand in the effluent from the digester in year  $y$  (tCOD/yr.)
- $COD_{PJ,effl,lag,y}$  = Quantity of chemical oxygen demand in the effluent of the open lagoon or dewatering facility in which the effluent from the digester is treated in year  $y$  (tCOD/yr.)
- $F_{PJ,effl,dig,m}$  = Quantity of effluent from the digester in month  $m$  (m<sup>3</sup>/month)
- $w_{COD,effl,dig,m}$  = Average chemical oxygen demand in the effluent from the digester in month  $m$  (t COD/m<sup>3</sup>)
- $F_{PJ,effl,lag,m}$  = Quantity of effluent from the open lagoon or dewatering facility in which the

effluent from the digester is treated in month  $m$  ( $\text{m}^3/\text{month}$ )

$W_{\text{COD,effl,lag},m}$  = Average chemical oxygen demand in the effluent from the open lagoon or dewatering facility in which the effluent from the digester is treated in month  $m$  ( $\text{t COD}/\text{m}^3$ )

The quantity of methane generated from COD disposed to the open lagoon or in dewatering facility is calculated as follows:

$$MCF_{PJ,y} = f_d \times f_{PJ,T,y} \quad (14)$$

Where:

$MCF_{PJ,y}$  = Project methane conversion factor (fraction) in year  $y$ , representing the fraction of  $(\text{COD}_{PJ,\text{effluent},y} \times B_o)$  that degrades to  $\text{CH}_4$

$f_d$  = Factor expressing the influence of the depth of the lagoon or dewatering facility on methane generation

Apply the following values for the corresponding average depth of the open lagoon or the sludge pit:

Depth > 5 m: 70%

Depth 1 – 5 m: 50%

Depth < 1 m: 0%

### 3. “Tool to determine methane emissions avoided from disposal of waste at a solid waste disposal site” (Version 06.0.1) EB 66 ANNEX 46 March 2012

The amount of methane produced in the year  $y$  ( $BE_{CH_4,SWDS,y}$ ) is calculated as follows:

$$BE_{CH_4,SWDS,y} = \varphi \cdot (1 - f) \cdot GWP_{CH_4} \cdot (1 - OX) \cdot \frac{16}{12} \cdot F \cdot DOC_F \cdot MCF \cdot \sum_{X=1}^Y \sum_J W_{j,X} \cdot DOC_j \cdot e^{-k_j(y-X)} \cdot (1 - e^{-k_j}) \quad (15)$$

Where:

$BE_{CH_4,SWDS,y}$  = Methane emissions avoided during the year  $y$  from preventing waste disposal at the solid waste disposal site (SWDS) during the period from the start of the project activity to the end of the

year  $y$  (tCO<sub>2</sub>-e).

$\Phi$	=	Model correction factor to account for model uncertainties (0.9).
$F$	=	Fraction of methane captured at the SWDS and flared, combusted or used in another manner.
$GWP_{CH_4}$	=	Global Warming Potential (GWP) of methane, valid for the relevant commitment period.
$OX$	=	Oxidation factor, (reflecting the amount of CH <sub>4</sub> from SWDS that is oxidized through soil and other material covering the waste.
$F$	=	Fraction of methane in the SWDS gas (volume fraction)(0.5)

The UNFCCC methodologies shown above, have been used to quantify emissions of CH<sub>4</sub> and N<sub>2</sub>O from implemented CDM projects. The performance of these methodologies will be discussed in further detail in section 4.1.5.

## 2.5 PROJECT AIMS

### ➤ Aim 1

Develop an understanding of fundamental emission generation processes for CH<sub>4</sub> and N<sub>2</sub>O and identify key chemical, biological and physical parameters of influence.

### ➤ Aim 2

Develop and validate standardised sampling methods for dissolved methane in anaerobic effluent and biogas resultant from uncovered treatment processes.

#### 2.5.1 Rationale

Based on the initial review of scientific literature and existing quantification methodologies, there arises a need to understand the influencing factors of dissolved methane, which remain relatively unknown. In addition to this, the contribution of dissolved methane is not currently accounted for in existing methodologies and as such requires further investigation for potential incorporation.

The existing methodologies currently provide incomplete guidance and underestimates on emissions due to incorrect emission factors and exclusion of key emission sources. This remains a particular issue for the quantification of N<sub>2</sub>O emissions for which current default

emission factors are based on a single study. Therefore, a greater understanding of how complex chemical and biological processes interact during wastewater treatment processes is needed.

Current scientific literature has highlighted the significant shortfalls that exist in available environmental and physical data for the various treatment methods and processes currently in use today. In order to build an inventory of field data, it is important to establish appropriate and reliable parameters to be measured and develop credible methods of data collection from defined emission sources. The ongoing study of GHG emissions and climate change should be committed to physiochemical identification, inventories, measurement and assessment methods as well as the quantitative study of the anthropogenic sources and its direct contributions (Listowski et al., 2011).

Furthermore, there is consistent absence of regulatory requirements for managing gaseous emissions from wastewater treatment. Because of this, fugitive emission monitoring has been conducted primarily for academic purposes only or as part of CDM Projects. When direct monitoring is not undertaken, the fugitive emissions are estimated based on observable plant data only. The methods developed for monitoring are often complex and expensive with limited practical application. This study will look at developing practical methods of sampling and monitoring for implementation into regular plant operating protocols.

## CHAPTER 3. METHODOLOGY

### 3.1 DEVELOPMENT OF BIOGAS SAMPLING PROCEDURE

#### 3.1.1 Field Sampling Site

The study site (Figure 5) is a privately owned facility that treats wastewater from a meat processing facility. The plant treats approximately 500m<sup>3</sup> of high strength wastewater per day using an EEI hybrid anaerobic reactor (EEI-HAR) of 6,500m<sup>3</sup> capacity. The treatment process also involves advanced nitrogen removal using the custom-built ANRUP© system. The anaerobic reactor (Figure 6) uses a modified version of Upflow Anaerobic Sludge Bucket (UASB) technology to suit treatment of meat processing effluent. The treatment process involves the development of a dense granulated sludge thus allowing for high volumetric COD loadings compared with other anaerobic processes (Kurup, 2012).



Figure 5: Aerial Photograph of Study Site (nearmaps)



### 3.1.2 Field Methane and Nitrous Oxide Measurements



**Figure 6: EEI Hybrid Anaerobic Reactor**

The anaerobic reactor at the site is not currently covered. In order to capture the gas flux rate over a period of time and to collect and analyse the gas produced, a gas collection system was installed. This system consisted of two main components; a floating inverted half 200L HDPE drum (Figure 7) and a secondary collection unit (Figure 8).

The half 200L HDPE drum was deployed on the surface of the large uncovered anaerobic digester with a concrete weight tied underneath to provide sufficient down-weight to avoid uplifting and to keep the apparatus level. Prior to sample collection, the floating apparatus was completely immersed in the digester liquid with the vacuum valve left open to purge the drum headspace. The valve was then closed and the drum was allowed to float back to the effluent surface creating a headspace under slight vacuum. A long plastic hose was connected to the valve on top of the drum and connected to the secondary gas collection unit at ground

level. The gas collection unit at ground level consisted of a half metal drum sitting inside a HDPE drum filled with water. The secondary collection unit was used to determine the volume of gas released over a period of time by measuring the drums displacement in the water bath. The emission flux rate could be determined by measuring the volume of gas collected over a given period of time and scaling up to integrate over the total surface area of the reactor. A T bar valve was fitted to the secondary collection unit allowing for the direct sampling of the captured gas into 1litre Tedlar sample bags (Figure 9).



