Greenhouse Gas Emissions from Three Full-Scale Metropolitan Wastewater Reclamation Plants

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This Thesis is dedicated to Ferruccio Bellucci and Costanza Guerrieri, most caring parents, who have always left me the freedom to explore.

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LIST OF ABBREVIATIONS

NH_3-N : ammonia nitrogen

NO_3-N: nitrate nitrogen

NO_2-N: nitrite nitrogen

WWTP(s): wastewater treatment plant(s)

GHG(s): greenhouse gas(es)

GC: gas chromatography

SP: site preference

EF: emission factor

Pe: person

TKN: total Kjeldahl nitrogen

SS: suspended solids

TOC: total organic carbon

COD: chemical oxygen demand

BOD: biological oxygen demand

BOD5: 5-day biological oxygen demand

BNR: biological nitrogen removal

GWP: Global Warming Potential

HCFC: hydrochlorofluorocarbon

IPCC: Intergovernmental Panel on Climate Change

MWRDGC: Metropolitan Water Reclamation District of Greater Chicago

USEPA: United States Environmental Protection Agency

SUMMARY

Domestic and industrial wastewater treatment plants (WWTPs) have been estimated to be the 7th highest contributors to atmospheric concentrations of both nitrous oxide (N_2O) and methane (CH_4), respectively. The total contribution to greenhouse gases (GHGs) from wastewater treatment has been estimated to be 24.4 x 10^{12} g carbon dioxide (CO_2) equivalents during the year 2007. This project identified the sources of N_2O and CH_4 within three conventional activated-sludge plug-flow WWTPs, quantified their annual total fluxes, and compare them to theoretical fluxes modeled following the Intergovernmental Panel on Climate Change (IPCC) guidelines. Additionally, this project characterized these GHG emissions, using carbon and nitrogen isotope measurements, to investigate the possible biological sources of these gases, particularly of N_2O. In fact, whether N_2O is produced by nitrification or denitrification within the aeration basins of single-stage nitrification plants is subject to debate.

Sampling was conducted at the Stickney, North Side, and Egan WWTPs in the Chicago area. Most of the treatment processes were sampled for N_2O and CH_4 analysis. The results show that the aeration basins represent the main source (>85%) of N_2O. Methane is produced by a variety of processes where anaerobic conditions develop, such as primary treatment and anaerobic digestion, possibly including bacterial floc anaerobic micro-sites in the aeration basins. Within the aeration basins, the N_2O is mainly produced when the dissolved oxygen ranges from 0.2 to 2.5 mg/L. A significant contribution to total GHG fluxes from the plants is also constituted by the numerous process-specific

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plant exhausts. The calculated cumulative fluxes from the Stickney WWTP were 5.9 x 10^5 kg N_2O/y (204 g/Pe/y), and 2.8 x 10^6 kg/y of CH_4 (1122 g/Pe/y). The calculated cumulative fluxes for the North Side WWTP were 1.7 x 10^4 kg/y N_2O (12.3 g/Pe/y), and 8.6 x 10^4 kg/y $_{CH4}$ (61.1 g/Pe/y). The calculated cumulative fluxes from the Egan WWTP were 1.6 x 10^4 kg/y N_2O (91.8 g/Pe/y), and 6.0 x 10^4 $_{CH4}$ (353.6 g/Pe/y). About 0.94%, 0.16%, and 0.97% of the incoming total Kjeldahl nitrogen (TKN) is emitted as N_2O at Stickney, North Side, and Egan respectively. Although our data are in good agreement with calculated CH_4 fluxes, our results for N_2O total fluxes are 1.5 orders of magnitude higher than those calculated following the IPCC model.

The study of the site-specific stable nitrogen isotope distribution in N_2O showed a site preference (SP, intramolecular distribution of ^{15}N between the central and later nitrogen in the linear N-N-O molecule) averaging ~0‰. This datum indicates that this GHG is produced mainly by denitrification in the aeration basin designed for nitrification of ammonia. This is probably due to inhibition of a key denitrifier enzyme (nitrous oxide reductase) by increasing levels of dissolved oxygen along the flow-path of the wastewater within the basin. Between 5 and 20% of the nitrate produced by ammonia oxidation is emitted as N_2O. The study of bulk stable nitrogen isotope ratios of nitrate and ammonia showed a trend that can be modeled with ammonia nitrification plus a variable amount (5

SUMMARY (Continued)

to 20%) of nitrate denitrification. This was the first time that site-specific nitrogen isotope analyses of N_2O were applied to determine the source of N_2O in a WWTP in the US. Furthermore, to the best of the author's knowledge, this was the first study that modeled in detail the isotopic mass-balance within the aeration basin of a WWTP.

This study provided some unique information about the sources of N_2O and CH_4 within conventional single-stage nitrification WWTPs: the total fluxes of N_2O and CH_4 to the atmosphere from the three WWTPs investigated, and the mechanism of production of N_2O within the aeration basins, which are the main sources of this GHG within conventional WWTPs.

Some of the most striking conclusions are: (1) the *measured* total N_2O flux from the WWTPs could be consistently 1.5 orders of magnitude higher than the flux predicted by the currently used mathematical method; (2) the N_2O is mainly produced by incomplete denitrification within aerobic processes; (3) the dissolved oxygen level is a key factor in N_2O production and emission control. This information will prove fundamental for designing tanks that minimize the wastewater treatment input of GHGs to the atmosphere.

CHAPTER 1

BACKGROUND INFORMATION

1.1 INTRODUCTION

Domestic and industrial wastewater treatment plants (WWTPs) have been estimated to be the 7th highest contributors to atmospheric concentrations of both nitrous oxide (N_2O) and methane (CH_4), respectively (USEPA 2010). The total contribution to greenhouse gases from wastewater treatment has been estimated to be 24.4 x 10^{12} g carbon dioxide (CO_2) equivalents during the year 2007 (USEPA 2009). Nitrous oxide can be released as a by-product of nitrification and denitrification during biological water treatment. Methane is an expected end product of anaerobic treatment of the excess sludge; however, CH_4 emissions can also occur in anoxic micro-sites within aerobic processes. Additionally, CO_2 is produced in considerable amounts both during biological oxidation of organic matter, endogenous respiration of cells, and during anaerobic digestion of sludge through bacterial fermentation, acetogenesis and methanogenesis (Tchobanoglous et al., 2004). The greenhouse gas (GHG) formed can enter the atmosphere as fugitive emissions from tanks and also be released by the exhaust outlets of different treatment processes throughout the plant. Tank aeration can also enhance GHG emissions through a stripping effect. Only a few studies (Czepiel et al., 1995;

Sümer et al., 1995; Wicht et al., 1995; Kimochi et al., 1998; Sommer et al., 1998; Kampschreur et al., 2008; Ahn et al., 2010; Bellucci et al., 2010) have focused on *in situ* greenhouse gas monitoring from WWTPs, and no extensive studies on total N_2O, CH_4, and CO_2 fluxes from such plants have been published to date. The goal of this study is (1) to identify the sources of N_2O, CH_4, and CO_2 within three conventional activated-sludge plug-flow WWTPs, (2) quantify their annual total fluxes, (3) compare measured to theoretical fluxes modeled following the Intergovernmental Panel on Climate Change (IPCC) guidelines and to fluxes from other well established greenhouse gas sources (fossil fuel combustion, wetlands, farmlands, etc.), (4) investigate the possible biological sources of these GHG emissions, particularly of N_2O, using C and N isotope measurements; (5) implications of the results for design and management of WWTPs as well as the global inventory of greenhouse gases will be explored.

1.2 GREENHOUSE GAS EFFECT OF N_2O, CH_4, AND CO_2

Nitrous oxide, CH_4, and CO_2 are naturally occurring GHG that also have anthropogenic sources (**Table I,** USEPA 2010). The global atmospheric concentration of these gases has increased from the pre-industrial era (ending about the year 1750) to the present day. Nitrous oxide has increased from a value of 270 ppb to 319 ppb (18%); CH_4 has increased from a value of 715 ppb to 1732 ppb (148%); and CO_2 has increased from a

value of 280 ppm to 379 ppm (36%, IPCC, 2007) over this time period. Calculated values of global warming potential (GWP) for N_2O and CH_4 over a 100-year period are 310 and 21 respectively (IPCC, 2006), meaning that the radiative forcing induced by these gases in 100 years is expected to be 310 and 21 times more than the effect produced by an equal mass of CO_2. Residence times are estimated to be 114, 15, and 110 years for N_2O, CH_4, and CO_2 respectively (IPCC, 2007). Nitrous oxide is of particular concern, since its effect is not limited to radiative forcing potential alone, but also to its major role as an ozone-depleting chemical (Ravishankara et al., 2009). Quite inert in the troposphere, above 30 km N_2O undergoes photochemical decomposition, absorbing high-energy photons to produce molecular nitrogen and an excited oxygen atom (O*), according to the reaction:

$$N_2O + hv \rightarrow N_2 + O^*$$

Below 30 km, in the stratosphere, O* reacts with N_2O to produce NO radicals ($NO\cdot$):

$$N_2O + O^* \rightarrow 2NO\cdot$$

$NO\cdot$ acts as a catalyst for the destruction of ozone, and it is regenerated at the end of the cycle:

$$NO\cdot + O_3 \rightarrow \cdot NO_2 + O_2$$

$$\cdot NO_2 + O \rightarrow \cdot NO + O_2$$

Modeling done by Ravishankara et al. (2009) shows that the ozone depleting potential (ODP) of N_2O is comparable to that of many hydrochlorofluorocarbons (HCFCs) that are currently phased out under the Montreal Protocol (Montreal, 1987), while N_2O is still unregulated.

1.3 WASTEWATER TREATMENT PLANTS

Wastewater Treatment Plants are engineered to achieve an effluent water quality in line with the regulations imposed by the Federal Government (Clean Water Act, 1972; Water Quality Act, 1987; USEPA regulations). As such, physical and chemical parameters of the influent, effluent, and each treatment step are closely monitored. This provides a wide database of information on wastewater composition such as: Dissolved Oxygen (DO), Biological Oxygen Demand (BOD), concentration of N-species, total Kjheldal nitrogen (TKN, sum of organic nitrogen + ammonia), temperature, pH, total dissolved solids (TDS), total suspended solids (TSS). Operational unit parameters such as the volume of air supplied for grit chamber and aeration basin operations, and volumetric data on inflow/outflow are also monitored. In this way WWTP are maintained as close as possible to steady-state conditions and, as a consequence, so are the chemical and

TABLE I

RECENT TRENDS IN U.S. GREENHOUSE GAS EMISSIONS (data are in Gg CO_2 eq.)

		YEAR						
		1990	1995	2000	2005	2006	2007	2008
	CO_2	**5090049**	**5417330**	**5965343**	**6089031**	**6001920**	**6102951**	**5905470**
1	Fossil fuel combustion	4718945	5016877	5575723	5728608	5631767	5736487	5552330
2	Non-Energy Use of Fuels	118370	138233	144987	136421	141597	135501	132892
3	Iron and Steel Production &	109760	103116	95062	73190	76100	77370	74517
4	Cement Production	33278	36847	41190	45910	46562	45229	41147
5	Natural Gas Systems	37317	42249	29394	29472	29526	30816	29973
6	Lime Production	11533	13325	14088	14379	15100	14595	14344
7	Incineration of Waste	8049	11461	11270	12616	12684	13289	13128
8	Ammonia Production and Urea	16831	17796	16402	12849	12300	13968	11755
9	Cropland Remaining Cropland	7084	7049	7541	7854	7875	8319	7638
10	Limestone and Dolomite Use	5127	6651	5056	6768	8035	6182	7088
	CH_4	29209	29202	27907	26341	27058	27105	27015
1	Enteric Fermentation	6303	6844	6513	6509	6619	6723	6707
2	Landfills	7111	6860	5747	5980	6050	6023	6016
3	Natural Gas Systems	6169	6313	6223	4935	4907	4738	4591
4	Coal Mining	4003	3193	2881	2710	2776	2765	3206
5	Manure Management	1395	1612	1837	2011	2015	2183	2144
6	Petroleum Systems	1613	1524	1439	1344	1344	1372	1384
7	**Wastewater Treatment**	1120	1183	1199	1158	1166	1162	1158
8	Forest Land Remaining Forest	152	203	681	467	1027	953	568
9	Rice Cultivation	339	363	357	326	282	295	343
10	Stationary Combustion	353	340	315	312	294	309	319
	N_2O	1041	1107	1118	1062	1066	1060	1029
1	Agricultural Soil Management	656	664	678	696	681	681	696
2	Mobile Combustion	142	174	172	119	108	98	84
3	Nitric Acid Production	64	71	70	59	58	69	64
4	Manure Management	47	50	54	54	56	56	55
5	Stationary Combustion	41	43	47	47	47	47	46
6	Forest Land Remaining Forest	9	12	39	27	58	54	33
7	**Wastewater Treatment**	12	13	14	15	15	16	16
8	N_2O from Product Uses	14	15	16	14	14	14	14
9	Adipic Acid Production	49	56	18	17	14	12	7
10	Composting	1	3	4	6	6	6	6

biological transformations that take place in the wastewater throughout the plant. Therefore, we should expect consistent and non-random GHG emissions from the various process steps. However, fluctuations in the chemical composition of the incoming wastewater, such as total organic and inorganic carbon (C) and nitrogen (N) during the day complicate this pattern and should be reflected in changes in GHG emissions.

The WWTPs investigated for this study are the Stickney, North Side, and Egan WWTP (**Figure 1**), operated by the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC). All three plants are plug-flow and employ activated-sludge single-stage nitrification reactors to eliminate ammonia (NH_3) and decrease the chemical oxygen demand (COD), but differ significantly in size, amount of wastewater treated, aeration technology used, incoming total nitrogen, and tank design.

By definition, the activated-sludge treatment process consists of three basic steps: (1) a reactor where the microorganisms responsible for treatment are kept in suspension and aerated; (2) a liquid-solid separation unit, usually constituted by settling tanks; and (3) a recycle system to return the solids removed in (2) back to the reactor (Tchobanoglous et al., 2004). Usually these three fundamental steps are preceded by physical process units that remove settleable and floatable solids, and grit (sand, gravel, cinders, and other heavy solid materials that have subsiding velocities or specific gravities substantially higher than those of the organic putrescible solids in wastewater).

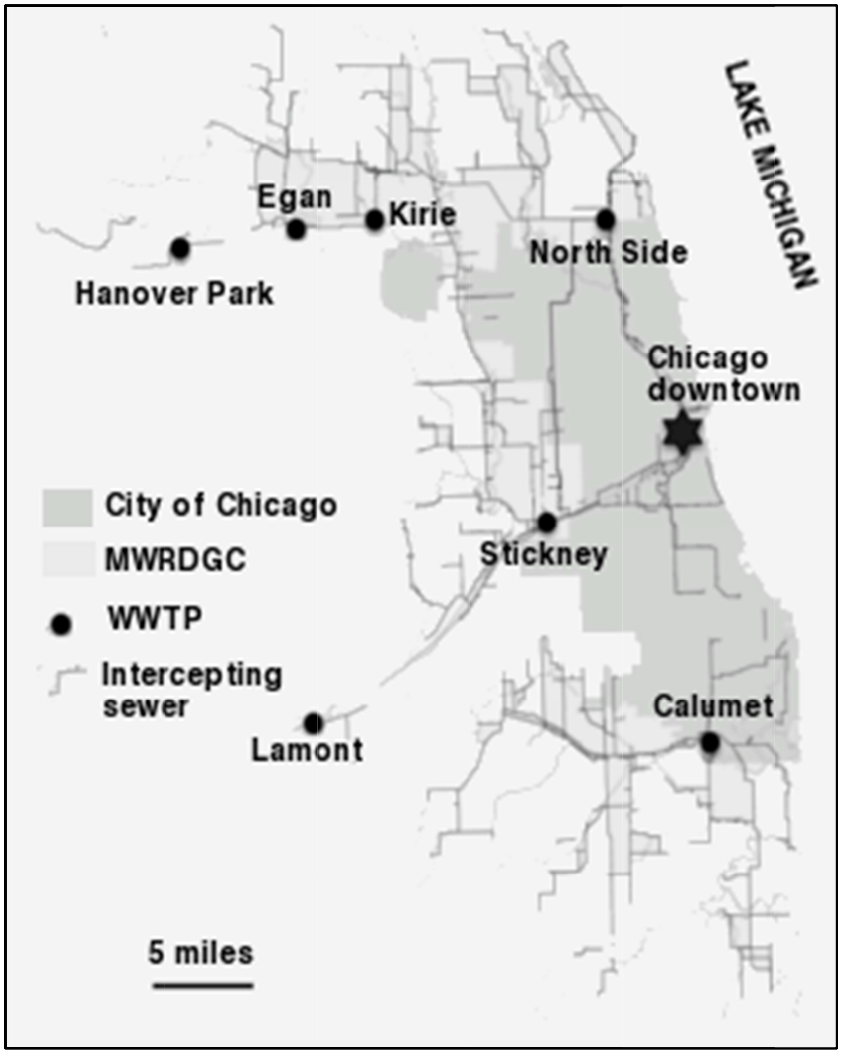

Figure 1. Location of the seven metropolitan WWTP in the Chicago area. The plants: Stickney, North Side, and Egan were investigated in this study.

After step 2, the treated water is returned back to the natural water system (Stickney, North Side), or sent to tertiary treatment (Egan) for chlorination or UV disinfection. Scum from the primary settling tanks and the excess of sludge produced in the aeration basins are pumped to mesophilic (~36 °C) anaerobic digesters, enclosed anaerobic tanks where the biological material is used as substrate for fermentation and methanogenesis. Anaerobic digesters are present at Egan and Stickney, the latter also treating the excess sludge from North Side. An overview of the physical and biological processes involved is reported in **Figure 2** and **Table II**.

The preliminary treatment includes removal of wastewater constituents such as rags, sticks, and floatables, employing coarse and fine screens. The grit is removed in a dedicated tank, the grit chamber. Air is pumped along one side into the rectangular grit chamber, to create a spiral flow pattern perpendicular to the flow through the tank, and to decrease the density of the liquid medium, which promotes particle settling. Particles with higher settling velocities deposit at the bottom of the tank and are mechanically removed and disposed of to landfills. Light, principally organic, particles remain in suspension and pass through the tank. Grit chambers are designed to remove 0.21 mm diameter or larger particles. Once free of grit, the wastewater is directed to settling tanks dedicated tank, the grit chamber. Air is pumped along one side into the rectangular grit chamber, to create a spiral flow pattern perpendicular to the flow through the tank, and to decrease the density of the liquid medium, which promotes particle settling. Particles with higher settling velocities deposit at the bottom of the tank and are mechanically

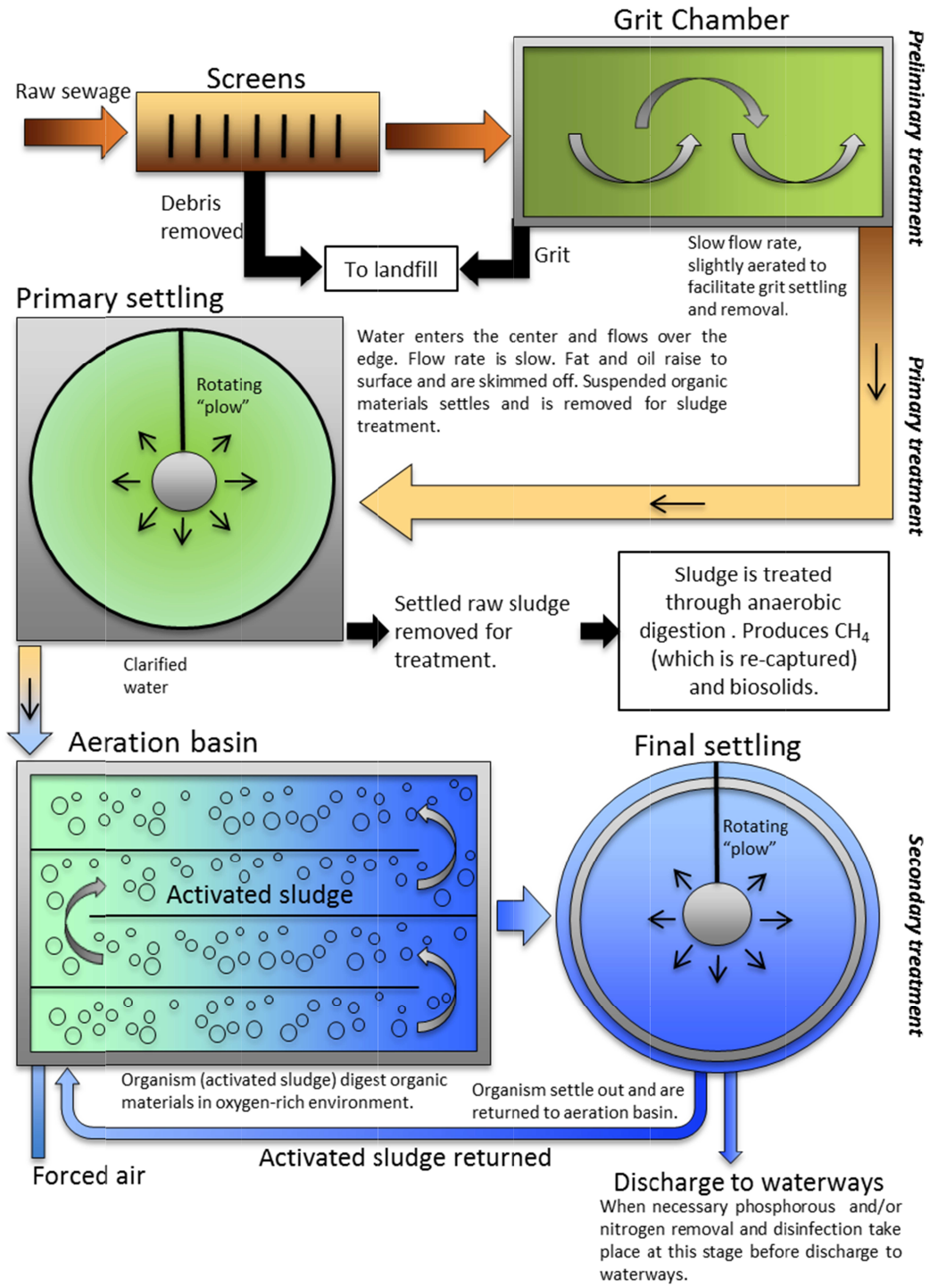

Figure 2. General sketch for an activated sludge WWTP.

TABLE II

SUMMARY OF PHYSICAL AND BIOLOGICAL PROCESSES FOR ACTIVATED-SLUDGE WASTEWATER TREATMENT PLANTS

Treatment level	Type	Description	Operation or process
Preliminary	Physical	Removal of wastewater constituents such as rags, sticks, floatables, grit, and grease that may cause maintenance or operational problems with the treatment operations, processes, and ancillary systems.	Coarse and fine screens, grit chamber
Primary	Physical	Removal of a portion of the suspended solids and organic matter from the wastewater, removal of fine settleable solids	Primary settling tanks with scrapers
Secondary	Biological	Removal of biodegradable organic matter (in solution or suspension) and suspended solids, nitrification/denitrification	Aeration basin
Clarifiers	Physical	Separation of treated water from biological sludge through decantation	Secondary clarifiers
Sludge and scum treatment	Biological	Anaerobic biological removal of excess sludge biomass and residual organic matter	Anaerobic digesters

removed and disposed of to landfills. Light, principally organic, particles remain in suspension and pass through the tank. Grit chambers are designed to remove 0.21 mm diameter or larger particles. Once free of grit, the wastewater is directed to settling tanks for primary treatment. Primary treatment is designed for removal of a portion of the suspended solids and organic matter from the wastewater, and of fine settleable solids.

Primary tanks remove 50-70% of suspended solids and 25-40% of 5-day biological oxygen demand (BOD5) (Tchobanoglous, 2004). Generally, the primary settling tanks are equipped with scraper flights attached to a conveyor belt (rectangular tanks) or a single scraper with circular motion (round tanks). The scrapers skim the surface and the bottom to collect floating material and settled solids respectively, which are transferred to the anaerobic digesters for further treatment. Therefore, the solids are constantly being removed from the tank. An older type of primary tanks, called “Imhoff” tanks, are still in use at the Stickney WWTP; these tanks are not equipped with scrapers and the settling of particles happens solely by gravity. These tanks have to be scraped manually, and accumulate organics at the bottom, where anoxic conditions can develop.

Due to the high BOD5 load (usually 100-500 mg/L; MWRDGC monthly reports, 2009), and the low dissolved oxygen (DO) levels, the wastewater entering the plant is expected to maintain nearly anoxic conditions throughout the preliminary and primary treatment steps. However, the introduction of air in the grit chamber complicates this pattern, as local aerobic micro-sites may develop. The primary settling tanks, characterized by slow water flows, usually develop strictly anaerobic conditions.

After preliminary and primary treatment, the wastewater enters reactors (aeration batteries), where atmospheric air is pumped into the water via submerged diffusers to supply oxygen for an aerobic bacterial mass (activated sludge) that consumes the BOD5 and nitrifies the NH_3 present in the wastewater or produced during BOD5 consumption. At the three plants that are the objects of this study, the aeration basins are constituted by

several tanks, each one subdivided in 3-4 sections (passes). The wastewater from the inlet point flows through the passes in sequential order, therefore the DO content increases along the path from the first to the last pass. The chemistry of the aeration basins is the result of complex interaction between organic (e.g. microbial respiration, synthesis, oxidation of organic matter, nitrification, denitrification) and inorganic (e.g. formation of carbonates, inorganic oxidation) processes.

The microbiology of the mixed liquor (wastewater + microorganisms) in the aeration basin is complex and varies from plant to plant (Curtis and Crane, 1998). However, some groups of bacteria are present in the vast majority of activated-sludge plants. These are typically *alpha*, *beta*, and *gamma Proteobacteria*, *Planctomycetes*, and members of the *Fibrobateres-Chlorobi-Bacteroidetes* ("*FCB*") group (Blackall et al., 1998). The most common genera responsible for ammonia oxidation are *Nitrosomonas* and *Nitrosospira* (Wang et al., 2010; Bae et al., 2011), while denitrifying microorganisms usually belong to the genera *Pseudomonas* and *Paracoccus* (Tchobanoglous, 2004).

Assuming COHNS as representative (but non-stoichiometric) composition of the organic matter in the wastewater, and $C_5H_7NO_2$ as the average composition of bacterial cells (Hoover and Porges, 1952), the following set of reactions can be considered a simplified, non-stoichiometric representation of the main biochemical processes occurring in the aeration basin (Tchobanoglous et al., 2004):

Oxidation of organic matter and synthesis of new cells:

(1.1) $COHNS + O_2 + \text{nutrients} \rightarrow CO_2 + NH_3 + C_5H_7NO_2$ (new cells) + other products

Endogenous respiration of bacterial cells:

(1.2) $C_5H_7NO_2 + 5O_2 \rightarrow 5CO_2 + 2H_2O + NH_3 + \text{energy}$

Nitrification (two-step process, requires both NH_3-oxidizer and nitrifier bacteria):

(1.3) $NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$

(1.4) $2NO_2 + O_2 \rightarrow 2NO_3^-$

Denitrification:

(1.5) $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

where the electron donor can be represented by: COD in the wastewater, COD produced by endogenous decay of bacteria, or an exogenous source.

The anaerobic digesters operate under strictly controlled mesophilic (~36°C) anaerobic conditions allowing microorganisms to use the excess sludge as substrate to produce inorganic matter (mainly sulfates), CH_4 and CO_2 (Parker and Owen, 1986). The

production of CH_4 is so prominent in the digesters, that the majority of the gas is recovered and used as a power source for the boilers located within the treatment facility. The anaerobic digestion process involves three steps: 1) hydrolysis of the particulate material into soluble compounds; 2) fermentation of amino acids, sugars, and fatty acids, to produce acetate, hydrogen, CO_2, and minor amounts of formic acid, methylamine, and carbon monoxide; 3) methanogenesis, where the products of fermentation are used as substrate by strictly anaerobic methanogens to produce CH_4, CO_2, H_2O, and minor amounts of NH_3 (McCarty and Smith, 1986).

The solids obtained after anaerobic digester treatment are rich in nutrients and are centrifuged to remove excess water, and shipped to drying beds where they are periodically overturned to facilitate evaporation of the residual water. Once dry, these bio-solids are made available as class B biosolids for fertilization. Until completely dry, the microorganisms present in the biosolid piles continue degrading the organic material.

The three plants investigated for this study employ similar physical and chemical processes for wastewater treatment; however, marked differences exist between them, (**Table III**). The differences between the plants allow for comparative analysis to determine factors most important in controlling GHG production.

The Stickney WWTP located in Stickney, Illinois is a single stage nitrification sludge plant that has a design average capacity of 1.2 billion gallons per day and serves 2.5 million people. In 2009, the plant treated an average of 761 million gallons of wastewater per day (MGD) with average influent concentrations of 1114 mg/L total

solids, 33 mg/L TKN, and 220 mg/L BOD5. The incoming wastewater is split into two separate process streams (**Figure 3**). The West Side influent process flow is as follows: 1) Screens; 2) Skimming tanks; 3) Grit chambers; 4) Imhoff primary tanks; 5) Aeration batteries; 6) Secondary settling tanks; and 7) Discharge. The West Side Imhoff sludge process train is as follows: (1) Floating cover anaerobic digesters; (2) Post digestion

TABLE III
SUMMARY OF DIFFERENCES BETWEEN THE THREE PLANTS STUDIED

	WW treated (MGD)	People served (M)	Primary tanks	Imhoff tanks	Aeration basins	Secondary clarifiers	Anaerobic digesters	TS (mg/L)	TKN (mg/L)	BOD5 (mg/L)
Stickney	750	2.5	Rectangular with scraper flights on conveyor belt	Yes	Side diffusers	Round with rake	Yes	1114	33	220
North Side	227	1.4	Square with single scraper in circular motion	No	Side diffusers (South) and full bottom diffusers (North)	Round, adapted from square with rake	No (treated at Stickney)	748	19.5	101
Egan	28	0.17	Round with single scraper in circular motion	No	Side diffusers	Round with rake	Yes	906	28	195

MGD = Million gallons per day; M = million; TS = total solids; TKN = total Kjeldahl nitrogen; BOD5 = biological oxygen demand (5 days).

centrifuge; and (3) Biosolid drying beds. The Southwest Side influent process is as follows: (1) Screens; (2) Aerated grit tanks; (3) Primary settling tanks; (4) Aeration batteries; (5) Secondary settling tanks; and (6) Discharge. Effluents from the West Side

Imhoff tanks and Southwest Side primary settling tanks are combined prior to entering the aeration batteries. The Southwest Side preliminary sludge is concentrated in concentration tanks and combined with the waste activated sludge and North Side WWTP sludge. The combined sludge process train is (1) Pre-digestion centrifuge; (2) Anaerobic digesters; (3) Post-digestion centrifuge or facultative lagoons; and (4) Biosolid drying beds. There are eight aerated grit tanks, 16 skimming tanks, 20 primary settling tanks, 96 secondary settling tanks, and 24 anaerobic digesters. There are four aeration batteries (A-D), each having eight tanks with four passes; the aeration tanks employ spiral roll diffuser plate systems. Additionally, there are three Imhoff batteries with 36 tanks in each battery. The North Side WWTP located in Skokie, Illinois is a single stage nitrification plant that has a design average capacity of 333 MGD and serves 1.4 million people. In 2009, the plant treated an average of 245 MGD with average influent concentrations of 748 mg/L total solids, 19.5 mg/L TKN, and 101 mg/L BOD5. The wastewater influent process flow is as follows: (1) Coarse screens; (2) Aerated grit tanks; (3) Fine Screens; (4) Primary settling tanks; (5) Aeration batteries; (6) Secondary settling tanks; and (7) Discharge. The primary and secondary sludge collected during treatment is pumped to the Stickney WWTP for treatment. There are six aerated grit tanks, 16 primary settling tanks, and 64 secondary settling tanks. There are four aeration batteries (A-D) where three aeration batteries (A-C) have 12 tanks and are single pass systems. The final aeration battery (D) has seven tanks, which are double pass systems. All aeration tanks employ spiral roll diffuser plate systems.

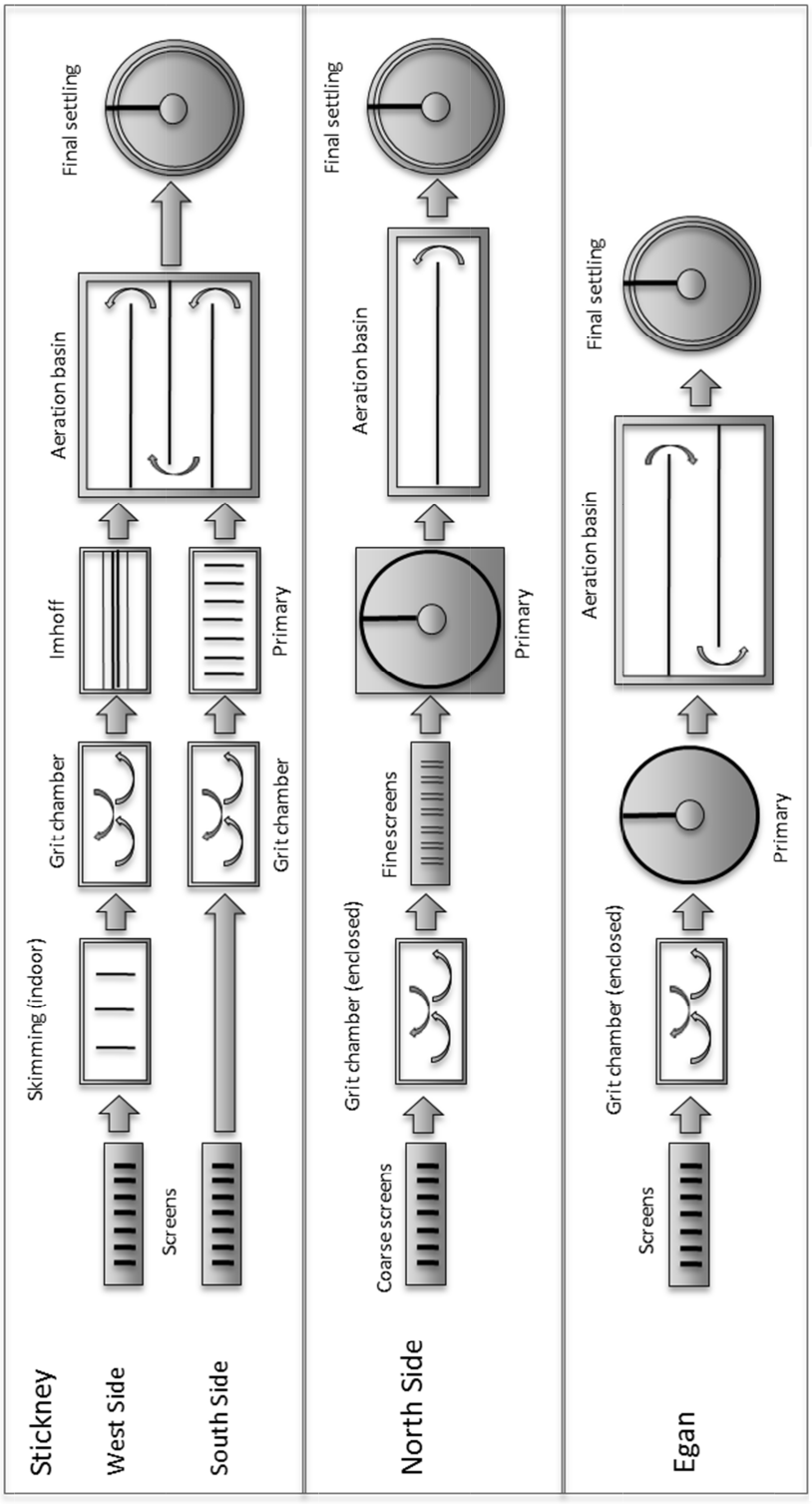

Figure 3. Influent flow for Stickney, North Side, and Egan WWTP.

The Egan WWTP located in Schaumburg, Illinois is a single stage nitrification and tertiary filtration plant that has a design average capacity of 30 MGD and serves 0.17 million people. In 2009, the plant treated an average of 28 MGD with average influent concentrations of 906 mg/L total solids, 28 mg/L TKN, and 195mg/L BOD5. The wastewater influent process flow is as follows: (1) Coarse and fine screens; (2) Aerated grit tanks; (3) Primary settling tanks; (4) Aeration batteries; (5) Secondary settling tanks; (6) Seasonal chlorination in contact tanks; (7) Dual media filter beds; and (8) Discharge. The primary and secondary sludge are combined and treated according to the following solids train: (1) Gravity Belt Thickeners; (2) Fixed cover anaerobic digesters; (3) Post digestion centrifuge; and (4) Drying beds or land application. There are four aerated grit tanks, four primary tanks, and eight secondary settling tanks. There are four aeration batteries where each battery has three tanks with three passes. The North Aeration Battery has full floor diffuser plate coverage, tapered aeration, and a baffle in the first pass for each tank. The South Aeration Battery has spiral roll aeration.

1.4 POTENTIAL SOURCES OF GREENHOUSE GAS

1.4.1 Nitrous oxide

Nitrous oxide can be released as a by-product of incomplete nitrification and denitrification during biological water treatment (Equations 1.3-1.5), which mainly

occurs in the aeration basin. Nitrification is a two-step process where each step is carried out by a specific group of microorganisms. Ammonium-oxidizing bacteria and archaea convert ammonia (NH_3), which at the typical wastewater pH ~7 is present as NH_4^+, to nitrite (NO_2^-), while nitrite-oxidizing bacteria convert NO_2^- to nitrate (NO_3^-). Even though N_2O is not present as an intermediate in the main catabolic path of nitrification, ammonium oxidizing bacteria are known to produce N_2O. This has been predominantly associated with nitrifier denitrification, a well-known metabolic pathway used by ammonium-oxidizing autotrophic bacteria. Denitrifying nitrifiers employ ammonium (NH_4^+) as the electron donor at first to produce NO_2^-, and then use the NO_2^- as electron acceptor effectively employing both nitrification and denitrification metabolic pathways at the same time (Ritchie and Nicholas, 1972; Bock et al., 1995). Nitrous oxide emissions due to chemical reactions of unstable biological intermediates have also been observed (Colliver and Stephenson, 2000).