**Figure 7: Gas Collection Unit**



**Figure 8: Secondary Collection Unit**



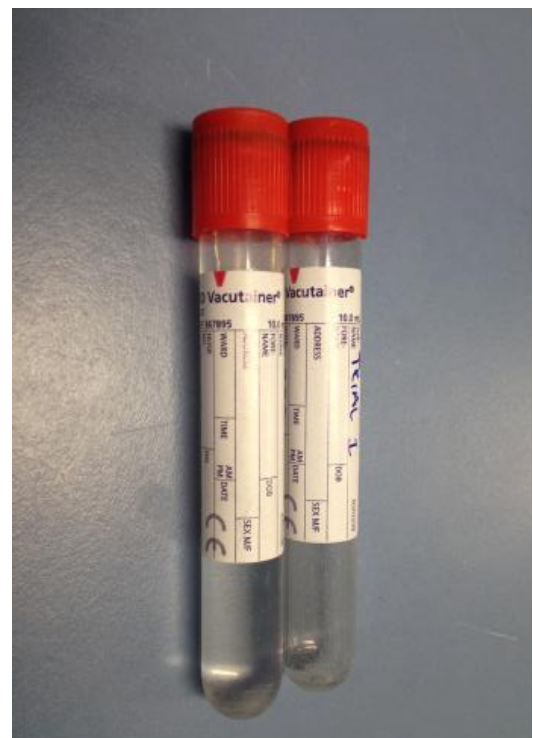
**Figure 9: 1 litre Tedlar Sample Bag**

### 3.2 DEVELOPMENT OF FIELD DISSOLVED METHANE SAMPLING PROCEDURE

Dissolved methane was sampled and analysed based upon the methodologies described in Alberto et al. (2000), Guisasola et al. (2008) and Foley et al. (2009).

The procedure involved procuring samples of effluent from the anaerobic digester at the study site with a 1L glass bottle (Figure 10). The glass bottle used as the primary apparatus for methane generation and consisted of a rubber stopper at the top with a small plastic tube fitted through the centre and a double-ended hypodermic needle pierced through to one side. The plastic tube was connected to a 20ml plastic syringe via a length of rubber hose approximately 40cm long with appropriate diameter to fit tightly on the end of the syringe. To obtain samples of effluent, a siphoning process was used in order to limit the exposure of effluent to the ambient atmosphere and avoid significant aggravation.

**Figure 10: Gas Sampling Apparatus and Vacutainer Sample Tubes**



Once the sample bottle was filled to capacity with effluent and had undergone sufficient siphoning, an initial temperature and pH reading was taken. In order to create a vacuum within the glass bottle, the syringe was drawn to remove 20ml of effluent from the 1L bottle. This was done to create a small headspace at the top of the glass bottle. The sample was then manually aggrivated for approximately 3 minutes. This allowed for the dissolved methane in

solution to partition into the vacuumed headspace. The resulting gas released into the headspace was sampled into 10ml BD vacutainer tubes (Prod #367895) by pushing the vacutainer down on the small rubber stopper atop the hypodermic needle until the needle pierced through both the stopper and the vacutainer septum. A second temperature reading was taken after each gas sample was obtained. The sample vacutainers were then weighed to determine the amount of gas obtained.

### 3.2.1 Calculation of Dissolved Methane Concentration

The concentration of dissolved methane in wastewater is proportional to its concentration in the headspace. Therefore the dissolved concentrations can be calculated with a predetermined partition coefficient at a given temperature (Lomond and Tong, 2011).

The following calculation for the determination of dissolved methane concentration was based upon similar calculations performed by Lomond and Tong (2011). A methane partition coefficient was used in the analysis, as partition coefficient calculations yield concentrations as mass-per-volume and do not involve partial pressures.

The partition coefficient between methane and water is defined as:

$$K_{gl} = \frac{C_g}{C_l} \quad (16)$$

Where  $C_g$  is the concentration (mg/V) of methane in the headspace and  $C_l$  is the concentration of methane in the sample bottle at equilibrium. The total mass of methane in the sample bottle,  $m_o$  is equal to:

$$m_o = C_l V_l + C_g V_g \quad (17)$$

Where  $V_g$  and  $V_l$  are volumes of the gas phase and liquid phase respectively. Combining the two equations,  $K_{gl}$  can be redefined as:

$$K_{gl} = \frac{C_g V_l}{m_o - C_g V_g} \quad (18)$$

The initial concentration of dissolved methane in the sample can then be determined by firstly rearranging Equation 18 in terms of  $m_o$ :

$$m_o = C_g \left( \frac{V_l}{K_{gl}} + V_g \right) \quad (19)$$

Furthermore, dividing through Equation 19 with  $V_l$  gives an expression for initial dissolved concentration,  $C_{w,o}$ :

$$C_{w,o} = \left( \frac{1}{K_{gl}} + \frac{V_g}{V_l} \right) C_g \quad (20)$$

Methane has a high partition coefficient due to its relatively low molar mass and high volatility. In the study performed by Lomond and Tong (2011), the partition coefficient  $K_{gl}$  for methane was determined to be 128 at 30°C. The vacutainers were weighed before and after sampling to determine the sample volume collected and the concentration of methane in the gas phase is determined using gas chromatography. With these parameters, the initial concentration can be calculated using Equation 20.

## CHAPTER 4. RESULTS AND DISCUSSION

### 4.1 FINDINGS OF CRITICAL LITERATURE REVIEW

#### 4.1.1 Factors Affecting Methane Generation: Key Findings

Methane emissions from wastewater treatment are resultant from the anaerobic metabolism of organic carbonaceous material via a complex process in which target microorganisms act symbiotically (Foley and Lant, 2008).

##### *Dissolved Methane*

The study by Cakir and Stenstrom (2005) on processes of anaerobic treatment at WWTPs found the mass of dissolved  $\text{CH}_4$  discharged in the anaerobic effluent to be as large as the  $\text{CH}_4$  released during treatment, especially for low strength wastewater. The mass of dissolved methane was calculated using Henry's Law and the measured value of  $\text{CH}_4$  partial pressure in the anaerobic reactor gas. The mass balance was undertaken using a mathematical model developed in a previous study (Cakir and Stenstrom, 2003). In the study performed by Matsuura et al. (2010) it was also reported that the amount of dissolved methane was roughly the same as the amount of  $\text{CH}_4$  produced from the USAB. However, the recovered dissolved methane was higher than that of the difference between the influent and effluent, suggesting that significant methane generation occurs in the effluent after leaving the UASB. These findings warrant further investigation before dissolved methane emission factors can be developed for inclusion in future methodologies.

Studies performed by Guisasola et al. (2008) and Hartley and Lant (2006) reported super-saturation conditions occurring in closed-system rising mains and discharged anaerobic effluents. The subsequent losses of dissolved methane upon discharge from digesters can be between 38-85% of total generated methane, depending on waste on physical reactor properties and influent strength (Hartley and Lant, 2006). These reported results do seem rather extreme and if true, would present a significant OH & S issue with opportunities for fire and/or explosion at the outlet from anaerobic reactor.

##### *Dissolved Oxygen (DO)*

The presence of DO in wastewater effluent was found to be inhibitory to methane generation as all methanogens are strictly and obligately anaerobic (Bitton, 2005). Using mechanical aeration, DO concentration increases, causing inhibition of methane generation processes.



However there is often still some quantity of methane released as a result of dissolved methane being stripped during mechanical aeration (Rajagopal and Béline, 2011). A comprehensive understanding of how DO concentration inhibits methane generation is still lacking, however in a recent study performed by Rajagopal and Béline (2011) it is suggested that the DO concentration plays a major role in CH<sub>4</sub> flux in aerobic and oxic systems. According to Wang et al. (2011), the DO concentration in anaerobic tanks tends to be more stable and is therefore not considered a major contributing factor to CH<sub>4</sub> generation during digestion. This statement appears to be at odds with the principles of thermodynamics for anaerobic digestion, as DO tends to change the redox potential subsequently altering the electron transfer in the main reaction. The effect of DO concentration on anaerobic digestion requires further research to validate such claims.

### *Temperature*

Temperature has a significant effect on the physiochemical properties of the components found in the digestion substrate and also on growth rate and metabolism of microorganisms. Typically an increase in temperature (up to a certain threshold level) will improve digester performance with increased solubility of the organic compounds, enhanced biological and chemical reaction rates (Appels et al., 2008) and an increase in CH<sub>4</sub> production (IPCC, 2006).

Currently the existing IPCC guidelines for wastewater treatment and discharge (IPCC, 2006) highlight temperature as a major factor in the production of CH<sub>4</sub> when operating at temperatures above 15°C. However, the IPCC guidelines have not included temperature into the emissions quantification methods for both domestic and industrial wastewater treatment.

The UNFCCC approved methodologies and tools for wastewater treatment use different methods for incorporating the effect of temperature on CH<sub>4</sub> production. The approved consolidated methodology ACM0014 uses the Van't Hoff-Arrhenius equation given below, with upper and lower limits for incorporating the effect of temperature on degradation of COD:

$$f_{T,m} = \begin{cases} 0 & \text{if } T_{2,m} < 283 \text{ K} \\ \exp\left(\frac{E \times (T_{2,m} - T_1)}{R \times T_1 \times T_{2,m}}\right) & \text{if } 283 \text{ K} < T_{2,m} < 303 \text{ K} \\ 1 & \text{if } T_{2,m} > 303 \text{ K} \end{cases} \quad (21)$$

Where:

$f_{T,m}$	=	Factor for expressing the influence of temperature on CH <sub>4</sub> generation in month, $m$ .
$E$	=	Activation energy constant (15,175 cal/ mol)
$T_{2,m}$	=	Average temperature at the project site in month $m$ , (K)
$T_1$	=	303.16 K
$R$	=	$R$ = Ideal gas constant (1.987 cal/K mol)
$M$	=	Months of year $y$ for the assessment period

The current NGERS method for estimating the mass of gas emitted includes a temperature component in the calculation as shown below:

$$M_{jet} = \frac{MM_j \times P_{ct} \times FR_{ct} \times C_{jet}}{8.314 T_{ct}} \quad (22)$$

Where:

$M_{jet}$	=	The mass of emissions in tonnes of gas type (j) released per second.
$MM_j$	=	The molecular mass of gas type (j) measured in tonnes per kilomole which: (a) For methane is $16.04 \times 10^{-3}$ or (b) Nitrous oxide is $44.01 \times 10^{-3}$ .
$T_{2,m}$	=	Average temperature at the project site in month $m$ , (K)
$P_{ct}$	=	303.16 K
$FR_{ct}$	=	The flow rate of the gas stream in cubic metres per second at the time of measurement.
$C_{jet}$	=	The proportion of the gas type (j) in the volume of the gas stream at the time of measurement.
$T_{ct}$	=	The temperature in degrees Kelvin, of the gas at the time of measurement.



Temperature is considered a significant factor affecting the rate of methanogenic activity, where the rate of methane production increases with increasing temperature (Lettinga and Haandel, 1993). For anaerobic systems, controlled digestion can be divided into psychophilic (10-20°C), mesophilic (20-40°C) or thermophilic (40-60°C) digestion (De Mes et al., 2003). For treatment plants operating within these different temperature ranges, considerations must be made regarding waste volumes and retention times. Typically, psychophilic digestion requires long retention time and therefore a large reactor capacity whereas thermophilic digestion can process high loadings in a relatively short period of time.

The effect of temperature is often considered to be less than predicted by the Van't Hoff equation (Massé and Masse, 2001). In the study performed by Tallec et al. (2008), results indicated that temperature had a significant effect on COD removal, with low temperatures resulting in low COD removal efficiencies. These results are in contrast with the recent Rajagopal and Béline (2011) study which could not find any significant relationship between CH<sub>4</sub> emissions and temperature in the processing units ( $R^2 < 0.2$ ). The facility assessed in the Tallec et al. (2008) study operated over a greater temperature range (6- 31°C) compared to (12- 24°C) and was also treating low strength wastewater. Furthermore, the study performed by Massé and Masse (2001) found that lowering the operating temperature from 30°C to 25°C did not greatly affect the specific methane production rate. It was only when the temperature was lowered to 20°C that a three-fold decrease in methane production was observed. From these results no conclusive comments can be made regarding temperature range thresholds, as there are several differences in the conditions of the studies being compared.

For methane formed in sewer systems, Foley et al. (2011) observed a significant difference between summer and winter emissions for CH<sub>4</sub> in the gas phase. The Foley et al. (2011) reported that CH<sub>4</sub> emissions were approx. 80% higher in summer than in winter suggesting that temperature is an important parameter determining the formation of CH<sub>4</sub> in sewers. For development of Australian guidelines, the effect of temperature on CH<sub>4</sub> generation is likely to be significant for summer months where averages can be very high.

### *pH*

Typically, methanogenic bacteria function in a pH range between 6.7 and 7.4, with an optimal performance between 7 and 7.2 (Gerardi, 2006). The generation of CH<sub>4</sub> was examined for pH dependence by linear regression analysis in the study performed by Rajagopal and Béline (2011), however no significant relationship was found. This suggested that pH did not play a

major role in CH<sub>4</sub> generation at the full-scale WWTP. That being said, it is still critical to provide conditions that promote digestion in a neutral environment to obtain greatest level of process efficiency.

#### *Hydraulic Retention Time*

The retention time is an important factor in the production of CH<sub>4</sub> from anaerobic and aerobic treatments for both solid and liquid wastes. Typically, shorter retention time for covered anaerobic reactors and lagoons results in significant emissions from digestate treatment and storage (Kurup, 2011).

#### *Feed Material*

The type of feed material governs the amount of CH<sub>4</sub> produced during anaerobic treatment. For wastewater, the main parameter is chemical oxygen demand (COD) or 5-day biological oxygen demand (BOD<sub>5</sub>), which is used instead of volatile solids (VS). The COD/BOD<sub>5</sub> parameter represent the organic content in the wastewater (Kurup, 2011). Based on stoichiometric calculations, the theoretical value of CH<sub>4</sub> generation is 0.35L CH<sub>4</sub>/g COD digested or 250 kg/tonne of COD digested (Tchobanoglous et al., 2003). This value was adopted as the default value for IPCC 2006 Guidelines.

**Table 1: Summary of Findings - CH<sub>4</sub>**

PARAMETER	SIGNIFICANCE	COMMENTS
Dissolved Methane	High	Requiring further study to determine correction factors for adoption by current methodologies
Dissolved Oxygen	Moderate	Comprehensive understanding still lacking
pH	Low	Most WWTPs operate in neutral range (6.7-7.4 pH)
Temperature	High	High seasonal variation. Inconsistency in current methodologies.
Hydraulic retention time	High	Current methodologies do not incorporate HRT.
Feed Material	High	Default values vary for different methodologies.

#### 4.1.2 Factors Affecting Nitrous Oxide Generation: Key Findings

In a recent report released by the Global Water Research Coalition (GWRC) in 2011, N<sub>2</sub>O emissions from WWTPs in Australia, USA, France and the Netherlands were measured. This represented the most comprehensive full-scale study on N<sub>2</sub>O emissions conducted to date. There was significant variability in emissions among the 26 WWTPs studied as well as seasonal and diurnal variability at each WWTP. The formation of N<sub>2</sub>O is very complex and can result from both autotrophic and heterotrophic bacterial processes (Foley et al., 2011). Bacterial processes show a dynamic response to changing influent loads, treatment process conditions and environmental factors (Yang et al., 2009).