Nitrous oxide is also an intermediate product of denitrification; therefore incomplete denitrification can lead to N_2O emission. Many denitrifying microorganisms are facultative denitrifiers, capable of using NO_2^- or NO_3^- as alternative oxidants to oxygen. (Robertson et al., 1989). It is generally agreed that anaerobic heterotrophic denitrification is the dominant denitrification pathway in wastewater treatment. However, laboratory-scale experiments by Otte et al. (1996), and Colliver and Stephenson (2000) have shown that both nitrifier denitrification and aerobic denitrification yield more N_2O than heterotrophic denitrification. Non bacterially-mediated reactions between NO_2^- and

hydroxylamine can produce N_2O (Van Cleemput, 1998), but to make this contribution significant, hydroxylamine production by ammonia oxidizing bacteria is required, which complicates the distinction between chemical and biological N_2O production (Kampschreur et al., 2009). Identification of the processes responsible for N_2O emissions from wastewater treatment is essential if these emissions will require mitigation in the near future.

1.4.2 Methane

Methanogens utilize end products of anaerobic fermentation under anaerobic conditions to produce CH_4, CO_2, and H_2O. Methanogens can use a number of substrates for their metabolism. In wastewater treatment, the most common substrates available to them are hydrogen, acetate, formic acid, CO_2, carbon monoxide, and minor amounts of methylamine and methanol (McCarty and Smith, 1986). A representative set of methanogenic reactions using these substrates are (Madigan et al., 1997):

(1.6) $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$

(1.7) $4HCOO^- + 4H^+ \rightarrow CH_4 + 3CO_2 + 2H_2O$

(1.8) $4CO + 2H_2O \rightarrow CH_4 + 3CO_2$

(1.9) $4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$

(1.10) $4(CH_3)_3N + H_2O \rightarrow 9CH4 + 3CO_2 + 6H_2O + 4NH_3$

(1.11) $CH_3COOH \rightarrow CH_4 + CO_2$

Methane is an expected end product of anaerobic treatment of the excess sludge in the anaerobic digesters from where it can leak out, depending on the type of cover on the digesters. However, anaerobic conditions favorable to methanogens may also develop during preliminary and primary wastewater treatment, particularly within Imhoff-type primary tanks, due to the inefficient solid removal that leads to accumulation of organic matter at the bottom. Finally, residual anaerobic pockets might be present as micro-sites in the aeration basins, especially in the section close to the inlet that receives the primary treated water and within the bacterial floc.

1.4.3 Carbon dioxide

Among the GHG emissions produced by wastewater treatment, CO_2 is the most common, both by the number of biological processes through which it is produced, and by total amounts released as off-gas. In aerobic processes, CO_2 is an end-product of oxidation of organic matter, synthesis of new bacterial cells, and endogenous respiration (reactions 1.1-1.2). In anaerobic processes, CO_2 is an end-product of both fermentation and methanogenesis (reactions 1.6-1.11). As such, CO_2 emissions are predominant in both aeration basins and anaerobic digesters, and are expected in minor amounts throughout the treatment plant. In accordance with the IPCC reporting guidelines, special consideration is necessary when reporting carbon dioxide emissions from biomass to ensure that there is no double counting. Carbon dioxide emissions from the aerobic treatment of domestic wastewater are not to be included in inventories as it is assumed

that the biomass is produced in a sustainable manner, and therefore CO_2 is assumed to be carbon-neutral. The CO_2 released by the degraded biomass is replaced by growing biomass, which in turn reabsorbs the same amount of atmospheric carbon as was given during the aerobic wastewater treatment process. This assumption is true only if the biomass is produced without fossil fuel input, which is rarely the case, as fossil fuels are commonly used directly or indirectly to power the machinery employed both in agriculture and in wastewater treatment (Bani Shahabadi et al., 2010). Anthropogenic CO_2 can also be produced by wastewater treatment at petroleum refineries (USEPA 2009). Methane and nitrous oxide emissions must be reported for wastewater treatment as there is no reverse biogenic mechanism by which replacement biomass removes these emissions from the atmosphere (IPCC, 2006).

1.5 PREVIOUS STUDIES

1.5.1 Estimate of GHG emissions from WWTPs based on IPCC Guidelines

Wastewater-derived N_2O and CH_4 emissions have been reported in the yearly USEPA “Inventory of U.S. Greenhouse Gas Emissions and Sinks” published yearly since 1996. To date, the reported data cover the period 1990-2008. The USEPA evaluation of these GHGs is based on the mathematical models developed in the IPCC Guidelines (Doorn and Eklund, 1995; Doorn and Irving, 2006). These models do not involve direct

measurement of N_2O and CH_4 emissions, and have some uncertainties. The model assumes that N_2O sources from WWTPs are limited to denitrification in anoxic zones (USEPA, 2010). Furthermore, the IPCC Guidelines for estimating N_2O emissions assume that N_2O production within the WWTPs can be considered negligible, and that the only significant N_2O source is subsequent denitrification of residual N in the WWTP effluent. According to the IPCC Guidelines, the contribution of the WWTPs to N_2O emissions is calculated as follows (Doorn and Irving, 2006):

(1.12) $$N_2O_{PLANTS} = P \bullet T_{PLANT} \bullet F_{IND-COM} \bullet EF_{PLANT}$$

where:

N_2O_{PLANTS} = total N_2O emissions from plants in the inventory year, kg N_2O/y

P = human population

T_{PLANT} = degree of utilization of modern, centralized WWTPs, %

$F_{IND-COM}$ = fraction of industrial and commercial co-discharged protein; default value = 1.25, based on data in Tchobanoglous et al. (2004)

EF_{PLANT} = emission factor, assumed to be 3.2×10^{-3} kg N_2O/person/year for non-BNR treatment, and 7.0×10^{-3} kg N_2O/person/year for BNR treatment.

The contribution of denitrification of residual nitrogen to N_2O emissions in the effluent can be calculated as follows:

(1.13) $$N_2O_{Emissions} = N_{Effluent} \bullet EF_{Effluent} \bullet \frac{44}{28}$$

where:

N_2O *Emissions* = N_2O emissions in inventory year, kg N_2O/y

N *Effluent* = nitrogen in the effluent discharged to aquatic environments, kg N/y

EF *Effluent* = emission factor for N_2O emissions from discharged to wastewater, kg N_2O-N/kg N

The factor 44/28 is the conversion of kg N_2O-N into kg N_2O.

Based on limited field data, the default IPCC emission factor (EF) for N_2O emissions from domestic wastewater nitrogen effluent ranges from 0.005 to 0.25 kg N_2O-N/kg N, 0.005 being the standard value used when no other information is available, and therefore representing a conservative estimate.

CH_4 emissions from *domestic* wastewater are calculated as follows:

(1.14) $$CH_{4Emissions} = \left[\sum_{i,j}\left(U_i \bullet T_{i,j} \bullet EF_j\right)\right] \bullet (TOW - S) - R$$

where:

CH_4 Emissions = CH_4 emissions in inventory year, kg CH_4/y

TOW = total organics in wastewater in inventory year, kg BOD/y

S = organic component removed as sludge in inventory year, kg BOD/y

U_i = fraction of population in income group i in inventory year

$T_{i,j}$ = degree of utilization 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

EF_i = emission factor, kg CH_4/kg BOD

R = amount of CH_4 recovered in inventory year, kg CH_4/y

EF values are country-specific, and require a correction factor depending on type of wastewater treatment. The CH_4 emission factor for the j^{th} domestic wastewater treatment/discharge pathway or system is calculated as follows:

(1.15) $$EF_j = B_0 \bullet MCF_j$$

where:

EF_j = emission factor, kg CH_4/kg BOD

j = each treatment/discharge pathway or system

B_0 = maximum CH_4 producing capacity, kg CH_4/kg BOD

MCF_j = methane correction factor (fraction); suggested MCF values are reported

by Doorn and Irving, 2006.

Country-specific data for B_0 should be used where available. If country-specific data are not available, default values of 0.6 kg CH_4/kg BOD5 removed or 0.25 CH_4/kg COD removed can be used (Doorn and Irving, 2006). CH_4 emissions from *industrial* wastewater are calculated as follows:

(1.16) $$CH_{4Emissions} = \sum_i \left[(TOW_i - S_i) \right] \bullet EF_i - R_i$$

where:

CH_4 *Emissions* = CH_4 emissions in inventory year, kg CH_4/y

TOW*i* = total organically degradable material in wastewater from industry *i* in inventory year, kg COD/y

i = industrial sector

S_i = organic component removed as sludge in inventory year, kg COD/y

EF_i = emission factor for industry *i*, kg CH_4/kg COD for treatment/discharge pathway or system(s) used in inventory year. If more than one treatment practice is used in an industry this factor would need to be a weighted average.

R_i = amount of CH_4 recovered in inventory year, kg CH_4/y.

An EF value of 0.25 CH_4/kg COD removed is used if measured EF values are not available. Therefore, the EF constitutes the biggest source of error in this model, as a direct measurement is often impractical and would require a detailed study of each specific treatment facility and wastewater pathway. The model is therefore a tool to quantify total GHG fugitive emission fluxes, but does not provide any information regarding the specific processes that cause the emissions. However, the IPCC model can be quickly applied to each specific wastewater treatment facility to estimate the magnitude of expected GHG emissions. For example, the IPCC model applied to Stickney yields values ranging from $7.4x10^3$ to $9.3x10^3$ kg/y for N_2O, and from $5.6x10^6$ to $14.6x10^6$ kg/y for CH_4 emissions respectively, depending on which EF values are chosen. Additionally, Bani Shahabadi et al. (2010) proposed a mathematical model that takes into account the various steps of the wastewater treatment, and also considers the off-site emissions due to factors such as power production to run the facility, and transportation of materials to and from the treatment plant.

1.5.2 Compound-specific GHG emissions from WWTPs

Early full-scale and lab-scale studies on WWTP emissions generally focused on quantification, modeling, and control of hazardous volatile organic compounds (VOCs) and odors, rather than GHG (DeHollander, 1997, and references therein). With the recognition of WWTPs as significant sources of GHGs (Sahely et al., 2006), several models and field studies have been developed to quantify these emissions and their

specific sources. Due to its high GWP (310; IPCC 2007) and ODP (0.017; Ravishankara et al. 2009), N_2O has been the main focus of most direct studies. Literature reviews report high variability in the fraction of nitrogen emitted as N_2O from wastewater treatment, with values ranging from 0 to 4% for full-scale studies and from 0 to 95% for lab-scale studies (Kampschreur, 2009, and references therein). It is agreed, however, that biological nitrogen removal is a significant contributor to atmospheric N_2O, and that N_2O production mainly occurs during aerobic nitrogen removal. A single study reported the N_2O emissions from different types of WWT bioreactors in 12 U.S. facilities (**Table IV**, Ahn et al., 2010), finding diurnal variability in the N_2O production, and a good correlation between the variations of TKN, NO_2^- and N_2O emissions throughout the day. Their calculated emission factors show a wide range, from 0.28 to 140 g N_2O/person/year (g/Pe/y). No studies were found where N_2O or CH_4 emissions from each step of the wastewater treatment were reported.

1.5.3 Stable isotope studies and bacterial N fractionation

The majority of the isotopic studies that can be related to wastewater treatment concern N_2O. The main focus of these studies was to distinguish the production mechanism of N_2O, particularly nitrification/denitrification. Isotope studies on the biological N-cycle report wide variations in the degree of N isotopic fractionation both during nitrification and denitrification (Heaton, 1986). For the overall nitrification process:

TABLE IV

SUMMARY OF N_2O INVENTORY MEASURED AT SEVERAL FULL-SCALE WWTPS

WWTP configuration	Water T (℃)	Emission fraction (% of TKN)
Separate stage nitrification	14.7	0.05
Four-stage Bardenpho	13.6	0.18
Step-feed BNR	29.4	3.2
Step-feed	17.4	0.26
Plug-flow 1	11.4	0.6
Plug flow 2	11	0.1

(1.17) $\text{Organic-N} \rightarrow NH_4^+ \rightarrow NH_3OH \rightarrow NO_2^- \rightarrow NO_3$

it has been observed that, while the conversion of organic-N to NH_4^+ involves very little fractionation (about 0 ‰), the following steps, yield large kinetic fractionations, between -38 and -5‰ (*Nitrosomonas* and *Nitrosospira,* Casciotti et al., 2003; unidentified soil denitrifiers, Mariotti et al., 1980). Similar values have been reported for denitrification processes:

(1.18) $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

for which fractionations of -35‰ (unidentified groundwater denitrifiers, Vogel et al. 1981), -40 to -30‰ (unidentified oceanic denitrifiers; Cline and Kaplan, 1975), and of -33 to -10‰ (laboratory experiment; Mariotti et al., 1982) have been reported. Similar values were also reported by numerous studies on denitrifiers from the genera *Pseudomonas* and *Paracoccus* (Yoshida, 1984; Toyoda et al., 2005; Sutka et al., 2006; Ostrom et al., 2007). In general, both nitrification and denitrification processes yield a ^{15}N-depleted metabolic product and a substrate that is passively enriched in ^{15}N. Mariotti et al. (1982) demonstrated that the rate of fractionation during denitrification increases as the rate of reduction decreases. For extensive denitrification in wet tropical forest soils, Perez et al. (2000) found that isotopically heavy N_2O can form as residual N_2O, and that the N_2O isotopic signature was regulated both by the isotopic composition of the substrate and by the N_2O emission rate. Due to its high variability, the sole use of bulk $\delta^{15}N$ to constrain the metabolic pathway responsible for N_2O production can be inconclusive in some cases (Koba et al., 2009).

In recent years, however, Sutka et al. (2006) have demonstrated that quantification of the relative abundances of ^{15}N in the central (α) and terminal (β) N atoms in the N_2O molecule ("site preference" or "isotopomer ratio") can be used to isotopically distinguish nitrification by denitrification. Isotopic studies on N_2O production by the denitrifiers have shown that the isotopomer ratios (site-specific intermolecular N isotope ratio analysis) of

N_2O reflect production and consumption of this GHG gas. This parameter is named "Site Preference" (SP), and is defined as:

(1.19) $$SP = \delta^{15}N_{\alpha} - \delta^{15}N_{\beta}$$

where α and β indicate the central and end N atom in the linear N-N-O molecule respectively. The SP has been shown to yield information that is independent of conventional (bulk) isotopic ratio. For example, Toyoda et al (2005) found that during denitrification experiments in lab reactors using *Paracoccus dentrificans* and *Pseudomonas fluorescens*, the SP is almost constant while the bulk $\delta^{15}N$ varied by 10-20‰. Sutka et al. (2006) found a distinctive N_2O SP value of 33‰ for nitrification by ammonia oxidizing and nitrifying microorganisms (*Nitrosomonas europaea, Nitrosospira multiformis*) and of 0‰ for denitrification by both denitrifiers (*Pseudomonas chlororaphis and Pseudomonas aureofaciens*) and nitrifying denitrifiers (*Nitrospira multiformis*). A study on the biological nitrogen removal (BNR) reactor of an advanced metropolitan WWTP in Tokyo showed that isotopomeric data can be used to quantify the relative contributions of nitrification and denitrification to N_2O production (Toyoda et al., 2011). The BNR operation at this plant includes anaerobic, anoxic and oxic steps; on the basis of bulk N and isotopomeric N compositions, the authors conclude that (1) N_2O is mainly produced by denitrification and partly reduced in the anoxic tank; (2) hydroxylamine oxidation and NO_2^- reduction contribute nearly equally to the N_2O

production in the entrance of the oxic tank; and (3) NO_3^- reduction (nitrifier-denitrification) is the main pathway of N_2O production from the middle to the end of the oxic tank, and (4) hydroxylamine oxidation slightly dominates over NO_2^- reduction in the secondary settling tank and N_2O is partly reduced. For these distinctive results, isotopomer analysis of N_2O is rapidly becoming a popular technique to determine the biological processes responsible for N_2O production (Toyoda et al., 2005; Wesley et al., 2006; Jinuntuya-Nortman et al., 2008; Toyoda et al., 2011).

1.6 TIMELINE AND OBJECTIVES OF THIS STUDY

This study is constituted by a three-year project that had three main objectives: (1) Identify the main sources of N_2O and CH_4 emissions from the Chicago metropolitan WWTPs of Stickney, North Side, and Egan managed by the MWRDGC; (2) determine measured full-scale total fluxes for N_2O and CH_4 and their emission factors; and (3) identify the biological reactions responsible for N_2O production.

The project was subdivided in three stages. Stage 1 (September-November 2008) was constituted by a pilot study on the Stickney WWTP to evaluate the rate of emissions of N_2O and CH_4 from various steps of the wastewater treatment process. The primary objectives of this reconnaissance study were to determine the magnitude of GHG emissions from different treatment steps, and to identify which sources carried the

highest environmental impact. A secondary objective was to test a variety of sampling and analytical methods. This initial approach included the collection and analysis of 55 samples.

Stage 2 (June-December 2009) was an extensive survey to determine the total fluxes of N_2O and CH_4 from the different treatment processes and plant exhausts from the WWTPs of Stickney, North Side, and Egan. All three plants employ single-stage nitrification reactors but differ significantly in size, amount of wastewater treated, aeration technology used, incoming Total Kjeldahl Nitrogen (TKN), and tank design. Therefore, the comparison of these WWTPs and effluents provided a thorough characterization of potential greenhouse gas emission and per capita variations. The results were compared to the N_2O and CH_4 emissions obtained following the IPCC protocol for the calculation of GHG emissions from WWTPs.

Stage 3 (June-November 2010) consisted in a detailed study on N_2O, CH_4, and CO_2 emissions from aeration battery B at the Stickney WWTP. The main objective at this stage was to understand which biological pathway/s is responsible for N_2O production within the aeration basins. We used concentrations, and bulk and site-specific nitrogen stable isotope data on $N_2O(g)$ and aqueous N species (ammonia nitrogen, NH_3-N and nitrate nitrogen, NO_3-N) to determine: (1) distribution of the aqueous N species along the flow path of the wastewater in a single aeration basin tank; (2) stable isotope trends in the aqueous N species along the wastewater flow path that could be related to nitrification and/or denitrification processes; (3) production mechanism of N_2O based on the site

preference (SP) data; (4) a N isotope mass balance for a single tank of the aeration basin. An additional objective was to isotopically characterize the CH_4 and CO_2 emissions from the aeration basin, the anaerobic digesters, and the Imhoff tanks.

CHAPTER 2

METHOD DEVELOPMENT AND ADOPTED EXPERIMENTAL METHODOLOGY

2.1 SAMPLING AND STORAGE METHOD TESTS

Four methods were tested for collection and storage of fugitive emissions, ambient air, or exhaust gas samples from unit processes; these methods are described in the following section.

Method 1: 60 mL plastic syringe with gas-tight valve and pre-evacuated vial system. A 60 mL plastic syringe was used for sample collection; the syringe needle was inserted into the desired source. The syringe plunger was drawn and released three times with the gas sample to flush the syringe volume. A final 50 mL gas sample was then collected; 10 mL were flushed out before inserting the syringe needle into a pre-evacuated ($P < 10$ μTorr) 20 mL evacuated glass vial with an Exetainer™ gas-tight rubber septum top. About 25-35 mL of the gas sample was pushed into the vial to ensure a positive pressure (2-10 psi) to prevent contamination by atmospheric air in case of leakage.

Method 2: 150-500 mL pre-evacuated glass bulbs with stopcock inlet. The glass bulbs were pre-evacuated ($P < 10$ μTorr). Upon sampling, the bulb inlet was positioned at the

desired source, and the stopcock was slowly opened. A gas sample was drawn inside the bulb, and the stopcock was closed to preserve the sample.