The first full-scale study on municipal wastewater performed by Czepiel et al. (1995) indicated N<sub>2</sub>O-N emissions to be less than 1% of total nitrogen load, however subsequent studies, such as Park et al. (2000), Kampschreur et al. (2008), have shown emission percentages of 4.6% and 7% respectively. For plants treating high strength wastewater, higher N<sub>2</sub>O-N emissions have been reported, in some cases, as high as 55% of total N influent (Itokawa et al., 1996). The large variation in reported N<sub>2</sub>O emissions from WWTPs can be attributed to the fact that N<sub>2</sub>O is formed during nitrification and denitrification, and that different physical characteristics influence the formation of N<sub>2</sub>O during these processes. The scale and frequency of changes in process conditions depend on the type of WWTP, reactor geometry, mixing intensity and aeration mode (Kampschreur et al., 2009).

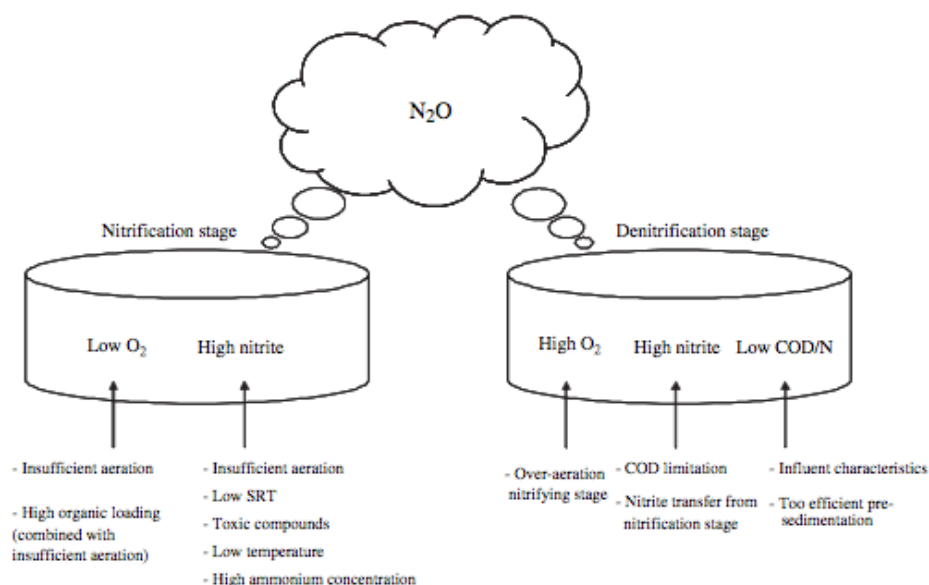
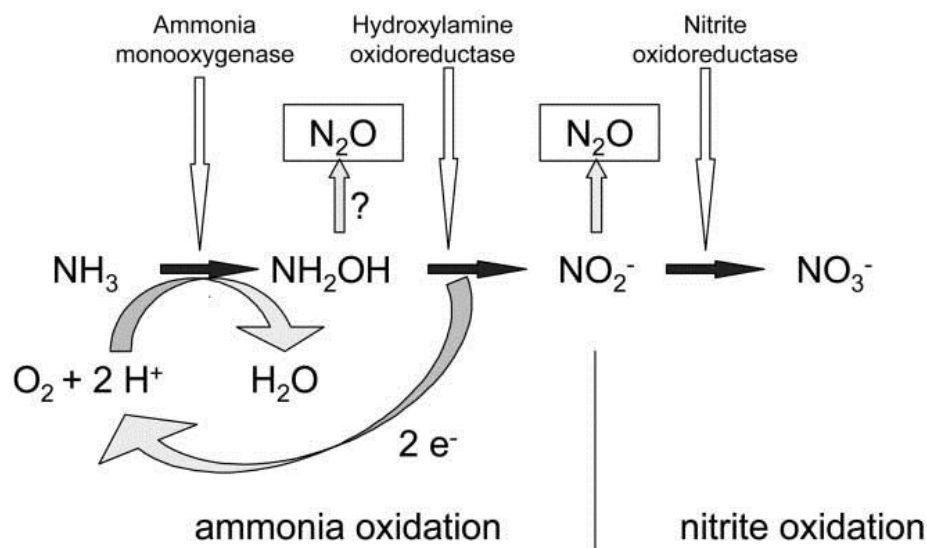


Figure 11: Factors affecting N<sub>2</sub>O generation (Kampschreur et al., 2009)

Denitrification in anoxic zones is implicated as the dominant source of  $\text{N}_2\text{O}$  from BNR activated sludge reactors (Scheehle and Doorn, 2003). However, nitrification can also play a role in  $\text{N}_2\text{O}$  generation and emission from WWTPs especially when cycling between anoxic and aerobic conditions (Kampschreur et al., 2008), as is common in BNR reactors. The significance of aerobic  $\text{N}_2\text{O}$  emissions has been validated by a comprehensive study performed by Foley and Lant (2009). A rigorous mass balance approach was used for individual reactor zones, which found that emission of  $\text{N}_2\text{O}$  occurs predominantly in the aerated zone due to significantly larger mass transfer coefficients. Under aerobic conditions nitrite is known to accumulate when the rate of ammonia oxidation to nitrite by the ammonia oxidizing bacteria (AOB) exceeds the rate of nitrite oxidation to nitrate by nitrite oxidising bacteria (NOB). This is likely due to competing rates of NOB and AOB constantly fluctuating. Foley and Lant (2009) also reported fluctuations in emissions over relatively short timeframes as well as temporary spikes in generation resultant from process perturbations. These findings suggest that the magnitude and variability of  $\text{N}_2\text{O}$  emissions are significantly influenced by process design and variability in operating process conditions.



**Figure 12: Nitrification pathway and enzymes involved (after Wragge et al. (2001))**

The nitrification pathway in Figure 12 shows the formation of  $\text{N}_2\text{O}$  as an intermediate in the reaction, however the formation mechanisms are still under debate (Ni et al., 2011). Existing literature suggests that the efficiency of the  $\text{NH}_4^+$  to  $\text{N}_2\text{O}$  conversion is higher at low dissolved oxygen (DO) concentrations and high  $\text{NH}_4^+$  and  $\text{NO}_2^-$  concentrations (Kampschreur et al., 2008, Sivret, 2008, Foley et al., 2010, Kampschreur et al., 2009).

### *Dissolved Oxygen*

It has been shown consistently that DO concentration is an important parameter for mitigating N<sub>2</sub>O emissions (Tallec et al., 2006, Zheng et al., 1994). Lower concentrations of DO within the nitrifier-denitrifier pathway have been known to increase the level of N<sub>2</sub>O emissions (Kampschreur et al., 2008). This is due to autotrophic ammonia oxidizers using nitrite as the terminal electron acceptor to save oxygen for the oxygenation reaction of ammonia to hydroxylamine (Kampschreur et al., 2009). For well-aerated conditions, N<sub>2</sub>O emissions from the nitrification pathway are minimal compared with the anoxic denitrification pathway (Park et al., 2000, Itokawa et al., 2001, Meyer et al., 2005, Schulthess and Gujer, 1996). Many studies have reported low DO concentrations cause a significant increase in the production of N<sub>2</sub>O during the denitrification phase (Foley and Lant, 2008). DO inhibits both synthesis and activity of denitrification enzymes and N<sub>2</sub>O reductase is more sensitive to oxygen than other commonly occurring enzymes, leading to N<sub>2</sub>O emission during denitrification (Otte et al 1996). The inhibitory effect of DO on N<sub>2</sub>O reductase was found to be reversible when a system was reverted back to anaerobic conditions (Schalk-Otte et al., 2000).

### *Nitrite Accumulation*

There is a known positive correlation between N<sub>2</sub>O emissions and the bulk accumulation of nitrite in the system (Hanaki et al., 1992, Park et al., 2000). This is most likely due to the inhibition of N<sub>2</sub>O reductase by high concentrations of nitrite intermediate and/or nitric oxide (Itokawa et al., 2001). High nitrite concentrations during denitrification lead to lower denitrification rate and subsequent build-up of NO and N<sub>2</sub>O (Schulthess et al., 1995). The system sensitivity to changes in nitrite is relatively large, with the study by (Tallec et al., 2006) showing four to eight-fold increases in N<sub>2</sub>O observed during nitrification with the addition of small nitrite pulses.

### *Indirect Nitrate Accumulation*

Some of the parameters identified in the literature as being key influences in N<sub>2</sub>O generation might not be directly related to emission generation, rather they alter other process parameters that subsequently lead to N<sub>2</sub>O production (Kampschreur et al., 2009). Short SRT, presence of toxic compounds (i.e. hydrogen sulphide), low temperatures, high salinity and high ammonium concentrations have all been linked to increased nitrite accumulation and subsequent inducement of N<sub>2</sub>O emission (Schonharting 1998; Colliver and Stephenson 2000).

### *pH*

Studies by Hynes and Knowles (1984) and Foley and Lant (2008) found higher pH values to result in greater production of NO and N<sub>2</sub>O during both aerated and non-aerated phases. However, it was noted that other parameters such as oxygen concentration, aeration rates and conversion rates are of more influence. Moreover, most WWTPs conduct operations in a pH range between 7 and 8 suggesting the pH effect to be relatively minor.

### *COD/N*

The results of the study undertaken by Schulthess and Gujer (1996), suggested that limited availability of biodegradable carbon dioxide can lead to an increase in N<sub>2</sub>O formation during denitrification. For an intermittently aerated bioreactor treating high strength wastewater, Itokawa et al. (2001) found that 20-30% of the nitrogen was being emitted as N<sub>2</sub>O when COD/N ratio was lower than 3.5. Hanaki et al. (1992) suggests that the increased emissions may not be a direct response of denitrifying bacteria of limiting COD availability, but could be caused by nitrite accumulation. Further studies such as Park et al. (2000) noted significant reductions in N<sub>2</sub>O emissions (from 4.5% to 0.2% of total nitrogen load) with provision of an external organic carbon source i.e. methanol to force the denitrification phase to completion.

**Table 2: Summary of Findings - N<sub>2</sub>O**

PARAMETER	SIGNIFICANCE	COMMENTS
Dissolved Oxygen	Moderate	Important effect on N <sub>2</sub> O emissions from denitrification pathway
Nitrite	High	Both direct and indirect nitrite accumulation lead to significant N <sub>2</sub> O emission from nitrification pathway
pH	Low	Redox potential is a more relevant parameter.
COD/N	Moderate	Negative effects can be easily mitigated with addition of external carbon source.

#### 4.1.3 Emission Mitigation Strategies

In view of the emerging and existing political agendas on mitigation of climate change, it is important to accurately quantify current GHG emissions and savings from wastewater treatment, and to set achievable goals for the future contributions towards the mitigation efforts in the waste management industry (Gentil et al., 2009). The significance and magnitude of  $N_2O$  emissions has become more apparent in recent years and as such the development of appropriate mitigation strategies should be considered. As discussed previously, the three most important operational parameters that result in  $N_2O$  emissions are:

- Low DO concentration during the nitrification stage;
- Increased nitrite concentrations in both the nitrification and denitrification stages; and
- Low COD/N ratio in the denitrification phase.

Therefore, in order to reduce the generation of  $N_2O$  emissions; mitigation strategies should be focused on operational measures that limit these conditions.

##### *Dissolved Oxygen Concentration*

Biological nitrification and denitrification using aerobic and anaerobic processes with low dissolved oxygen has gained recent attention because of its lower energy consumption (Yoo et al., 1999). However, it is commonly understood that a significant amount of  $N_2O$  is generated during this process. During the nitrification stage, the oxygen supply should be sufficient to both minimize  $N_2O$  emission through nitrifier-denitrification, and avoid nitrite accumulation induced  $N_2O$  emissions (Kampschreur et al., 2009). For treatment plants operating simultaneous nitrification-denitrification processes, the control on the efficient concentration of oxygen is very difficult to achieve, as higher level of oxygen will cause inhibition of denitrification. Furthermore, low dissolved oxygen concentration in the nitrification stage will lead to a local oxygen limitation and subsequent increase in  $N_2O$  production (Park et al., 2000). This presents a dilemma for plant operators as to how to achieve optimum oxygen concentration to avoid  $N_2O$  generation. It is proposed that off gas  $N_2O$  monitoring be undertaken as part of plant operation protocols to determine efficient air supply and detect process failure, as was suggested in (Sivret, 2008).

Plant operators should endeavour to control DO concentration so as to avoid operating in the 0.2-0.5 mg/l range as studies have shown this to range to correspond with  $N_2O$  emission peaks (Park et al., 2000). Lower than this suggested threshold, nitrification is too low to

produce  $\text{N}_2\text{O}$  and higher than the threshold, DO concentration is favourable for complete nitrification subsequently avoiding major production of  $\text{N}_2\text{O}$ .

#### *Aeration*

The use of intermittent aeration has been shown to significantly reduce the percentage emission of  $\text{N}_2\text{O}$  for activated sludge reactors (Osada et al., 1995). There is a tendency for plant operators to steer away from mechanical aeration due to the high operation costs involved and potential reduction in  $\text{CO}_2$  emissions. However several studies have reported that the global warming effect of  $\text{N}_2\text{O}$  emissions resultant from anoxic conditions far outweigh the savings in  $\text{CO}_2$  reduction (Park et al., 2000).

#### *COD/N*

The COD/N ratio of a WWTPs influent cannot be controlled. However, if COD is limiting the completion of denitrification, pre-sedimentation of organic carbon in the influent could be minimised and emissions could be prevented through additional dosing of organic carbon (Kampschreur et al., 2009).

#### *Sludge Alkaline Fermentation Liquid*

A relatively new method for mitigating  $\text{N}_2\text{O}$  and NO generation in low DO anaerobic-aerobic nutrient removal processes is the use of waste activated sludge alkaline liquid as a carbon source. Acetic acid is the main organic component in municipal wastewater and has been the most commonly used carbon source of anaerobic-low DO wastewater treatment processes. In the study performed by Zhu and Chen (2011) it was reported that the use of sludge fermentation liquid resulted in a 68.7 % and 50% reduction in  $\text{N}_2\text{O}$  and NO emissions respectively. These findings are relatively new and untried; therefore, further validation is suggested before extensive implementation of this method into plant operating protocols.

#### *HRT*

Retaining the wastewater in the anoxic phase for a long duration allowed for the intermediate  $\text{N}_2\text{O}$  formed during denitrification to be used as an electron donor and consequently denitrifiers were able to further reduce the  $\text{N}_2\text{O}$  to  $\text{N}_2$  (Rajagopal and Béline, 2011).

#### **4.1.4 Mitigation of Dissolved Methane**

The current knowledge on contributions of dissolved methane to total plant emissions is limited. Therefore, the development of mitigation strategies requires further knowledge on generation processes and sources. In light of this, a recent study conducted by Matsuura et al.



(2010) looked into the use of a post treatment down-flow hanging sponge (DHS) reactor to recover dissolved methane as useful energy gas. The study reported 99% recovery of dissolved methane via the two-stage system. For larger WWTPs treating high strength wastewater, such technologies could be justified in future mitigation efforts.