Method 3: 60 mL plastic syringe with gas-tight valve. Same procedure as per Method 1, but the sample was preserved inside the syringe instead of being transferred to a pre-evacuated vial. The needle was removed after collection, with the valve closed to isolate the sample; two models of valves were tested.

Method 4: AC'SCENT vacuum chamber with gas-tight 1L polyvinyl-fluoride (TEDLAR™) bags. The sample was withdrawn from the desired source using flexible plastic tubing connected to the vacuum chamber sampling input valve. A pre-evacuated 1 L sampling bag was placed inside the vacuum chamber. During equilibration, each sample bag in the vacuum chamber was conditioned allowing air to inflate/deflate the bag. After the equilibration time the sampling line was flushed for 3-10 second with the sample gas before a sample was collected in the bag. Sampling time was 0.5-2 minutes. The vacuum chamber was evacuated using a built-in air pump, causing the sample bag inside to inflate, while about 500 mL of sample was passively drawn into and collected inside the bag. The bag valve was closed and the bag stored until analysis.

These four methods were tested using a standard gas mix containing 100 ppmv of N_2O and 1000 ppmv of CH_4. Samples were collected in triplicate for each method, and each sample was analyzed by gas chromatography (GC) as described in section (2.3). Analytical results are reported in **Table V** and in **Figures 4-5**. Methods 1 and 2 presented the lowest standard deviations and were the most accurate among the four methods

considered, while the syringe storage proved to be the least accurate method, possibly due to leaky stopcocks and/or valves. Additionally, Methods 1 and 2 were faster (< 1 minute per sample) than Method 4 (10-15 minutes per sample). To further test the shelf life of gas samples stored in the Exetainer™ glass vials, four samples were prepared using a gas mix of about 100 ppmv N_2O and 650 ppmv of CH_4. These four samples were analyzed by GC at 0.5, 44.5, 71.0, and 240.0 hours after sample preparation (**Figure 6)**. No significant variation were observed between the four runs, showing that the samples still maintained their N_2O and CH_4 initial concentrations after 10 days shelf time. Methods 1 and 2 were used, sometimes interchangeably, as methods of choice during the 2009-2010 extensive sampling campaigns at the Stickney, North Side, and Egan WWTPs. Method 1 was the main sampling method. All sample vials were let equilibrate at laboratory temperature (20°C) overnight before GC analysis, and all analyses were completed within 3 days from collection, to ensure that sample characteristics did not change due to a longer shelf time.

2.2 FIELD METHODS

2.2.1 Off-gas emissions capture

All gas samples, from all sources, were collected at least in duplicate for GC analysis; when other types of analyses were required, an appropriate number of additional

TABLE V

ANALYTICAL RESULTS FOR A 100 PPMV N_2O AND 1000 PPMV CH_4 STANDARD GAS MIXTURE USING FIVE DIFFERENT COLLECTION DEVICES.

Method	N_2O (ppmv)	CH_4 (ppmv)	Average N_2O (ppmv)	Stdev	Average CH_4 (ppmv)	Stdev
Vial 1	99	989				
Vial 2	104	1023	99.7	4.0	1003	17.6
Vial 3	96	998				
Bulb 1	95	964				
Bulb 2	91	1012	96.3	6.1	989	24.1
Bulb 3	103	991				
Syr 1 (white)	79	936				
Syr 2 (white)	93	981	91.7	12.1	980	43.5
Syr 3 (white)	103	1023				
Syr 1 (blue)	105	1041				
Syr 2 (blue)	95	977	96.0	8.5	988	48.9
Syr 3 (blue)	88	945				
Bag 1	94	1023				
Bag 2	87	976	91.7	4.0	992	26.9
Bag 3	94	977				

Stdev = standard deviation; Syr = syringe (blue/white = color-coded valves).

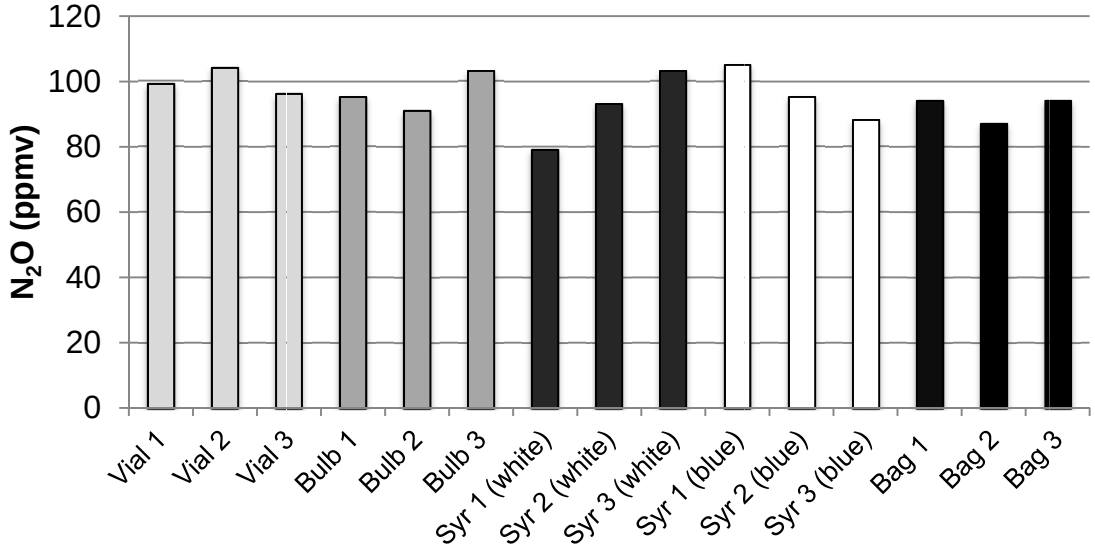

Figure 4. N_2O concentrations from different gas collection devices containing a standard gas mixture (see Table V).

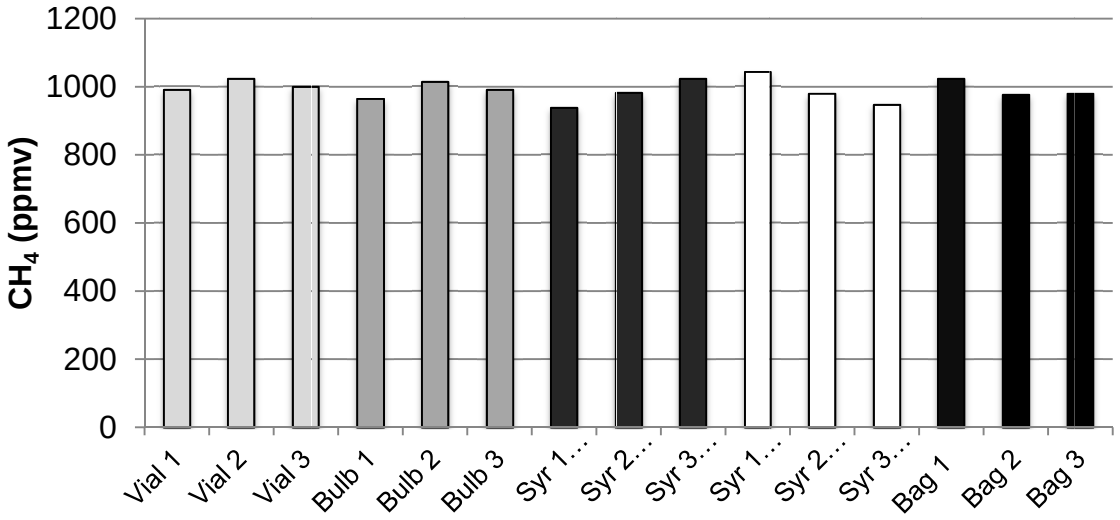

Figure 5. CH_4 concentrations from different gas collection devices containing a standard gas mixture (see Table V).

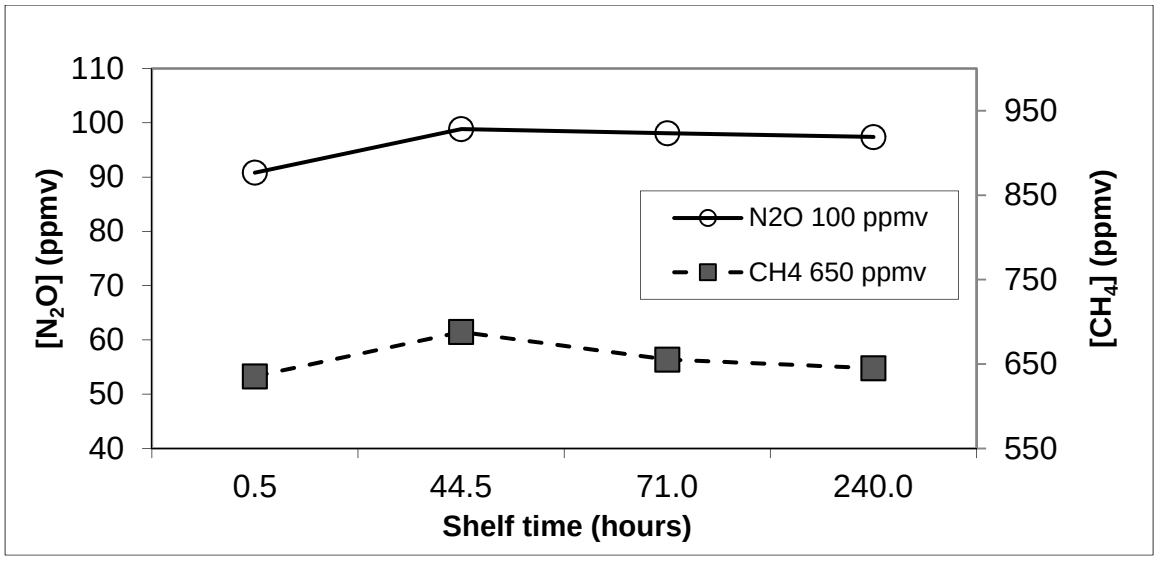

Figure 6. Concentration of N_2O and CH_4 in glass vials containing a standard gas mixture (100 ppmv N_2O, 1000 ppmv CH_4) vs. shelf time.

samples were also collected. Plant intakes and exhausts were sampled through Method 1 or 2, withdrawing the sample directly from the source. The cross-sectional area of the exhaust was recorded and the exhaust velocity measured using a TSI Velocicheck™ air velocity meter. Temperatures were recorded at all sampling locations using a thermocouple thermometer with an accuracy of ± 0.1 °C.

Off-gas emissions from liquid surfaces and biosolid drying beds were captured using floating off-gas hoods of different surface area (0.13 and 3.0 m^2) and volume (0.025 and 0.84 m^3), depending on the process. The 0.13 m^2 area/ 0.025 m^3 volume hoods (*Type 1*) were stainless steel AC'SCENT™ flux hood chambers manufactured by Saint Croix Sensory Inc., equipped with a tire inner tube to ensure flotation (**Figure 7**). When

not used for active surfaces (aerated basin and aerated grit chamber) gas sample collection, this hood was also equipped with a 12V 4” diameter fan to ensure proper gas mixing within. Samples were collected per Method 1 through a gas tight port equipped with a pierceable rubber septum or through a flexible rubber tube. The 3.0 m^2 area/0.84 m^3 volume floating hoods (*Type 2*) were used exclusively for aeration basin and grit chamber sampling at Stickney. They were custom built and equipped with a fitted elbow joint and a 5 cm ID flexible plastic hose to ensure proper gas flow and minimal pressure build-up (**Figure 8**). Gas samples were collected using Method 1 through a needle-size hole located approximately 3 m from the hose outlet.

To collect the off gas from the ~15 cm wide annular space between the floating cover and wall of the anaerobic digesters at Stickney, a special chimney device was constructed. The sampling device (chimney) was made by attaching the end of a 15 cm diameter plastic funnel to a 50 cm polyvinyl chloride pipe. At the top of the pipe is a T-intersection equipped with a brass fitting sealed by a pierceable septum to allow sampling using a syringe. To sample, the bell end of the funnel was placed about 1” below the sludge surface channeling the off gas up through the apparatus, allowing Method 1 to be employed. A flexible Tygon™ tube coming out of the sampling apparatus was connected to the T-intersection of a 10 mL glass flow meter that allows for flux measurement (**Figure 9**). The funnels were allowed to equilibrate for 30-60 minutes, depending on the flux, so about 3 bed volumes of fugitive gases were flushed through the funnels before a sample was collected. The travel time of the gas through the flow meter from the 0 mL to

10 mL gradation was recorded. Three funnels were used at each digester, at different locations, and for each funnel 15 flux measurements were taken, therefore a total of 45 flux measurements were averaged for each digester in order to estimate an average flux (m^3/yr). Flux calculations are described below in section 2.4.

2.2.2 Sample collection for isotopic analysis

Samples for NH_4^+ isotope analysis were filtered through a 0.45 μm filter, and the filtrates were collected in 1 L polyethylene bottles with Polyseal caps. Each sample was preserved by adding 2 mL concentrated H_2SO_4 to achieve a pH value < 2 and stored at 4°C until analysis. Samples for NO_2^-/NO_3^- isotope analysis were filtered through 0.45 μm filters, and stored in 125 mL polyethylene bottles. Samples were preserved by adding one reagent-grade "pellet" of NaOH to achieve a pH value of 10-11, and stored at 4°C until analysis. Gas samples for CH_4 isotope and N_2O isotope and isotopomer analysis were collected by attaching 500 mL pre-evacuated glass bulbs to the hose and withdrawing sample gas until the bulb was full (Method 2). The bulbs were also stored at 4°C before analysis. Samples for suspended solids isotope analysis were collected on the 0.45 μm silica-glass fiber filters. The filters were freeze-dried in laboratory and preserved at -4°C until analysis. Samples for CO_2 isotope analysis were collected per Method 1 and analyzed the following day after equilibration at laboratory temperature overnight.

Figure 7. Type I flux hood used for a variety of liquid surfaces and biosolid drying beds sampling.

Figure 8. Type II flux hoods used for sampling at the aeration basins and grit chamber at Stickney. The chamber in the picture is approximately 2m x 1.5m in size.

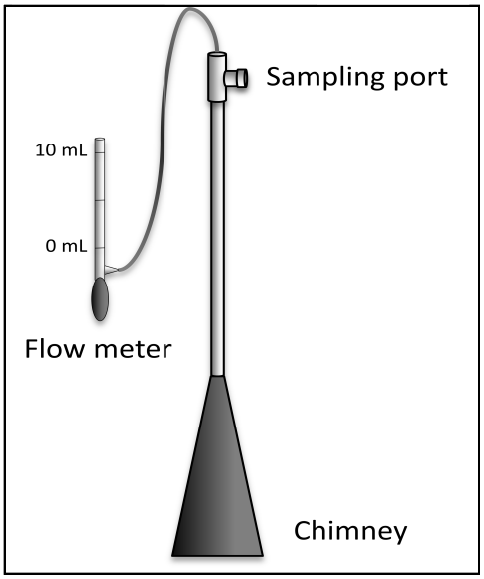

Figure 9. Sketch of the custom-built chimney device used for off-gas sampling of the floating-cover anaerobic digesters.

2.2.3 Sample collection for water quality analysis

During certain sampling events in the aeration basins and grit chamber at Stickney, associated mixed liquor samples (2 gallons) were collected for NH_3, NO_2^-, NO_3^-, total organic carbon (TOC), TKN, BOD, chemical oxygen demand (COD), and TSS analyses. The raw samples were collected using a plastic 500 mL scoop and transferred to two 1-gallon plastic containers. All samples were immediately stored at -4°C until analysis, and analysis completed within three days from collection at the Stickney Water Reclamation Plant Analytical Laboratory Division using standard procedures described by Eaton et al. (2005). Temperature, pH, and DO content were also measured in situ using dedicated probes.

2.3 LABORATORY METHODS –GAS CHROMATOGRAPHY ANALYSIS

All gas samples were transported to the UIC Environmental Isotope Geochemistry Laboratory for GC analysis of CH_4, N_2O, and CO_2. Samples were allowed to equilibrate at room temperature and were analyzed within three days from collection. All samples were analyzed by gas chromatography using mainly a SRI Instruments Greenhouse-Gas Gas Chromatograph, or alternatively a Hewlett Packard (HP) 5890 gas chromatograph operating in split mode. The HP chromatograph analyzed N_2O using a Restek QPlot capillary column coupled with an electron capture detector (ECD) and CH_4 using a

Restek Molecular Sieve capillary column coupled with a flame ionization detector (FID). The SRI gas chromatograph was used to simultaneously analyze N_2O, CH_4, and CO_2 using two Haysep-D columns coupled with an ECD (for N_2O detection) and a FID-Methanizer (for CH_4 and CO_2 detection) and no make-up was used (**Figure 10**). The make-up gas in similar GC instruments is usually N_2 or He, and it is used to increase the total flow through the ECD detector to improve the stability of the signal. However, in the SRI apparatus this would also lead to an increased total gas flow through the FID-Methanizer, which in turns introduces instability in the signal from this second detector. The SRI GC inlet and outlet were modified (**Figure 11**) to allow for rapid evacuation of the sampling loop, for equalization of the sample pressure to atmospheric pressure, and for rapid injection of standards; this achieved a run time of 7 minutes/sample for the determination of all three compounds of interest. However, in the initial stages of the study, an inlet GC system that allowed for sample pressure equalization was not available. Therefore, the effect of sample pressure on the ECD and FID-Methanizer signals was tested to determine the appropriate correction for the data to account for different pressures of injection. Six samples were prepared as per Method 1 using a standard gas mix containing 100 ppmv N_2O, 1000 ppmv CH_4, and 1000 ppmv CO_2. Different amounts of gas were injected into the glass vials to obtain a range of different sample pressures upon injection (0.74 – 1.56 atm); samples were then analyzed using the SRI GC. The results (**Table VI** and **Figure 12**) show that the intensity of the GC peak is strongly dependent on the pressure of injection. Pressures < 1 atm strongly affect

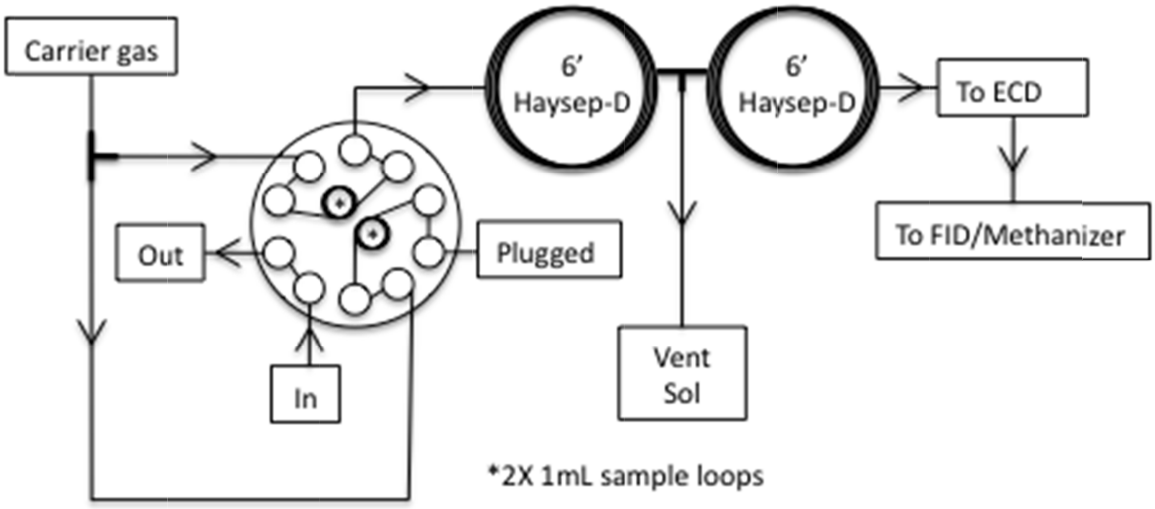

Figure 10. Schematics of the SRI GC gas flow during sample analysis.