#### 4.1.5 Existing Uncertainties for Current Methodologies

##### *Methane*

The IPCC calculation for methane emission is a combination of the estimated mass of methane produced during the treatment of wastewater ( $[\sum_{i,j}(U_i \cdot T_{i,j} \cdot EF_j)](TOW - S)$ ) and the measured mass of methane captured (R). A difference between the two expressions represents a loss of methane to the atmosphere. For uncovered treatment systems, the value of R is zero. This type of emission methodology is heavily dependent on default emission and correction factors. The maximum theoretical yield ( $B_o$ ) of methane from the removal of COD is 0.25 kgCH<sub>4</sub> per kgCOD removed and is governed by the stoichiometry of methane (IPCC, 2006). The default values of maximum CH<sub>4</sub> production used in various approved methodologies are provided in Table 3:

**Table 3: Summary of Default Theoretical Yield Values**

Default values of maximum CH <sub>4</sub> production ( $B_o$ )	Reference (methodology)
250 kg/t of COD digested	Table 6.2, Chapter 6, IPCC 2006
265 kg/t of COD digested	AM0025, Version 12 (UNFCCC)
210 kg/t of COD digested	ACM0014, AM0039 (UNFCCC)

A review of several existing CDM projects from around the world has been summarised in Table 4:

**Table 4: Summary of Yield Factors Used in CDM Projects (Kurup (2011))**

CDM Project	Description	Methodology	Comments
Project 4265: Indonesia.	AD with biogas extraction, treatment of tapioca starch.	ACM0014 $B_o = 210 \text{ kg CH}_4/\text{t}$	Research from a tapioca starch wastewater treatment

		of COD	in Thailand report, estimate $B_o = 220\text{--}240 \text{ kg CH}_4/\text{t}$ of COD.
Project 3759: China.	Methane recovery, high starch content treated anaerobically.	ACM0014 $B_o = 210 \text{ kg CH}_4/\text{t}$ of COD	Given the nature of the wastewater, consider using $B_o = 240 \text{ kg CH}_4/\text{t}$ of COD.
Project 3686: Malaysia	AD and methane capture system, palm oil facility.	ACM0014 $B_o = 210 \text{ kg CH}_4/\text{t}$ of COD	Full year study performed by (Yacob et al., 2006) showed average $B_o = 238 \text{ kg CH}_4/\text{t}$ of COD for anaerobic ponds.
Project 1919: Chile	AD with enclosed flare followed by activated sludge system, Swine waste.	IPCC 2006, $480\text{m}^3 \text{CH}_4$ per tonne of dry matter.	Included various parameters from CDM methodologies.
Project 4660: Hunan Province, China	Installation of 20,000 household biogas digesters for treatment of manure.	IPCC 2006, $290 \text{ m}^3 \text{CH}_4$ per tonne of volatile solids	Project 4723 also used same emission value.

The CDM projects summarised in the Table 4, applied default values based on the relevant UNFCCC methodology or IPCC 2006 guidelines. Based on the reported generation factors resultant from long-term studies, the default values for methane generation can be deemed adequate. Of the reviewed CDM projects, only projects 4265 and 1919 considered  $\text{N}_2\text{O}$  emissions. Project 1919 utilised the default IPCC 2006 factor of  $0.005 \text{ kg N}_2\text{O-N}/\text{year}$  for manure waste management and Project 4265 considers only  $\text{N}_2\text{O}$  emissions from land application of digestate.

Further to the discussion of current CDM projects, the UN assessment report conducted in 2011 offered a number of key recommendations for current approved UNFCCC methodologies. These recommendations have been summarised in Table 5:

**Table 5: Summary of UNFCCC Methodology Assessment (Kurup (2011))**

Methodology	Description	Comments
AM TOOL 04 EB 55	“Tool to determine CH <sub>4</sub> emissions avoided from disposal of waste at a solid waste disposal site”	The accuracy of fraction of CH <sub>4</sub> in biogas (F), DOC <sub>F</sub> and other default parameters can be improved by referencing known parameters in current literature.
AM0025	“ Method of Estimation of CH <sub>4</sub> emissions from wastewater”	Value of Bo is too conservative (0.265). MCFp values provided by IPCC 2006 can be used for other substances other than sewage sludge. Currently no temperature correction factor, Recommend adoption of Van’t Hoff Arrhenius method.
ACM0014	“ Mitigation of greenhouse gas emissions from treatment of industrial wastewater”	Depth factor in anaerobic lagoons is questionable. Correction factors need to be applied. Methodology requires extensive field data

The methane correction factor (MCF) represents a measure of conversion efficiency of COD to CH<sub>4</sub> for a particular treatment process. Table 6 represents the current IPCC 2006 default methane correction factors for treatment of domestic wastewater:

**Table 6: Summary of Methane Correction Factors**

Type of Treatment	Comments	MCF	Range	Emission Factor (MCF × B <sub>0</sub> ) CH <sub>4</sub> /KG COD
Centralized aerobic treatment plant	Well managed, CH <sub>4</sub> can be emitted from settling basins	0	0 - 0.1	0
Centralized aerobic treatment plant	Poorly managed, Overloaded	0.3	0.2 - 0.4	0.075
Anaerobic sludge digester	No consideration of CH <sub>4</sub> recovery	0.8	0.8 - 1.0	0.20
Anaerobic reactor	No consideration of CH <sub>4</sub> recovery	0.8	0.8 - 1.0	0.20
Shallow anaerobic lagoon	Depth < 2m	0.2	0 – 0.3	0.05
Deep anaerobic lagoon	Depth > 2m	0.8	0.8 – 1.0	0.20

The values presented in the table are not based on any published studies, but rather on expert opinion and judgment of the lead authors. Many recent studies have reported methane emissions significantly less than the 0.25 kgCH<sub>4</sub>.kgCOD<sup>-1</sup> suggested by the IPCC (Flesch et al., 2011, Moller et al., 2009, Börjesson and Berglund, 2007).

This was highlighted further in an extensive literature review on methane emissions factors performed by Foley and Lant (2008). They found that many scientific studies on closed anaerobic systems reported emission factors much less than the suggested IPCC factor (Toprak, 1995, Kalogo and Verstraete, 1999, Paing et al., 2000). The discrepancy between emission and correction factors is mainly attributed to the failure of most scientific studies to consider the loss of dissolved CH<sub>4</sub> in the released anaerobic effluent (Foley and Lant, 2009). The level of dissolved methane is highly dependent on mass transfer kinetics, therefore levels vary greatly with different physical plant characteristics and processes. The occurrence of CH<sub>4</sub> super-saturation in anaerobic systems is not well understood, with difficulty arising in the application of COD mass balances at thermodynamic equilibrium (Pauss et al., 1990).

#### *Nitrous Oxide*

In early IPCC guidelines the estimation guidelines for N<sub>2</sub>O emissions from wastewater handling assumed minimal nitrogen removal occurred during treatment and hence all influent nitrogen was discharged into rivers/estuaries where it would undergo mineralisation,

nitrification and denitrification under natural processes (Foley and Lant, 2009). The current IPCC default accounting method for fugitive N<sub>2</sub>O includes direct emissions from municipal WWTPs with “controlled nitrification and denitrification steps” (IPCC, 2006). The default N<sub>2</sub>O emission factor is 0.0032 kgN<sub>2</sub>O/person.yr which is considered to be very simple and grossly inaccurate as it is based on only one scientific study (Czepiel et al., 1995). The study by Czepiel et al. (1995) was undertaken at a moderately sized secondary treatment plant with no nitrogen removal system. Based on a wastewater nitrogen loading of 16g·person<sup>-1</sup>·d<sup>-1</sup> (Tchobanoglous et al., 2003), the emission factor equates to approximately 0.00035 kgN<sub>2</sub>O-N/kgN.

The review conducted by Foley and Lant (2008) highlighted the lack of existing data for nitrification-denitrification systems under Australian conditions representing a serious knowledge gap.