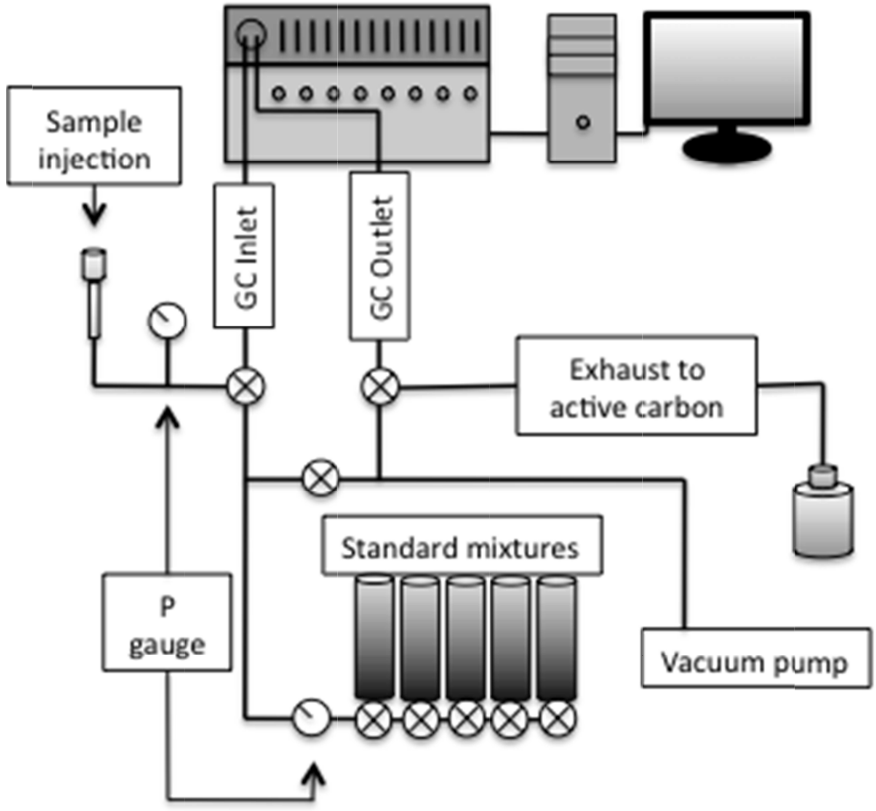

Figure 11. Schematics of the custom-built injection system for the SRI GC.

the ECD signal, while P > 1 atm strongly affect the FID-Methanizer signal. However, there is good linear correlation between pressure of injection and signal on the detectors ($0.87 < R^2 < 0.97$). When the samples were injected at different pressures (2008 sampling campaign only), a linear correction was therefore applied to the data to normalize them to atmospheric pressure. The majority of the samples had injection pressures ranging from 0.9 to 1.2 atm. Sample pressures from the 2009 and 2010 sampling campaigns were reduced to atmospheric pressure before injection, and no correction was needed. Standards mixes of CH_4 and CO_2 were analyzed every 3 to 8 samples to ensure proper calibration of the instruments throughout the analyses. The absence of make-up gas made the calibration of the ECD challenging, as the calibration curve was not linear, particularly at high concentration; for that reason N_2O standards (having similar concentrations to the samples) were run every 3-4 samples. A list of the standards used for calibration is reported in **Table VII**. Lower detection limits on both machines for CH_4, N_2O, and CO_2 were 0.4 ppmv, 0.3 ppmv, and 100 ppmv, respectively; any analytical result below the respective detection limit was considered to be zero for the purpose of calculating total fluxes. All gas concentrations were corrected for temperature and ambient air concentrations (when appropriate) at the time of sampling. The air concentrations were assumed to be 0.35, 1.70, and 379 ppmv for N_2O, CH_4, and CO_2 respectively (IPCC, 2007).

TABLE VI

RESULTS FOR PRESSURE OF INJECTION TEST.

P of injection (atm)	CH_4 (ppmv)	CO_2 (ppmv)	N_2O (ppmv)	CH_4 % change	CO_2 % change	N_2O% change
0.74	612.0	609	50.8	39	39	50
0.97	953.6	850	69.0	5	15	32
1.00	999.3	1001	101.8	1	1	2
1.05	1217.3	1003	101.0	121	100	101
1.44	1519.8	1272	118.3	152	127	116
1.56	1854.3	1455	162.0	185	145	159

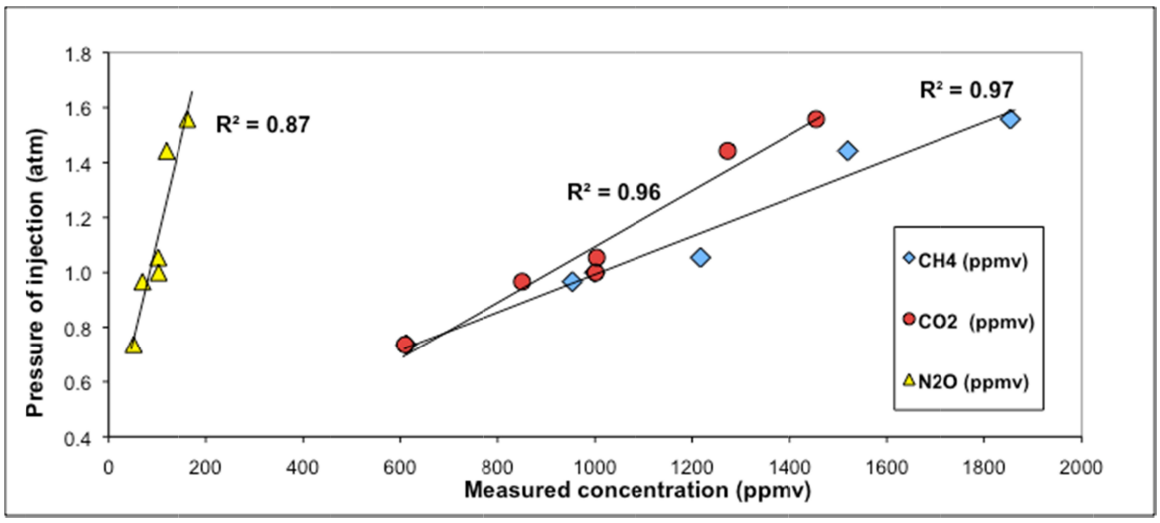

Figure 12. Dependency of ECD (N_2O) and FID-Methanizer (CH_4, CO_2) signal on pressure of injection. R^2 values for the linear regressions of the data are shown

TABLE VII

STANDARDS USED FOR GC CALIBRATION

Standard type	Gas	Concentration (ppmv)
Mix	N_2O	100
	CH_4	1000
	CO_2	1000
Mix	N_2O	300
	CH_4	1000
	CO_2	10000
Single	N_2O	0.3
Single	N_2O	10
Single	CH_4	100
Single	CO_2	1000

2.4 FLUX CALCULATIONS

2.4.1 Active surfaces (aeration basins and grit chamber) and exhaust points

Once an average concentration for the GHG of interest was obtained, the GHG flux (F_{GHG}) was estimated in kilograms/year (kg/y) from exhaust systems as follows:

(2.1)
$$F_{GHG} = Q \cdot \frac{\lfloor GHG_{(g)} \rfloor}{1x10^6} \cdot \frac{P}{RT} \cdot MW_{GHG} \qquad (2.1)$$

where:

Q = Gas flow rate (m^3/y)

$[GHG_{(g)}]$ = GHG concentration (ppmv)

MW_{GHG} = Molecular weight (kg/mol)

R = Universal gas constant (m^3-atm/mol-K)

T = Temperature at time of sampling (K)

P = Pressure (atm)

For aeration basins and grit chambers, Q was assumed to be equal to the amount of air that is pumped into the tanks, which is known from the air usage data from the MWRDGC Manteinance and Operation monthly operation reports (e.g. see **Table IX**). For the exhausts, Q was calculated by:

(2.2) $$Q = v \cdot A_p$$

where A_p is the source emission area, in m^2, and v is flow velocity in m/sec, measured in the field. For the anaerobic digesters, Q was measured directly using the flow meter attached to the gas sampling chimney.

2.4.2 Emissions from floating-cover anaerobic digesters

The GHG flux from the anaerobic digesters was calculated as follows:

(2.3) $$F_{GHG} = Q \cdot \frac{\lfloor GHG_{(g)} \rfloor}{1x10^{6}} \cdot \frac{A_p}{A_f} \cdot \frac{P}{RT} \cdot MW_{GHG}$$

where:

Q = Off gas flow rate (m^3/yr)

$[GHG_{(g)}]$ = GHG concentration (ppmv)

A_p = Annular space for the digester (m^2)

A_f = Cross sectional area of the chimney funnel (m^2)

MW_{GHG} = Molecular weight (kg/mol)

R = Universal gas constant (m^3-atm/mol-K)

T = Temperature at time of sampling (K)

P = Pressure (atm)

2.4.3 Passive surfaces (Imhoff tanks, primary settling tanks, secondary clarifiers, and biosolid drying beds)

The emissions from passive surfaces were calculated using one of the two following methods. The first one used a measured accumulation factor and fluxes were calculated as follows:

(2.4) $$F_{GHG} = \frac{\theta_{GHG} \cdot V_c}{A_c} \cdot A_p \cdot \frac{P}{RT} \cdot MW_{GHG} \cdot \frac{525600 \text{ min}}{yr}$$

where:

θ_{GHG} = Accumulation factor (ppmv/min)

V_c = Volume of the accumulation chamber (m^3)

A_c = Area of the accumulation chamber (m^2)

A_p = Area of the tanks (total, m^2)

MW_{GHG} = Molecular weight (kg/mol)

R = Universal gas constant (m^3-atm/mol-K)

T = Temperature at time of sampling (K)

P = Pressure (atm)

525600 = Minutes in one year

The accumulation factor (θ_{GHG}) was determined using a closed chamber build-up method modified from Rolston (1986). Briefly, a Type I hood was flushed with air and positioned on the liquid surface at the desired location. For each location, five to seven samples were collected periodically from a Type I hood over a 25–30 minute period as a buildup of the gas released from the tank was collected in the headspace. Theoretically, the gas concentration was expected to increase over time during the process as long as gas loss from the headspace did not occur. The gas concentrations were then plotted

versus the accumulation time and a slope was fitted to derive an accumulation factor (θ, ppmv/min; e.g. **Figure 13**). The second method used for passive surface flux calculations was based on the sweep air method proposed by Klenbusch (1986). Briefly, a Type I hood was flushed with air and positioned on the liquid surface at the desired location. Flexible plastic tubing connected the hood to a laboratory-grade N_2 gas tank ("sweep air"). The hood was constantly flushed with 3.0 L/m of the N_2 gas and it was equilibrated for 30 minutes to allow for over 3 bed volumes of gas to pass through the 25 L inner volume. At this point a sample was collected. The flux of the GHG of interest was then calculated as follows:

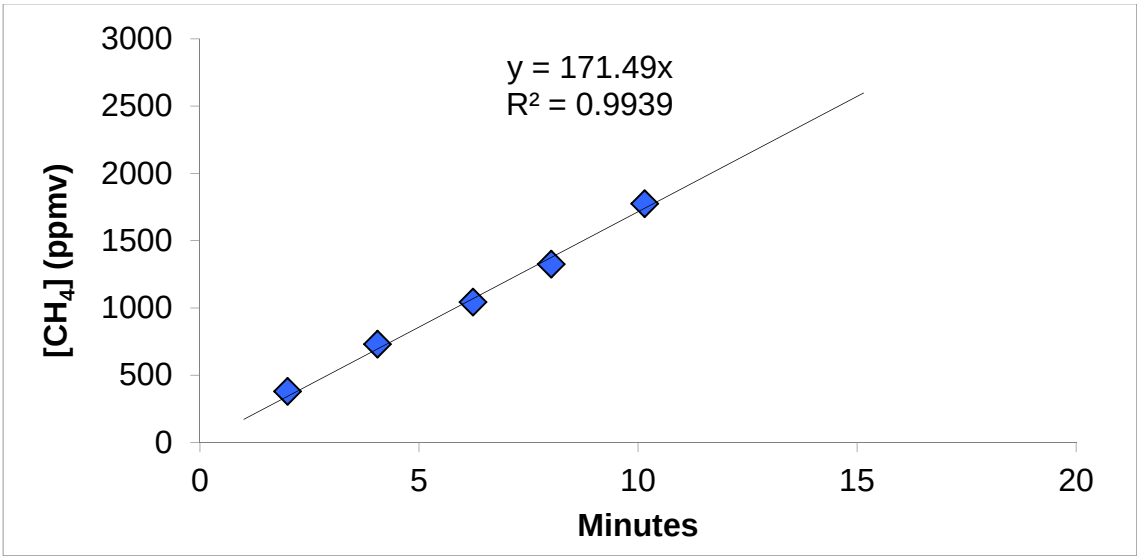

Figure 13. Example of application of the closed chamber build up method for CH_4 from the Imhoff tank 18, pass 1, tail section. The accumulation factor, θ, is the angular coefficient of the regression line, (R^2 = 0.99) = 171.49 ppmv/min. The regression line is forced through the origin to represent [GHG] = 0 at t = 0.

(2.5) $$F_{GHG} = Q_{sweep} \cdot \frac{[GHG_{(g)}]}{1x10^{6}} \cdot \frac{A_p}{A_c} \cdot \frac{P}{RT} \cdot MW_{GHG} \cdot \frac{5256000}{y}$$

where:

Q_{sweep} = N_2 (“sweep air”) flux rate (L/min)

$[GHG_{(g)}]$ = Volume of the accumulation chamber (m^3)

A_p = Area of the tanks (total, m^2)

A_c = Area of the accumulation chamber (m^2)

MW_{GHG} = Molecular weight (kg/mol)

R = Universal gas constant (m^3-atm/mol-K)

T = Temperature at time of sampling (K)

P = Pressure (atm)

525600 = Minutes in one year

The closed chamber build-up method was successfully applied to the Imhoff tanks at Stickney. The sweep air method was successfully applied to the primary settling tanks at Stickney. Primary settling tanks at North Side and Egan, secondary clarifiers in all three plants, and biosolid drying beds had low and/or inconsistent GHG emissions, and the accumulation factors and total fluxes could not be determined unequivocally. In those cases, only ranges of measured concentrations were reported.

2.5 AMMONIUM AND NITRATE/NITRITE STABLE ISOTOPE AND NITROUS OXIDE ISOTOPE AND ISOTOPOMER ANALYSIS

Samples of wastewater for N and O isotope ratio determination in NH_4^+ and NO_2^- /NO_3^- were analyzed at the USGS Reston Stable Isotope Laboratory (RSIL). The aqueous samples for NH_4^+ N stable isotope determination were analyzed following the procedure detailed by Hannon et al. (2008). The NH_4^+ was converted to NH_3 gas by adding MgO to the sample to obtain a pH >9. Subsequently the NH_3 gas was quantitatively trapped as $(NH_4)_2SO_4$ on a glass fiber filter saturated with $NaHSO_4$. The filter was dried and then combusted with a Carlo Erba NC 2500 elemental analyzer (EA) to convert the total nitrogen in the filter sample into N_2 gas. The N_2 gas was then transferred to continuous-flow isotope-ratio mass spectrometer (CF-IRMS) for $\delta^{15}N$ determination, defined as following:

$$\delta^{15}N = \left\{ \frac{\frac{^{15}N}{^{14}N}(sample) - \frac{^{15}N}{^{14}N}(reference)}{\frac{^{15}N}{^{14}N}(reference)} \right\} \cdot 1000 \quad (2.6)$$

where the N isotope reference is atmospheric N_2.

The aqueous samples for N and O stable isotope determination in NO_3^-/NO_2^- were analyzed following the bacterial method described by Sigman et al. (2001) and modified as in Coplen et al. (2004). Minor modifications of the method for O analysis are detailed

in Casciotti et al. (2002). The method is based on the quantitative conversion of NO_3^- /NO_2^- in the sample to N_2O through the bacterial activity of the denitrifier *Pseudomonas Aureofaciens*, lacking the nitrous oxide reductase enzyme and therefore unable to further reduce N_2O. The N_2O gas obtained is subsequently analyzed through CF-IRMS. The denitrifying bacterial cultures were prepared in an appropriate medium lacking any source of nitrogen. The cultures were sealed and purged with He gas to remove any atmospheric O_2 and N_2O present in the headspace. An aliquot of the sample was then added to the culture where NO_3^-/NO_2^- are quantitatively converted to N_2O. The gas was then stripped from each sample using a stream of He carrier gas, collected cryogenically, purified by gas chromatography and finally analyzed for N and O stable isotope using a Thermo Finnigan GasBench II sample preparation system connected to a Thermo Finnigan Delta Plus CF-IRMS. For NO_3^-/NO_2^- stable isotope ratios, the precision is better than 0.2‰ for $\delta^{15}N$ and 0.6‰ for $\delta^{18}O$. For NH_4^+ stable isotope ratios, the precision is generally better than 0.2‰.

The isotope and isotopomer composition of N_2O gas samples was determined at the Michigan State University Biogeochemistry and Paleoproteomics Laboratory following the method detailed in Ostrom et al. (2007). The samples were analyzed on a multicollector GV Instruments IsoPrime Mass Spectrometer interfaced with a continuous flow Trace Gas Inlet System for purification and concentration of N_2O. CO_2 and H_2O are eliminated from the gaseous sample using Carbosorb and magnesium perchlorate respectively as chemical scrubbers, and through cryogenic trapping. The N_2O is then

purified through gas chromatography using a Poraplot Q gas chromatographic column with He as the carrier gas within the Trace Gas system. The effluent from the Trace Gas system was then transferred to the multicollector mass spectrometer which simultaneously monitors 5 masses of interest for N_2O isotopologues; 30, 31, 44, 45, and 46. The precision of N_2O concentration measurements for replicate standards and samples is better than ± 5%. The precision for the isotope ratio measurement is better than 0.1‰. The central and outer N atoms in the linear N-N-O molecule are defined as α and β respectively (Toyoda and Yoshida, 1999), and the SP is defined as in equation 1.19.

2.6 STABLE ISOTOPE ANALYSIS OF OFF-GAS CARBON DIOXIDE AND METHANE, SUSPENDED SOLIDS, AND RADIOCARBON MEASUREMENTS ON OFF-GAS CARBON DIOXIDE

The stable isotope (C, O) composition of off-gas CO_2 was determined on duplicate gas samples collected at the same time as off-gas samples for GC analysis. After equilibration at 20°C overnight, the samples were analyzed by continuous flow isotope ratio mass-spectrometry using a Thermo-Finnigan Gas Bench II continuous flow interface coupled with a Delta Plus XL mass spectrometer. The precision is better than 0.2‰ and 0.4‰ for $\delta^{13}C$ and $\delta^{18}O$ respectively.

Values for $\delta^{13}C$ and δD in off-gas CH_4 were determined at the Isotech Laboratories

(Champaign, IL). Sample purification was obtained by gas chromatography, followed by combustion and dual-inlet isotope ratio mass spectrometry. When necessary, the sample was cryogenically enriched prior to analysis. Precision is better than 0.2‰ for $\delta^{13}C$ and better than 1‰ for δD.