**Table 7: Summary of Existing N<sub>2</sub>O Emission Factors**

Conditions	Emission Factor	Source
IPCC 2006 Default emission factor	0.00035 kgN <sub>2</sub> O-N / kgN	(Czepiel et al., 1995)
Municipal Wastewater Median	0.01 kgN <sub>2</sub> O-N / kgN	Literature review: (Foley and Lant, 2008)
Range of values (10 <sup>th</sup> – 90 <sup>th</sup> percentiles)	0.0003 – 0.03	
High Strength Wastewater Median	0.075 kgN <sub>2</sub> O-N / kgN	Literature review: (Foley and Lant, 2008)
Range of values (10 <sup>th</sup> – 90 <sup>th</sup> percentiles)	0.006 – 0.363	

Due to the high variability of percentage emissions with different treatment processes, it is difficult to estimate emissions using standard methodologies and default parameters. As research continues, the understanding of how certain process parameters influence emissions will improve allowing for the development of more robust methodologies for use in GHG accounting.

## 4.2 DISSOLVED METHANE SAMPLING PROCEDURE

### 4.2.1 Results

This study investigated the development of a practical replicable dissolved methane sampling procedure that could obtain samples with minimal error and be adopted into regular protocols by plant operators. Given the small size of the collected samples, Gas Chromatography was

the preferred method of analysis, however due to limitations regarding available laboratory equipment and resources it was not possible to test the samples and validate the developed method. In light of such events, alternative methods of obtaining dissolved methane samples were evaluated.

#### **4.2.2 Discussion**

There are several reported methods of dissolved methane sampling, many of which have acknowledged limitations. A significant drawback observed in current protocols was the exposure of gas samples to atmospheric conditions and possible oxygen interference (Alberto et al., 2000, Souza et al., 2011). In studies where samples were exposed to atmospheric conditions, a correction component was built into the concentration calculations, which assumed a globally averaged concentration value for ambient methane in the atmosphere. In addition to this, exposure and aggravation of samples would result in diffusion of dissolved gases into the atmosphere due to natural mass transfer kinetics. The use of a globally averaged ambient methane concentration represents a significant level of uncertainty in calculations as the ambient methane concentration at sampling locations is likely to be higher than the global average, especially for uncovered systems. Through identifying this limitation, the method used in this study endeavoured to eliminate exposure errors by syphoning the sample through a sealed vessel and sampling the gas under vacuumed conditions.

The practical application of the developed method proved difficult, particularly maintaining a vacuum within the sample apparatus in the field. During the sampling rounds, a vacuum in the sampling apparatus was created only twice, although not long enough for samples of gas to be obtained. The problem could be attributed to the failure the connector tubes, which after a number of lab tests and initial field tests became loose at their attachment points. Given that a vacuum was achieved in the sample bottle, albeit momentarily, with better apparatus components it should be possible to maintain a vacuum under field conditions for long enough to allow for the direct sampling of gas into vacuum tubes.

The dissolved methane sampling methods used by Guisasola et al. (2008) and Foley et al. (2009) avoided wastewater contact with the atmosphere by injecting effluent directly into vacutainer tubes using a hypodermic needle. The samples were then mixed overnight to allow for the equilibration of gas and liquid phases as mentioned in Alberto et al. (2000). This stage of the method represents a potential introduction of error given that the samples were

not preserved to prevent further anaerobic degradation and methane formation during storage. More recent dissolved methane studies have described a process of preventing continued methane production by either adding a preventative such as mercury (II) chloride (Rajagopal and Béline, 2011) or refrigeration (Souza et al., 2011) to inhibit bacterial activity. The method developed for this study does not require the use of preventative measures as it is obtaining gas samples directly into vacutainer tubes with no presence of effluent. The sampling process can also be performed within a matter of minutes, unlike other existing methods that involved equilibration of gas and liquid phase over 24 hours.

In a recent study performed by Daelman et al. (2012), the salting-out method was validated against the commonly used vacuum tube method. The salting-out method involved adding 50ml of effluent to bottles containing 20g NaCl. The bottles were sealed and shaken for a short period of time to speed up the dissolving of the salt. Under these conditions the sample is supersaturated and as a consequence of the high salt concentration, microbial activity is halted and the dissolved gasses are salted out (Gal'chenko et al., 2004). The results of the salting out method were compared to the vacuum tube method and it was found to be more accurate with a smaller standard deviation of results. There were a number of practical advantages in using the salting-out method as no filtering or toxic compounds were required for sample preservation. One other important finding of the study was the identification of residual methane inside the vacutainer tubes ranging from 248-400ppm. This could prove a limiting factor in the continued use of vacutainers for sample collection and analysis.

## **4.3 BIOGAS SAMPLE ANALYSIS**

### **4.3.1 Results**

There were a total of 10 samples collected on two separate occasions. The first round of sampling was performed on the 12<sup>th</sup> of September 2012 with the facilities sludge return system switched off. Unfortunately, due to unforeseen circumstances these samples could not be processed the following day and remained in the laboratory for some time. The second round of sampling was undertaken on the 24<sup>th</sup> of October 2012 from the same location and with the sludge return system switched on. All 10 samples were taken to the Process Expertise Group Laboratory at the Water Corporation's Woodman Point Wastewater Treatment Plant.



**Figure 13: Varian 450-GC**

The analysis of the collected biogas samples was done using a Varian 450-GC Gas Chromatograph (Figure 13). The gas chromatograph (GC) used a thermal conductivity detector (TCD) and employed detector tubes to identify and quantify the main components in the sample biogas. The TCD detector consists of an electrically heated wire, which changes temperature depending on the thermal conductivity of the gas flowing around it. Variances in the thermal conductivity that occur when constituent molecules displace some of the carrier gas cause a temperature rise in the element which is sensed as a change in resistance. The TCD is not as sensitive as other GC detectors but is non-specific and non-destructive.

The TCD was analysing for the quality of the main components of biogas: methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ). In addition to this, gas detector tubes were used to analyse for hydrogen sulphide content ( $\text{H}_2\text{S}$ ). Other components of biogas include nitrogen and trace elements of siloxanes, ethane, propane butanes, pentanes, hexanes, oxygen, hydrogen, sulphur dioxide, carbon monoxide, water vapour and helium. Due to limitations in the laboratory equipment, these components could not be quantified and as such are shown as the not detected (ND) component. Two rounds of analysis were performed for each of the collected