The suspended solids samples were weighted in tin capsules (0.5-1.5 mg) and introduced in a Costech 4010 CHNSO elemental analyzer through a Zero Blank Autosampler. The elemental analyzer combustion and reduction furnaces ware operating at 1000° and 780°C respectively; a chromatography column was then used to separate the N_2 and CO_2 formed, which were quantitatively transferred to a Thermo Finnigan Delta Plus XL mass spectrometer and analyzed by isotope ratio mass spectrometry. The precision is better than 0.2‰ for $\delta^{15}N$, and better than 0.2 and 0.4‰ for $\delta^{13}C$ and $\delta^{18}O$ respectively.

Off-gas CO_2 radiocarbon (^{14}C) data were collected at the Center for Accelerator Mass Spectrometry (CAMS) at the Lawrence Livermore National Laboratories. The Accelerator Mass Spectrometer (AMS) employs a cesium-sputter ion source, a 7MV tandem electrostatic accelerator, and two mass spectrometer (low and high energy, for negative and positive ions respectively). A magnetic quadrupole filter was used as focusing system and a multianode gas ionization detector was used to determine the relative abundance of ^{14}C in the sample (Vogel et al., 1995).

CHAPTER 3

PILOT STUDY AT THE STICKNEY WASTEWATER TREATMENT PLANT

3.1 INTRODUCTION

A pilot-scale monitoring study to evaluate the rate of emissions of N_2O and CH_4 from various steps of the wastewater treatment process was conducted at the Stickney WWTP between September and November 2008. The primary objectives of this reconnaissance study were to determine the magnitude of GHG emissions from different treatment steps, and to identify which sources carried the highest environmental impact. A secondary objective was to test a variety of sampling and analytical methods. This initial approach included the collection and analysis of 55 samples, including: 1) off-gas emissions from the water surfaces of the aeration batteries, primary settling tanks, secondary clarifiers, aerated grit chambers, and Imhoff tanks; 2) fugitive gas emissions from the floating cover anaerobic digesters and sludge concentration tanks; 3) gas emissions from the exhaust points of the digester, screens, and sludge thickening process buildings; and 4) off-gas emissions from a biosolid drying bed. A subset of gas samples was also analyzed for their major constituents (N_2, O_2, Ar) and CO_2. Additionally, samples were collected along the perimeter of the plant to determine the extent of lateral dispersion of these gases.

3.2 SAMPLING COVERAGE AND METHODS

All gas samples taken during the reconnaissance study were stored using Method 4 (see section 2.1). Either Type I hoods or a 6” diameter plastic funnel connected to the vacuum chamber through flexible plastic tubing were used for sample collection. In several cases the gas was collected using both approaches to compare the results. Equilibration times for the Type I hood or the funnel ranged from 5 to 35 minutes depending on the flux for each sampling site. Exhausts were sampled by introducing the sampling line of the vacuum chamber directly into the exhaust outlet. The size of the outlet was measured, and the velocity of the exhaust gas measured as described in section 2.2 to obtain the total exhaust flux. Samples were collected from different locations within the same treatment process: four locations each from the grit chamber and from the primary settling tanks, three locations from the Imhoff tanks, twelve locations from the aeration basin D, six locations from three different secondary clarifiers (center of the tank and outflow channel), three locations from a single floating-cover anaerobic digester, and nine exhausts. Additionally, three air samples were collected outside concentration tanks #4 and #8, two samples were collected from the biosolid drying beds, and nine samples were collected from locations along the perimeter of the WWTP (**Table VIII** and **Figure 14**). All samples were analyzed for N_2O and CH_4 using the HP 5890 GC following the method described in section 2.3. Additionally, N_2, O_2, Ar, and CO_2 concentrations were determined with a SRS-200 Residual Gas Analyzer (RGA) in some samples.

TABLE VIII

SAMPLING LOCATIONS AND FREQUENCY

Location	# of samples
Aeration Battery "D"	12
Aerated Grit Chamber	4
Anaerobic Digesters	3
Secondary clarifiers	6
Exhaust - Coarse Screens	1
Exhaust - Fine Screens	1
Exhaust - Pre-centrifuge Building	3
Exhaust - Post-centrifuge Building	3
Exhaust - Roof of Digesters building	1
Perimeter	9
Imhoff Battery "B"	3
Concentration Tank #4 and #8	3
Biosolid drying beds	2
Primary Settling Tank #6	2
Primary Settling Tank #10	2
Total	55

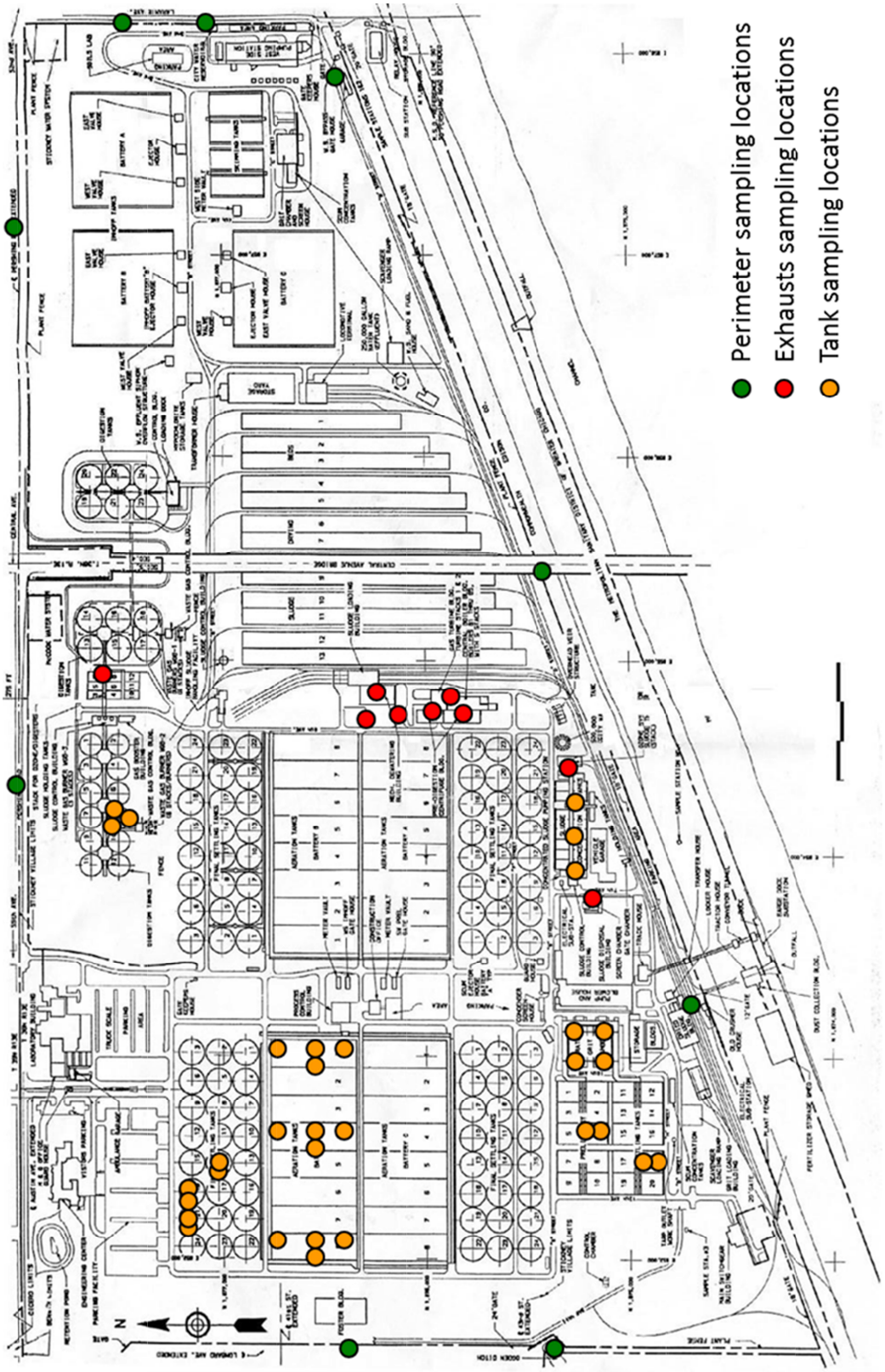

Figure 14. Off-gas and air sampling locations for perimeter, exhausts, and tanks at the Stickney WWTP.

Flux measurements were conducted for primary settling tanks, secondary clarifiers, and Imhoff tanks using the ‘sweep air” method detailed in section 2.4, applying a known flux of N_2 of 1.2-3.2 L/min to the emission isolation chamber. The fluxes were calculated based on the sample concentrations of N_2O, CH_4 and CO_2 using equation 2.5. When using N_2 fluxes < 3 L/min the equilibration time for flux hood was increased to allow for proper flushing of the hood (at least 3 bed volumes of N_2 before sampling). For aeration basin and grit chamber samples, the fluxes were calculated based on the amount of air used to aerate the tanks (Equation 2.1), which was 4.53×10^9 and 3.62×10^8 m^3/y respectively in 2008. Total gas flux from the exhaust points was measured as described in section 2.4 and calculated using equation 2.1. An attempt was made to measure the total gas flux from the digesters by collecting the gas with the sampling funnel into a 2” plastic tube. A port on the side of the tube allowed for the introduction of the TSI Velocicheck anemometer probe to record the off-gas speed. Data from aerated chambers (grit chamber and aeration basin) and exhausts were corrected for air, assuming air concentrations of 0.4, 1.7, and 379 ppmv for N_2O, CH_4, and CO_2 respectively.

3.3 RESULTS AND DISCUSSION

Concentrations of N_2O, CH_4, CO_2, O_2, N_2, and Ar are reported in **Table IX** in ppmv. The analytical error is ± 0.3 ppmv for N_2O, ± 1.0 ppmv for CH_4, and ± 100 ppmv

for CO_2. The analytical error for the measured concentrations of N_2, O_2, and Ar is ± 1.1%, ± 0.6%, and ± 0.01% for N_2, O_2, and Ar, respectively. For N_2O, CH_4, and CO_2, the concentrations reported are the measured concentrations minus the concentrations in air, assumed to be 0.4 ppmv N_2O, 1.7 ppmv CH_4, and 379 ppmv CO_2.

The highest N_2O concentrations were measured in the off-gas from the aeration basin (1.4-61 ppmv) and grit chamber (9.7-15.1 ppmv). The concentration of N_2O from the exhaust points ranged from below detection to 1.1 ppmv. The secondary clarifiers, sampled with the sweep air method, showed relatively small accumulation of N_2O; the center, sampled applying 1.2 L/min N_2 flux, reached a N_2O concentration of only 0.2 ppmv above air standard; this difference with air is smaller than the analytical error. The secondary clarifier outflow channel, however, sampled with 3.2 L/min N_2 flux, reached a N_2O concentration of 11.5 ppmv. The highest CH_4 concentrations were measured in the off-gas from the anaerobic digester (up to 10% CH_4), from the grit chamber (68-135 ppmv), and from the aeration basin (up to 65 ppmv). Primary settling tanks and Imhoff tanks, sampled with the sweep air method, showed accumulation of CH_4. When a 3.2 L/min N_2 flux was applied, an average CH_4 concentration of 130 ppmv and 3,800 ppmv was measured for primary settling tank and Imhoff tank samples respectively. Additionally, gas samples from some of the exhaust points showed relatively high CH_4 concentrations, which ranged from 35 to 54 ppmv and 0.5 to 190 ppmv for the fine + coarse screens exhausts and the post-centrifuge building exhausts respectively. Concentrations of CO_2 were high in the off-gas from the anaerobic digesters

TABLE IX
ANALYTICAL RESULTS FOR GAS SAMPLES

#	Sampling date	Location	Air T (℃)	Water T (℃)	N_2O (ppmV)	CH_4 (ppmV)	CO_2 (ppmV)	N_2 (%)	O_2 (%)	Ar (%)
1	11/24/2008	Primary Settling Tank #10	3	15	0	57	N/A	N/A	N/A	N/A
2	11/24/2008	Primary Settling Tank #1	3	15	0.1	160	N/A	N/A	N/A	N/A
3	10/10/2008	Aeration Battery "D" tank1	23	19	34	19	5,300	79	18	0.94
4	10/10/2008	Aeration Battery "D" tank1	23	19	27	24	5,300	82	17	0.97
5	10/10/2008	Aeration Battery "D" tank1	23	19	14.5	65	4,400	80	19	0.95
6	10/16/2008	Aeration Battery "D" tank 1, downwelling side	21	20.7	3.3	5	6,000	78	19	0.93
7	10/13/2008	Aeration Battery "D" tank4	25	21	0.9	1	2,800	79	20	0.93
8	10/13/2008	Aeration Battery "D" tank4	25	21	1.4	1	3,100	80	20	0.9
9	10/16/2008	Aeration battery "D", tank 4	21	20.7	61	2	6,300	80	18	0.94
10	10/16/2008	Aeration Battery "D" tank 4, downwelling side	21	20.7	12.9	1	300	77	20	0.92
11	10/10/2008	Aeration Battery "D" tank8	23	19	15.2	9	5,100	81	19	0.96
12	10/10/2008	Aeration Battery "D" tank8	23	19	22	0	6,200	80	19	0.94
13	10/16/2008	Aeration Battery "D" tank8	21	20.7	32	0	5,300	77	20	0.91
14	10/16/2008	Aeration Battery "D" tank8, downwelling side	21	20.7	11	0	1,700	78	21	0.92
15	10/13/2008	Grit Chamber #8	27	22	9.7	70	N/A	N/A	N/A	N/A
16	10/13/2008	Grit Chamber #8	27	22	14.2	77	2,300	78	20	0.93
17	10/13/2008	Grit Chamber #4	27	22	11.1	68	1,900	78	20	0.92
18	10/13/2008	Grit Chamber #4	27	22	15.1	135	2,600	79	21	0.93

Values of zero are reported for measured concentrations of N_2O, CH_4, and CO_2 equal or less than those in air. Concentrations that were below detection in the sample are reported as BD. Concentrations that were not measured are reported as N/A. The analytical error is ± 0.3 ppmv for N_2O, ± 1.0 ppmv for CH_4, and ± 100 ppmv for CO_2. The analytical error for the measured concentrations of N_2, O_2, and Ar is ± 1.1%, ± 0.6%, and ± 0.01% for N_2, O_2, and Ar, respectively.

TABLE IX (continued)

#	Sampling date	Location	Air T (℃)	Water T (℃)	N_2O (ppmV)	CH_4 (ppmV)	CO_2 (ppmV)	N_2 (%)	O_2 (%)	Ar (%)
19	10/30/2008	Imhoff Battery "B" Tank #31 (end)	11.5	16.5	0	24	300	79	21	0.94
20	10/30/2008	Imhoff Battery "B" Tank #26 (end)	11.5	16.5	0	21	250	78	21	0.93
21	10/30/2008	Imhoff Battery "B" Tank #37 (head)	11.5	16.5	0	9	250	78	21	0.93
22	10/16/2008	Anaerobic Digester #8 N side	21	N/A	0	860	12800	70	19	0.83
23	10/16/2008	Anaerobic Digester #8 SW side	21	N/A	0	1920	24800	61	17	0.72
24	10/16/2008	Anaerobic Digester #8 SE side	21	N/A	0	1130	13600	68	18	0.8
25	10/23/2008	Secondary clarifier #18 - center	16	19	0.2	0	N/A	N/A	N/A	N/A
26	10/23/2008	Secondary clarifier #14 - channel	16	19	4.7	0	800	78	21	0.93
27	10/23/2008	Secondary clarifier #14 - center	16	19	0	0	N/A	N/A	N/A	N/A
28	10/23/2008	Secondary clarifier #18 - channel	16	19	4.3	8	N/A	N/A	N/A	N/A
29	10/28/2008	Secondary clarifier #21 - center	8	17	0.4	4	90	77	21	0.91
30	10/28/2008	Secondary clarifier #21 - channel	8	17	11	3	2200	77	20	0.92
31	10/28/2008	Exhaust - Coarse Screens	8	N/A	0.6	35	100	78	21	0.92
32	10/28/2008	Exhaust - Conc. Tanks Fine Screens	5	N/A	1.1	54	90	77	21	0.92
33	10/28/2008	Exhaust - Pre-centrifuge bld, HOLDING TANK	3	N/A	0	1.7	10	78	21	0.93
34	10/28/2008	Exhaust - Pre-centrifuge bld, ROOM	3	N/A	0	0	20	79	21	0.93
35	10/28/2008	Exhaust - Post-centrifuge bld, MECHANICAL AREA	3	N/A	0.5	52	700	77	20	0.91
36	10/28/2008	Exhaust - Post-centrifuge bld, GENERAL AREA	3	N/A	0	7	30	78	21	0.93

TABLE IX (continued)

#	Sampling date	Location	Air T (℃)	Water T (℃)	N_2O (ppmV)	CH_4 (ppmV)	CO_2 (ppmV)	N_2 (%)	O_2 (%)	Ar (%)
37	10/28/2008	Exhaust - Post-centrifuge bld, CENTRATE	3	N/A	0	0	0	77	21	0.92
38	10/28/2008	Exhaust - Post-centrifuge bld, CENTRIFUGE	3	N/A	0.1	17	100	78	21	0.93
39	10/28/2008	Exhaust - Post-centrifuge bld, BELT	3	N/A	0.3	190	1400	77	21	0.92
40	10/29/2008	Perimeter - North Side next to Anaerobic Digesters - Top of fence	5	N/A	0	0	7	78	21	0.93
41	10/29/2008	Perimeter - North Side next to Imhoff Tanks - Top of fence	5	N/A	0	0	N/A	N/A	N/A	N/A
42	10/29/2008	Perimeter - NE corner next to water tank - Top of fence	5	N/A	0	0	N/A	N/A	N/A	N/A
43	10/29/2008	Perimeter - E side top of artificial hill - Top of fence	5	N/A	0	0	N/A	N/A	N/A	N/A
44	10/29/2008	Perimeter - SE corner between the last two buildings - Top of fence	5	N/A	0	0	N/A	N/A	N/A	N/A
45	10/29/2008	Perimeter - S side under bridge - Top of fence	5	N/A	0	0	N/A	N/A	N/A	N/A
46	10/29/2008	Perimeter - S side near Coarse Screens building - Top of fence	5	N/A	0	0	N/A	N/A	N/A	N/A
47	10/29/2008	Perimeter SW corner, Wood - Top of fence	5	N/A	0	0	N/A	N/A	N/A	N/A
48	10/29/2008	Perimeter - W side beyond deposit building - Top of fence	5	N/A	0	0	N/A	N/A	N/A	N/A
49	10/30/2008	Roof of Digesters building #127	11.5	16.5	0.3	5.7	300	79	21	0.94
50	10/30/2008	Concentration Tank #4 Outside/above	11.5	16.5	0	0.5	20	77	21	0.92
51	10/30/2008	Concentration Tank #8 Outside/above	11.5	16.5	0	19	20	78	21	0.94
52	10/30/2008	Biosolid pile I (temperature of the pile: 6℃)	15.3	N/A	0.1	0	10	78	21	0.93
53	10/30/2008	Biosolid Pile II (temperature of the pile: 6℃)	15.3	N/A	0.6	0	20	79	21	0.93

(12,800 to 24,800 ppmv), the aeration basin (up to 6,300 ppmv), and grit chamber (1,900 to 2,600 ppmv). The samples collected near the concentration tanks had CH_4 concentrations ranging 0.5 to 19 ppmv above the standard air concentration, suggesting that the concentration tanks leak CH_4 through their cover. All samples collected along the perimeter of the plant showed N_2O, CH_4, and CO_2 concentrations almost identical to standard air concentrations, and therefore lateral dispersion of GHGs from the plant seems to be insignificant, or the dilution by air is large enough that the flux from the WWTP is not measurable at these locations. For the biosolid drying beds, the "sweep air" method, even at low N_2 flux (1.2 L/min), yielded sample concentrations that were below detection. Therefore sampling was repeated by placing the flux hood on top of two distinct dry biosolid piles, allowing for 20 min equilibration time, and then a sample was collected. N_2O concentrations were 0.8 and 1.2 ppmv above air concentration respectively, while CH_4 concentrations were negligible. This method did not provide any flux information, but allowed to qualitatively determine if N_2O and/or CH_4 production was still active within the biosolid mass.

The aeration basin off-gas showed N_2 concentrations ranging 77 to 82%, O_2 ranging 19 to 21%, and Ar ranging 0.91 to 0.97%. These results suggest that only about 1 to 2.5% of the oxygen pumped into the basin is consumed by biological reactions; this corresponds to 4.3 to 10.9% air/liquid oxygen transfer efficiency. Therefore, the majority of the off-gas is constituted by the same air that is pumped into the basin, with the addition of variable amounts (< 1 to 2.5%) of N_2O, CH_4, and CO_2 produced by the

biological reactions taking place within the aeration basin, plus trace amounts of other volatile compounds. These observations also confirm the validity of the method used to calculate total GHG fluxes from aerated tanks (Equation 2.1). Average fluxes were calculated for each source when possible (**Table X**).

Average total fluxes for 2008 from the Stickney WWTP were estimated in kg/y at 1.6 x 10^5 N_2O, 2.3 x 10^6 CH_4, and 4.6 x 10^7 CO_2, corresponding to emission factors of 64, 920, and 18,400 grams per person per year (g/Pe/y) for N_2O, CH_4, and CO_2 respectively. The emission factor for N_2O falls within the wide range reported in literature (0.28-140, Ahn et al., 2010). The aeration basins were the main source of fugitive N_2O (92% of the total), but a significant flux of N_2O were measured also from the grit chamber (5%), and minor amounts were released through the plant exhausts (2%). CH_4 is mainly produced by the Imhoff tanks (85%) and anaerobic digesters (7%), and also released by plant exhausts (6%), and also produced in minor amounts in anaerobic pockets in the aeration basin (1%). Carbon dioxide is mostly produced in aeration basins (89%), and also released by plant exhausts (5%), and the grit chamber (3%). Other processes contribute to N_2O, CH_4, and CO_2 with minor emissions.

The anaerobic digesters release off-gas by slow bubbling through a scum foam blanket floating on top of the liquid; this generally results in low and intermittent off-gas flow. The velocity of the gas escaping, measured with the TSI Velocicheck anemometer, was variable, ranging from 0.03 to 10.7 m/min, but at these low flows the error on the instrument is large. Following a visual inspection of the amount and size of the gas

TABLE X

AVERAGE GHG FLUXES CALCULATED FOR THE STICKNEY WWTP

	N_2O flux (kg/y)	CH_4 flux (kg/y)	CO_2 flux (kg/y)	% of TOTAL N_2O flux	% of TOTAL CH_4 flux	% of TOTAL CO_2 flux
Grit Chamber	8,144	20,655	1,478,126	5	0.8	3.2
Primary Settling Tanks	0	21,898	9,266	0	0.9	0
Imhoff Batteries	0	2,076,744	546,049	0	84.7	1.2
Aeration Batteries (A+B+C+D)	150,403	26,893	41,430,298	92.3	1.1	89.3
Secondary clarifiers - center	46	0	513,596	0	0	1.1
Secondary clarifiers - channel	553	0	2,597	0.3	0	0
Anaerobic Digesters	0	167,627	78,700	0	6.8	0.2
Exhaust - Coarse Screens	600	12,079	97,738	0.4	0.5	0.2
Exhaust - Conc. Tanks Fine Screens	1,222	21,762	95,117	0.7	0.9	0.2
Exhaust - Digester Building	124	925	130,925	0.1	0	0.3
Exhaust - Pre-centrifuge HOLDING TANK	1	43	914	0	0	0
Exhaust - Pre-centrifuge ROOM	0	0	16,985	0	0	0
Exhaust - Post-centrifuge MECHANICAL AREA	222	8,036	305,305	0.1	0.3	0.7
Exhaust - Post-centrifuge GENERAL AREA	0	14	191	0	0	0
Exhaust - Post-centrifuge CENTRATE	0	0	10	0	0	0
Exhaust - Post-centrifuge CENTRIFUGE	1,540	65,456	1,096,088	0.9	2.7	2.4
Exhaust - Post-centrifuge BELT	134	29,650	598,989	0.1	1.2	1.3
Exhausts - Total	3,843	137,965	2,342,263	2.4	5.6	5
Total Fluxes	**162,989**	**2,451,782**	**46,400,895**			

bubbles escaping through the foam, gas velocities such as 10.7 m/min seem unrealistic. Additionally, the CH_4 concentration measured for the anaerobic digesters ranged from 859 ppmv to about 10% in volume. The biogas produced in the anaerobic digesters, however, is expected to contain up to 65% CH_4 in volume, and therefore the measured concentrations seem relatively low. The fluxes calculated using a gas velocity of 0.03 m/min, assuming a CH_4 concentration of 10%, result in 1.7×10^5 kg/y of CH_4 and 7.9×10^4 kg/y of CO_2. No significant fluxes were measured from the biosolid drying beds during the 2008 study. However, the "sweep air" method used for fluxes considerably dilutes the samples; as such, some of the lowest GHG emissions were below detection, while samples obtained from the same locations with no dilution showed small but nonzero GHG emissions.

3.4 CONCLUSIONS

Direct measurement of GHG emissions at a full-scale wastewater reclamation plant during this preliminary reconnaissance study has shown that: (1) the aeration batteries are the main source of N_2O; (2) leaks from floating-cover anaerobic digesters, taking place between the tank cover and the tank wall, constitute a significant source of CH_4; (3) the Imhoff tanks constitute, by a large margin, the main source of fugitive CH_4 at the Stickney WWTP. Replacement of these tanks with more efficient primary tanks

would significantly decrease the CH_4 emissions from the WWTP; (4) the grit chamber can be a significant source of N_2O, accounting for about 5% of the N_2O emitted; (5) similarly, the plant exhausts release significant amounts of N_2O and CH_4 (2.4 and 5.6% of the total N_2O and CH_4 respectively); (6) no significant lateral dispersion of N_2O or CH_4 from the WWTP was detected in the perimeter samples.

CHAPTER 4

GREENHOUSE GAS EMISSIONS FROM THREE METROPOLITAN WASTEWATER RECLAMATION PLANTS*

(**this chapter to be submitted for publication*)

4.1 ABSTRACT

We compared N_2O and CH_4 emissions for 2009 on a per-process basis at three plug-flow, activated-sludge, metropolitan Wastewater Treatment Plants (WWTPs) in the Chicago area (Stickney, North Side, and Egan WWTPs). Each plant receives substantially different amounts of wastewater and employs different aeration technologies and tank designs. CO_2 emissions also were measured for a subset of these treatment processes. Total N_2O fluxes were calculated to be 5.9×10^5 kg/y for Stickney, 1.7×10^4 kg/y for North Side, and 1.6×10^4 kg/y for Egan. Total CH_4 fluxes, excluding re-captured CH_4, were calculated to be 2.8×10^6 kg/y for Stickney, 8.6×10^4 kg/y for North Side, and 6.0×10^4 kg/y for Egan. The N_2O emissions were highest in the aerobic sections of the biological reactors (aeration basins), with 5.1×10^5 kg/y, 1.6×10^4 kg/y, and 1.4×10^4 kg/y for Stickney, North Side, and Egan WWTPs, respectively. Methane was emitted mostly from primary settling tanks, aeration basins, grit chambers, and as fugitive emissions from floating-lid anaerobic digesters. Grit chambers and plant

exhausts also contributed substantially to both N_2O and CH_4 emissions. Differences were observed in the per capita emissions at the three plants; N_2O emissions ranged from 204, 12, and 92 grams per person per year (g/Pe/y) for Stickney, North Side, and Egan respectively, while CH_4 emissions were 1122, 61, and 354 g/Pe/y for Stickney, North Side, and Egan respectively. These results suggest that several sources (e.g. grit removal, primary settling tanks, biological nitrogen removal, plant exhausts, and anaerobic digesters) contribute to overall N_2O and CH_4 fluxes, and that the choice of wastewater treatment technology employed has a significant impact on greenhouse gas emissions to the atmosphere. According to our results, the currently employed models might underestimate N_2O emissions by up to two orders of magnitude.

4.2 INTRODUCTION

According to the U.S. Environmental Protection Agency (USEPA), WWTPs are the 7^{th} highest anthropogenic contributors of both N_2O and CH_4 to the atmosphere in the US, with 5.0 and 24.5 Tg CO_2 equivalents in 2009, respectively (USEPA, 2010). The Global Warming Potential (GWP) of these two greenhouse gases is estimated to be 310 and 21 for N_2O and CH_4 respectively. Additionally, N_2O is rapidly becoming a main greenhouse gas of concern as it is also an ozone-depleting substance, and its impact on the atmosphere is comparable to that of many chlorofluorocarbons, which are being

phased out under the Montreal protocol (Ravishankara et al., 2009). A systematic database of measured N_2O and CH_4 fluxes from WWTPs does not currently exist. Few full-scale studies report N_2O emissions from WWTPs (Czepiel et al., 1995; Sümer et al., 1995; Wicht et al., 1995; Kimochi et al., 1998; Sommer et al., 1998; Kampschreur et al., 2008; Ahn et al., 2010) and only two of these reports were conducted in the United States (US). One focused on biological nitrogen removal (BNR) operations on 12 activated-sludge US WWTPs (Ahn et al., 2010), and one focused on a non-BNR WWTP in New Hampshire (Czepiel et al., 1995). None of these studies systematically reported both N_2O and CH_4 emissions from the various treatment processes.

Both gases can be produced during wastewater treatment through multiple biological pathways. The USEPA assumes that incomplete denitrification in anoxic zones during BNR is the main source of N_2O. The method used by the USEPA to estimate N_2O emissions from WWTPs operations is based on emission factors of 3.2 g N_2O/person (Pe)/year (y) for non-BNR treatment plants, and 7.0 g N_2O/Pe/y for BNR treatment plants. However, recent studies have shown that N_2O emissions are higher in the aerated sections of the BNR treatment, and emission factor values ranging from 0.28 to 140 have been reported (Ahn et al., 2010). This suggests that oxygen-inhibited denitrification and/or nitrification under variable DO conditions could be responsible for some of the N_2O production and emission (Ritchie and Nicholas, 1972; Knowles, 1982; Inamori et al., 1998). The high N_2O emissions values may also be amplified by a N_2O-stripping effect due to tank aeration. Emissions of N_2O may occur from any treatment step for

which chemo-physical conditions allow for either nitrification or denitrification to take place, including not anoxic systems but micro- and aerophyll systems as well..

Anaerobic fermentation and methanogenesis using fermentation products are exploited for CH_4 production in the anaerobic digesters at WWTPs (Tchobanoglous, 2004). The same reactions may also occur during the various treatment steps whenever anoxic conditions persist, e.g. during primary treatment or in low DO portions of the aeration basin. Moreover, CH_4 emissions may occur as leakage from anaerobic digesters, depending on the digester's design.

In this study, we determined the total fluxes of N_2O and CH_4 from the different treatment processes and plant exhausts from the WWTPs of Stickney, North Side, and Egan, located in the Chicago metropolitan area (**Figure 15**) and managed by the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC). All three plants employ single-stage nitrification reactors but differ significantly in size, amount of wastewater treated, aeration technology used, incoming Total Kjeldahl Nitrogen (TKN), and tank design. Therefore, the comparison of these WWTPs and effluents should provide a thorough characterization of potential greenhouse gas emission and per capita variations for comparable metropolitan areas.

The *Stickney* WRP located in Stickney, Illinois, is a single stage nitrification sludge plant that has a design average capacity of 1.2 billion gallons per day and serves 2.3 million people. In 2009, the plant treated an average of 761 million gallons of wastewater per day (MGD) with average influent concentrations of 1114 mg/L total

solids, 33 mg/L total Kjeldhal nitrogen (TKN), and 220 mg/L 5-day biological oxygen demand (BOD5). The incoming wastewater is split into two separate process streams (**Figure 16**). The West Side influent process flow is as follows: 1) screens; 2) skimming tanks; 3) grit chambers; 4) Imhoff tanks; 5) aeration batteries; 6) secondary settling tanks; and 7) discharge. The West Side Imhoff sludge process train is as follows: 1) floating cover anaerobic digesters; 2) post digestion centrifuge; and 3) biosolid drying beds. The Southwest Side influent process is as follows: 1) screens; 2) aerated grit tanks;

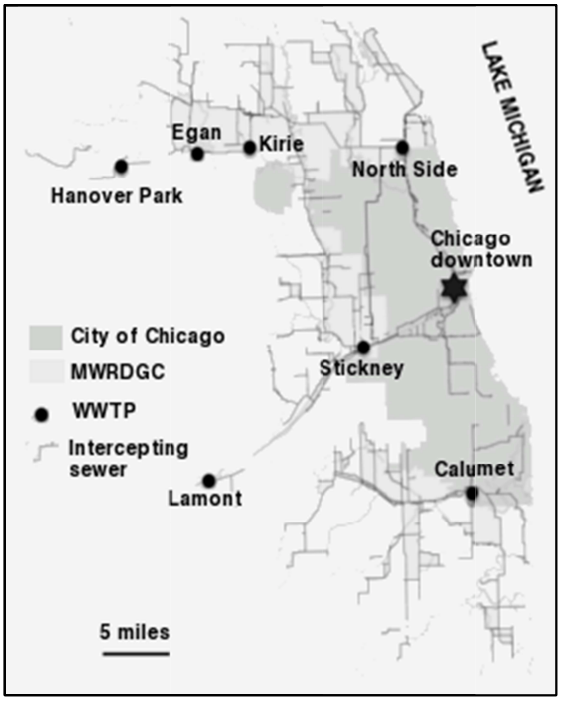

Figure 15. Location of the 7 WWTPs in the Chicago aerea operated by the MWRDGC. This study concerned the Stickney, North Side, and Egan facilities.

3) primary settling tanks; 4) aeration batteries; 5) secondary settling tanks; and 6) discharge. Effluents from the West Side Imhoff tanks and Southwest Side primary settling tanks are combined prior to entering the aeration batteries. The Southwest Side preliminary sludge is concentrated in concentration tanks and combined with the waste activated sludge and North Side WWTP sludge. The combined sludge process train is: 1) pre-digestion centrifuge; 2) anaerobic digesters; 3) post-digestion centrifuge or facultative lagoons; and 4) biosolid drying beds. There are eight aerated grit tanks, 16 skimming tanks, 20 primary settling tanks, 96 secondary settling tanks, and 24 anaerobic digesters. There are four aeration batteries (A-D), each having eight tanks with four passes; the aeration tanks employ spiral roll diffuser plate systems. Additionally, there are three Imhoff batteries with 36 tanks in each battery.

The *North Side* WRP located in Skokie, Illinois is a single stage nitrification plant that has a design average capacity of 333 MGD and serves 1.4 million people. In 2009, the plant treated an average of 245 MGD with average influent concentrations of 748 mg/L total solids, 19.5 mg/L TKN, and 101 mg/L BOD5. The wastewater influent process flow is as follows: 1) coarse screens; 2) aerated grit tanks; 3) fine Screens; 4) primary settling tanks; 5) aeration batteries; 6) secondary settling tanks; and 7) discharge. The primary and secondary sludge collected during treatment is pumped to the Stickney WWTP for treatment. There are six aerated grit tanks, 16 primary settling tanks, and 64 secondary settling tanks. There are four aeration batteries (A-D) where three aeration batteries (A-C) have 12 tanks and are single pass systems. The final aeration battery (D)

has seven tanks, which are double pass systems. All aeration tanks employ spiral roll diffuser plate systems.

The *Egan* WRP located in Schaumburg, Illinois is a single stage nitrification and tertiary filtration plant that has a design average capacity of 30 MGD and serves 0.17 million people. In 2009, the plant treated an average of 27 MGD with average influent concentrations of 906 mg/L total solids, 28 mg/L TKN, and 195mg/L BOD5. The wastewater influent process flow is as follows: 1) coarse and fine screens; 2) aerated grit

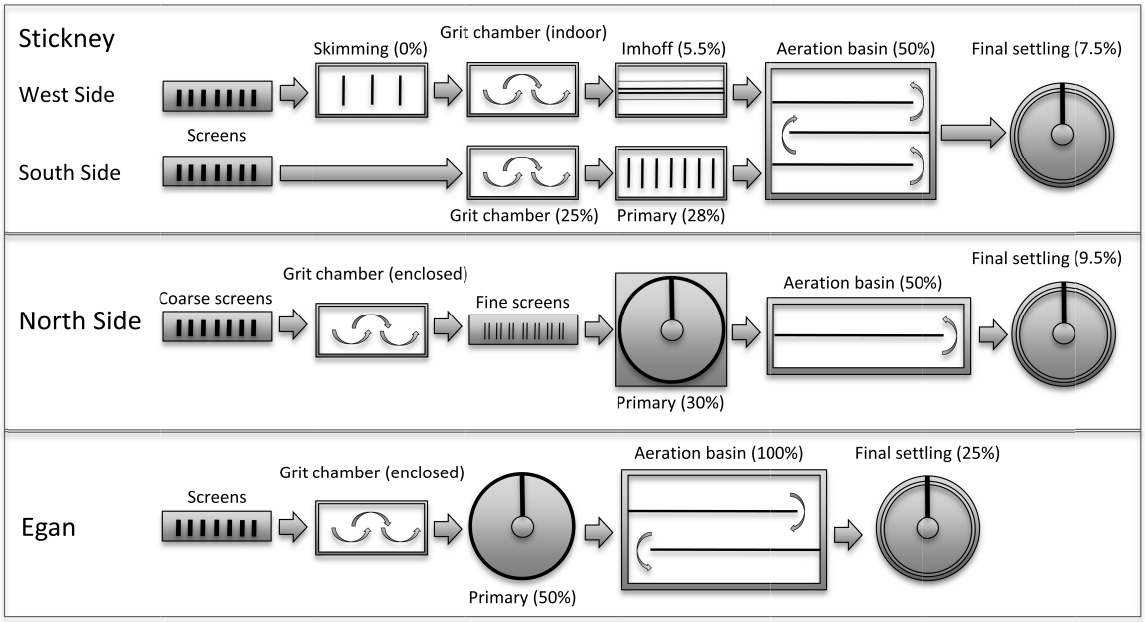

Figure 16. Wastewater influent process flow for Stickney (West and South Side), North Side, and Egan WWTPs and sampling coverage for each process (%). At Stickney and North Side the treated water is discharged after final settling, whereas at Egan tertiary treatment (seasonal chlorination and dual media filtration) is also employed before discharge.

tanks; 3) primary settling tanks; 4) aeration batteries; 5) secondary settling tanks; 6) seasonal chlorination in contact tanks; 7) dual media filter beds; and 8) discharge. The primary and secondary sludge are combined and treated according to the following solids train: 1) gravity belt thickeners; 2) fixed cover anaerobic digesters; 3) post digestion centrifuge; and 4) drying beds or land application. There are four aerated grit tanks, four primary tanks, and eight secondary settling tanks. There are four aeration batteries where each battery has three tanks with three passes. The north aeration battery has full floor diffuser plate coverage, tapered aeration, and a baffle in the first pass for each tank. The south aeration battery has spiral roll aeration.