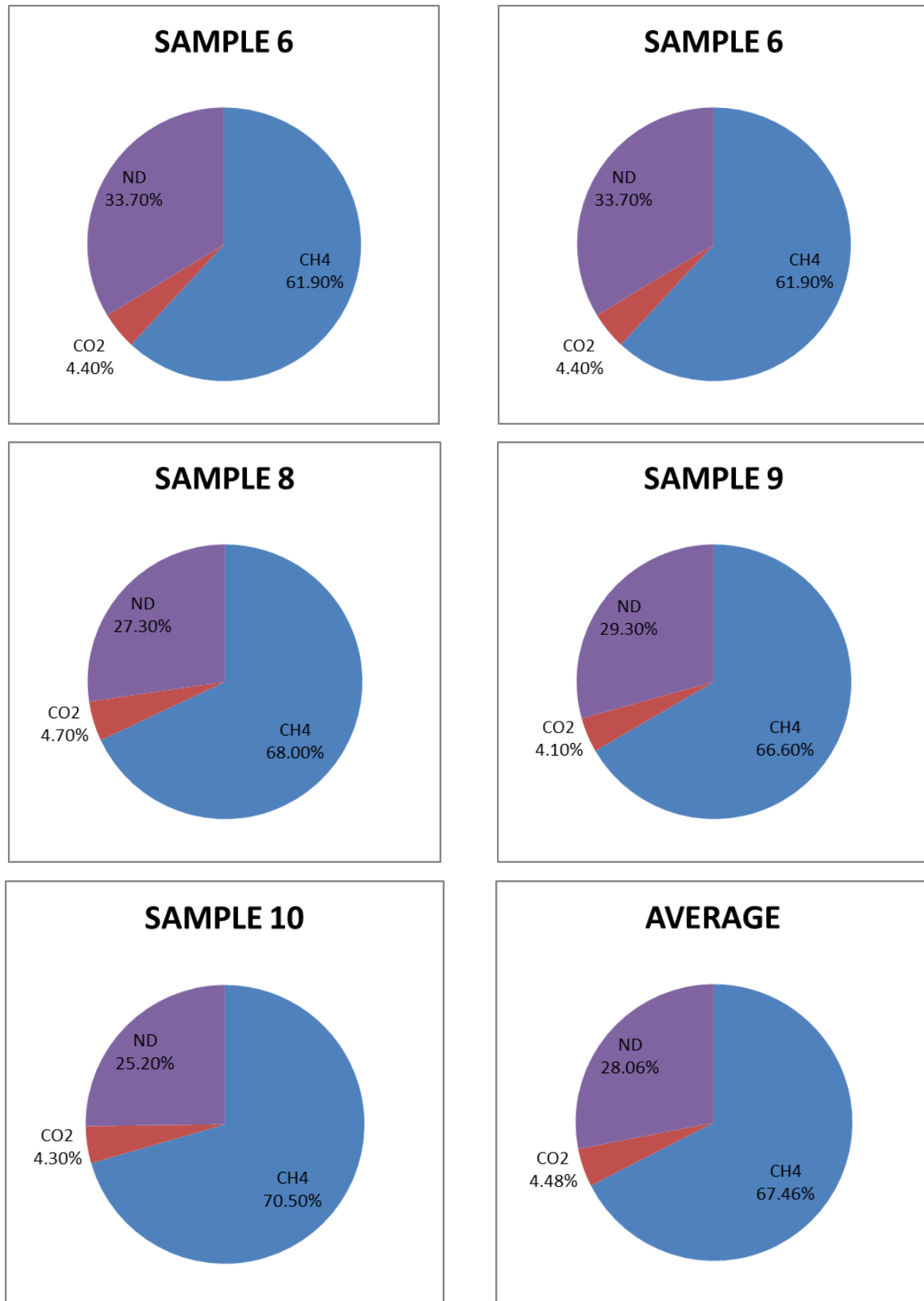
samples, each taking approximately 6 minutes to process. The results of the analysis are shown in Table 8:

**Table 8: Summary of Biogas Analysis**

<b>SAMPLE ID</b>	<b>CH<sub>4</sub> (%)</b>	<b>CO<sub>2</sub> (%)</b>	<b>H<sub>2</sub>S (ppm)</b>	<b>Comments</b>
<i>Sampling Round 1: 12 September 2012</i>				
Sample 1	37.3	2.0	0.40	
Sample 2	44.9	3.5	0.75	Tedlar bag leaking
Sample 3	42.3	3.3	1.50	
Sample 4	43.2	3.3	1.70	
Sample 5	18.6	1.4	0.75	Tedlar leaking substantially
<i>Sampling Round 2: 24 October 2012</i>				
Sample 6	61.9	4.4	ND	Possibly contaminated during sampling
Sample 7	70.3	4.9	ND	
Sample 8	68.0	4.7	ND	
Sample 9	66.6	4.1	0.05	
Sample 10	70.5	4.3	0.05	

### 4.3.2 Discussion

Figure 14: Visual Representation of Biogas Constituent Concentrations



The analysis of the Round 1 samples show severely impaired results. This can be attributed to the long time between sampling and analysis (over a month) where during such time gas would have leaked through the Tedlar sample bags. These results were not considered in the final analysis.

The analysis of the second round of samples showed results that are more consistent. The biogas samples were analysed one day after sampling avoiding any significant leakage. A summary of results are provided in the Table 9:

**Table 9: Summary of Round Two Results**

<b>Sampling Round Two</b>	<b>Average Values</b>
CH <sub>4</sub> (%)	67.46
CO <sub>2</sub> (%)	4.48
Not Detected (ND)	28.06
H <sub>2</sub> S (ppm)	0.02

The average CH<sub>4</sub> (%) value is in line with the literature range of 65-75%, however the average CO<sub>2</sub> (%) values are much lower than expected. Normally CO<sub>2</sub> makes up 25-30% of emitted biogas, therefore the low value detected suggests a significant presence of other gases that were not detected. The UASB study performed by Matsuura et al. (2010) found the average composition of biogas to be CH<sub>4</sub> (75%), CO<sub>2</sub> (5%) and N<sub>2</sub> (23%). Given the similarity of these results to the ones obtained in this study, it could be speculated that the major unknown component is N<sub>2</sub> however further analysis should be performed to determine the percentage of N<sub>2</sub>O present in the samples. The detection of N<sub>2</sub>O using gas chromatography requires a specific column which was unfortunately the use of which was not made available for the purposes of this study.

#### *Emission Flux Rate*

The emission flux rate was not successfully measure in this study. The half metal drum used for the secondary gas collection unit proved to be too heavy when sitting in the water bath. The metal drum was not able to lift up when gas was entering the headspace, instead the gas would remain in the first collection unit on the surface of the tank. Using a lighter plastic half drum with the correct dimensions to fit inside a HDPE half drum would be suggested for any

future sampling of biogas. However if adequate funds are available, the use of a gas flow metre would be more accurate and less troublesome.

## **CONCLUSIONS AND RECOMMENDATIONS**

### **CONCLUSION**

In light of the ongoing research to understand the fundamental CH<sub>4</sub> and N<sub>2</sub>O generation processes and key chemical and biological parameters of influence, it has become apparent that without sufficient field data from the various treatment processes in use today, methods of emissions quantification contain a significant level of uncertainty. The most current scientific literature continues to report significant variance in findings regarding all manner of influencing factors. When studied singularly, the characteristics and influence of chemical, biological and physical parameters on generation of emissions can be better understood. However, what remains an area of great uncertainty are the complex interactions that occur on a microbial level between each key influencing parameter.

The way forward in gaining a better understanding of the complex interactions between known factors of influence is the formation of comprehensive inventories of plant operational data (flow rates, reactor volumes, solids capture efficiencies, biosolids tonnages and composition, biogas production and composition) as well as analytical field data (COD, TN, Nitrite, Nitrate and DO).

This study has looked into the development of field sampling methods for dissolved methane in anaerobic effluent and biogas released during anaerobic digestion. With improvements made to sampling equipment and further validation, these methods have significant potential for integration into treatment plant operating protocols. With regular sampling and monitoring incorporated into WWTP protocols, the resulting data could be used by researchers to further develop and validate estimation methodologies as well as gain a better understanding of how individual processes and parameters contribute to GHG emissions. The collected data could also assist plant operators in developing effective mitigation strategies based on minimizing energy consumption and GHG emissions as well as recovery and use of biogas.

### **RECOMMENDATIONS**

Based on the findings of the extensive literature review on CH<sub>4</sub> generation in WWTPs, there is a significant knowledge gap in the understanding of dissolved methane formation and transport. For adoption of a dissolved methane parameter into existing methodologies, further

studies would need to identify the effect of parameters such as COD strength, reaction rate, HRT and mechanical aeration on dissolved methane. The goal of research would be to provide new methane correction factors that incorporate dissolved methane for the various treatment processes.

As outlined in the discussion, the two sampling methods require adjustments and improvements. With these made, further studies should be undertaken to validate the methods and explore the development of standard industry sampling and monitoring protocols.

A number of mitigation options were discussed in this study. Further to this, current methodologies should be assessed to identify potential for guidelines to incorporate mitigation options for individual wastewater treatment processes.

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