4.3 MATERIALS AND METHODS

4.3.1 Sampling coverage

The majority of the treatment processes were sampled for off-gas emissions at the three WWTPs. All accessible process exhausts vents were also sampled. Exhaust vents are part of the ventilation systems either for a specific treatment building or a specific process. Imhoff tanks, floating-lid anaerobic digesters, and biosolid piles are only present at the Stickney WWTP; skimming tanks and grit chamber for the West Side influent at Stickney are located indoors and were not sampled. Similarly, the grit chambers of North Side and Egan WWTPs are not open-topped and off-gas samples were not collected.

Eleven of the twenty-four anaerobic digesters were sampled at Stickney, for a 46% coverage. The sampling coverage for each process varies between 5.5 and 100% (see Figure 16). The low sampling coverage of the final settling tanks and Imhoff tanks is due to their large number, and is partially compensated by the fact that these tanks receive well-homogenized wastewater, and they are expected to produce similar fluxes of fugitive greenhouse gases. At the Stickney WWTP, the grit chamber and aeration basin were both sampled at regular intervals throughout the day to investigate diurnal variability in the greenhouse gas fluxes. The grit chamber was sampled at the inlet and at the outlet every two hours from 9:00 to 17:00. The aeration basins were sampled at the inlet, middle point, and outlet. Samples were collected every 2 hours from 6:00 to 20:00. The aeration basins at North Side and Egan were sampled at inlet, outlet, and seveeral more locations distributed at equal spacings along the flow paths.

4.3.2 Field methods

Off-gas emissions from different sources were captured using floating off-gas hoods of different surface area (0.13 – 3.0 m^2) and volume (0.025 – 0.836 m^3), depending on the process. For aerated surfaces (aeration basins and grit chambers) sampling, the 0.836 m^3 inner volume hoods were equipped with a 5 cm ID hose to ensure proper gas flow and avoid pressure build-ups. Passive surfaces (primary settling tanks, final settling tanks, Imhoff tanks, and biosolids drying beds) were sampled with 0.025 m^3 emission isolation hoods using a sweep air (Klenbusch, 1986) with N_2 or a closed chamber (gas

build up) method (Rolston, 1986). The anaerobic digesters at Stickney were sampled by inserting a funnel in the open space (~6”) between the floating lid and the containment wall. The funnel was equipped with a gas-tight sampling port and a glass flow meter (Section 2.2). Three funnels were used at each digester, at different locations, and for each funnel 15 flux measurements were taken and averaged. A total of 45 flux measurements were therefore averaged for each digester. The funnels were left to equilibrate for 30-60 minutes, depending on the flux, so about 3 bed volumes of fugitive gases were flushed through the funnels before a sample was collected in duplicate.

Gas samples were collected from the desired source using a 60 mL sterile plastic syringe fitted with a gas tight valve (Method 1, section 2.1). The syringe was flushed with three bed volumes of sample gas before a final 50 mL sample was collected. About 35 mL of the syringe sample was then stored in a pre-evacuated glass vial with a gas-tight cap holding a pierceable rubber septum. The vials were maintained at positive pressure (2-8 psi) to prevent contamination by atmospheric air in case of leakage, and they were let equilibrate overnight at room temperature (20º C) prior to analysis. Plant exhausts were sampled inserting the syringe directly inside the exhaust. The airflow through the exhaust was measured using an air velocity meter.

4.3.3 Analytical methods

The samples were analyzed using HP 5910 and SRI Instruments Greenhouse-Gas gas chromatographs (Section 2.3). Lower detection limits for CH_4, N_2O, and CO_2 were

0.4 ppmv, 0.3 ppmv, and 100 ppmv, respectively; any analytical result below the respective detection limit was considered to be zero for the purpose of calculating total fluxes. All gas concentrations were corrected for temperature and ambient air concentrations at the time of sampling, when appropriate. Dissolved oxygen (DO), temperature, oxidation-reduction potential (ORP), and pH were determined in-situ using dedicated probes. Water quality samples were analyzed for total suspended solids (TSS), VSS, chemical oxygen demand (COD), NH_4^+, NO_3^-, and NO_2^- using standard methods (Eaton et al., 2005). The analytical error is better than ±10% for N_2O and better than ±5% for CH_4 and CO_2. The analytical error for the water quality parameters is better than ±2%. CO_2 was only analyzed for a limited number of processes and was not analyzed for the majority of North Side and Egan samples.

4.3.4 Flux calculations

For aerated tanks, plant exhausts, and anaerobic digesters, the concentrations were averaged and the fluxes were calculated based on the overall off gas flow rate, which was known or was measured, using equation 2.1. Exhausts were assumed to be operational 24 hours a day for the whole year. For passive surfaces sampled with a closed chamber method a slope was fitted to derive an accumulation factor (θ_{GHG}, ppmv/min) and the fluxes calculated using equation 2.4. For the primary settling tanks at Stickney, sampled with a sweep air method, fluxes were calculated using equation 2.5.

4.4 RESULTS

Average concentrations and ranges for N_2O, CH_4, and CO_2 gas species are reported in **Table XI**. Values are highly variable. The highest N_2O concentrations were observed at the grit chamber and aeration basins. The highest CH_4 concentrations were seen at the grit chamber, inlet of the aeration basins, primary settling tanks, and anaerobic digesters. Calculated total fluxes are reported in **Table XII**. The error for the total fluxes calculated on a 95% confidence interval for Stickney is ± 22%, ±17%, and ± 6% for N_2O, CH_4, and CO_2 respectively. As North Side and Egan were sampled only once the limited number of data points does not allow for an accurate calculation of the error. Results are reported for each plant following the order of the tanks along the wastewater flowpath.

4.4.1 Stickney

The N_2O concentrations ranged from 0.6 to 452 ppmv, and CH_4 ranged from 3 to 1936 ppmv in the grit chamber samples (**Figure 17**). The highest concentrations were observed at the inlet of the tank. The primary settling tanks were sampled with a "sweep air" method (Klenbusch, 1986), and ranges of concentrations are not available. When a N_2 sweep air flux of 3.0 L/min was applied, the calculated fluxes were 1.8×10^2, 2.6×10^3, and 1.5×10^5 kg/y for N_2O, CH_4, and CO_2 respectively. One of the aeration basins sampled (battery D) was being overaerated to compensate for several broken plate

TABLE XI

GHG concentrations and ranges

				N_2O (ppmv)				CH_4 (ppmv)				CO_2 (ppmv)			
Plant	**Process**	**Location**	**T℃**	**min**	**max**	**Avg**	**S**	**min**	**max**	**avg**	**S**	**min**	**max**	**avg**	**S**
Stickney															
	GC	inlet	13	0.6	337	113	137	3	1940	800	867	160	9600	4500	4300
		outlet	13	29	452	109	169	120	630	310	173	3850	8400	6500	1550
	AB-B	P1	16	*BD*	19	5.2	10	44	340	149	71	4604	8000	6600	1200
		P2	16	35	163	71	30	1	8	4	1.9	12800	18700	15300	1750
		P3	16	19	189	70	43	*BD*	19	8	4.1	12550	18250	15800	1750
		P4	16	3.7	43	16	13	*BD*	1	0.1	0.5	10050	15250	12600	1750
	AB-D	P1	16	2.1	31	9.2	8.5	174	610	420	120	3700	8550	7700	1200
		P2	16	47	379	157	98	*BD*	8	3	2.5	9800	15600	12250	1600
		P3	16	45	406	186	109	*BD*	4	2	1.3	11100	15400	12550	1100
		P4	16	19	140	62	12	*BD*	3	1	0.3	9550	12800	11100	1500
	FST	Center	21	0.6	30	3.8	7.6	1	130	19	27	-	-	-	-
		Rake*	21	0.8	7.2	3.4	4.6	103	1030	550	674	-	-	-	-
	AD		32	1.0	57	11	8.6	304410	564900	429300	85100	95000	132000	117000	14900
	BP	wet (fresh)	21	*BD*	0.3	0.1	0.1	68	190	120	37	-	-	-	-
		dry (old)	24	19	111	64	26	*BD*	1	0.1	0.2	-	-	-	-
North Side															
	AB-B	1	19	-	-	3.1	-	-	-	200	-	-	-	-	-
		2	19	-	-	1.8	-	-	-	38	-	-	-	-	-
		3	19	-	-	9.0	-	-	-	4.6	-	-	-	-	-
		4	19	-	-	3.5	-	-	-	1.9	-	-	-	-	-
	AB-D	P1-1	21	-	-	12.5	-	-	-	15	-	-	-	-	-
		P1-2	21	-	-	3.5	-	-	-	97	-	-	-	-	-
		P1-3	21	-	-	0.6	-	-	-	24	-	-	-	-	-
		P1-4	21	-	-	4.4	-	-	-	14	-	-	-	-	-
		P2-1	21	-	-	20	-	-	-	8.0	-	-	-	-	-
		P2-2	21	-	-	9.7	-	-	-	2.4	-	-	-	-	-
		P2-3	21	-	-	0.8	-	-	-	1.0	-	-	-	-	-
		P2-4	21	-	-	8.2	-	-	-	5.8	-	-	-	-	-
	PST	center	23	0.1	0.5	0.1	-	*BD*	260	130	110	-	-	-	-
	FST	center	22	0.3	1.1	0.2	0.4	0.5	61	31	24	-	-	-	-
		channel	22	0.2	1.9	0.4	0.4	0.7	5	3	1.5	-	-	-	-
		corner	22	0.3	0.4	-	0.4	1.5	3	2	-	-	-	-	-
Egan															
	AB	1	18	-	-	6.6	-	-	-	34	-	-	-	6500	-
	South	2	18	-	-	46	-	-	-	21	-	-	-	9200	-
		3	18	-	-	28	-	-	-	6	-	-	-	7100	-
		4	18	-	-	18	-	-	-	1	-	-	-	6500	-
		5	18	-	-	13	-	-	-	0.4	-	-	-	6500	-
		6	18	-	-	6.1	-	-	-	*BD*	-	-	-	4850	-
		7	18	-	-	5.5	-	-	-	*BD*	-	-	-	5500	-
		8	18	-	-	4.0	-	-	-	*BD*	-	-	-	5300	-
	AB	1	21	-	-	8.6	-	-	-	240	-	-	-	-	-
	North	2	21	-	-	31	-	-	-	96	-	-	-	-	-
		3	21	-	-	35	-	-	-	53	-	-	-	-	-
		4	21	-	-	79	-	-	-	6	-	-	-	-	-
		5	21	-	-	80	-	-	-	6	-	-	-	-	-
		6	21	-	-	34	-	-	-	210	-	-	-	-	-
		7	21	-	-	6	-	-	-	19	-	-	-	-	-
		8	21	-	-	55	-	-	-	5	-	-	-	-	-
	FST	center	21	*BD*	*BD*	0.0	-	0.4	5	2	-	-	-	-	-
		channel	21	*BD*	0.4	0.2	-	0.4	3	1	-	-	-	-	-

S=standard deviation; BD=below detection; - datum not available; AB=Aeration Basin; BP=Biosolid Piles; FST=Final Settling Tanks; GC=Grit Chamber; PST=Primary Settling Tanks; *the rake datum was obtained allowing the accumulation chamber to follow the tank rake for one full rotation (45 minutes).

TABLE XII.

SUMMARY OF SIGNIFICANT GREENHOUSE GAS FLUXES AND SOURCES.

Plant	Process	N_2O flux (kg/y)	CH_4 flux (kg/y)	CO_2 flux (kg/y)	N_2O g/Pe/y	CH_4 g/Pe/y	CO_2 g/Pe/y
Stickney	Grit chamber	$7.5x10^4$	$1.3x10^5$	$3.8x10^6$	30.1	52.2	1515
	Aeration basins	$5.1x10^5$	$2.0x10^5$	$1.1x10^8$	202.9	78.3	42240
	Imhoff tanks	0.0	$2.2x10^6$	-	0.0	873.3	-
	Primary settling tanks	$1.8x10^2$	$5.2x10^3$	-	0.0	2.1	-
	Anaerobic digester	8.7	$1.4x10^5$	$3.9x10^4$	0.003	56.8	15.5
	Exhausts	$3.9x10^3$	$2.8x10^5$	-	1.6	112.0	-
	Biosolid piles	-	-	-	-	-	-
	Total:	**$5.9x10^5$**	**$2.8x10^6$**	**$1.1x10^8$**	**204.5**	**1122.5**	**42255**
North Side	Aeration basins	$1.6x10^4$	$6.4x10^4$	-	11.5	45.7	-
	Primary settling tanks	0.0	-	-	0.0	-	-
	Exhausts	$1.1x10^3$	$2.2x10^4$	-	0.8	15.4	-
	Total:	**$1.7x10^4$**	**$8.6x10^4$**	**-**	**12.3**	**61.1**	**-**
Egan	Aeration basins	$1.4x10^4$	$1.2x10^4$	-	84.2	71.2	-
	Primary settling tanks	0.0	$3.4x10^4$	-	0.0	198.3	-
	Exhausts	$1.3x10^3$	$1.4x10^4$	-	7.6	84.1	-
	Total:	**$1.6x10^4$**	**$6.0x10^4$**	**-**	**91.8**	**353.6**	**-**

diffusers. In the normal aeration basins, N_2O ranged from below detection to 190 ppmv, CH_4 from below detection to 340 ppmv, and CO_2 from 4,600 to 18,700 ppmv. The overareated battery showed higher average N_2O and CH_4, and lower average CO_2 concentrations in all passes, with N_2O ranging from 2.1 to 410 ppmv, CH_4 from below detection to 610 ppmv, and CO_2 from 3,700 to 15,600 ppmv. The highest CH_4 concentrations were observed toward the inlets. Systematic variations were observed in N_2O and CH_4 emissions along the flow path in the aeration basins (**Figure 18**). Methane decreases rapidly with distance from the inlet. Nitrous oxide emissions were generally low at the inlet (5-9 ppmv), and increased toward the middle point of the tanks (70-189 ppmv), where DO levels were 1-3 mg/L; subsequently, N_2O emissions tended to decrease toward the outlet of the tank (16-62 ppmv), where DO levels were 5-6 mg/L. Additionally, higher N_2O and CH_4 emissions were observed between 7:00-9:00 and 16:00-19:00 hours (**Figure 19**). The secondary clarifiers had N_2O concentrations ranging from 0.6 to 30 ppmv, and CH_4 concentrations ranging from 0.5 to 126 ppmv. However, when the accumulation chamber was attached to the tank scraper (which disturbs the sludge deposited at the bottom), CH4 concentrations reached 1032 ppmv. The anaerobic digesters had fugitive emissions (leak) constituted by 30-60% CH4, 1-13% CO2, and relatively low N2O (0.8 to 57 ppmv). The Imhoff tanks showed an average CH4 accumulation factor (θ, Equation 2.4) of 444 ppmv/min, and negligible N2O accumulation. Sampling of the Biosolid drying beds showed CH4 concentrations of 68-194 ppmv when freshly piled, and N2O concentrations of 19-110 ppmv when dry.

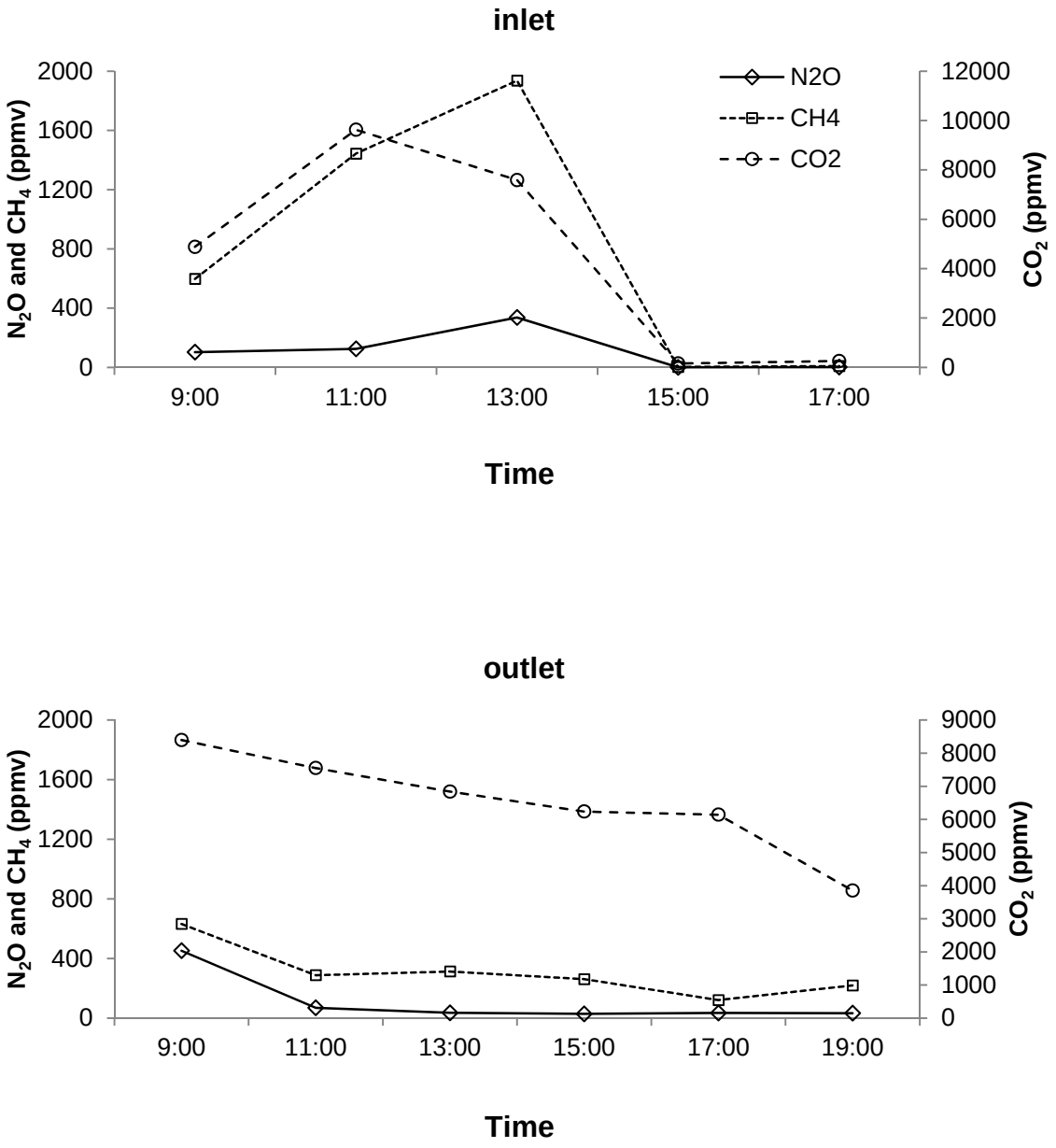

Figure 17. Variation of N_2O, CH_4, and CO_2 headspace concentrations measured at the inlet (top) and outlet (bottom) of the grit chamber versus time of the day.

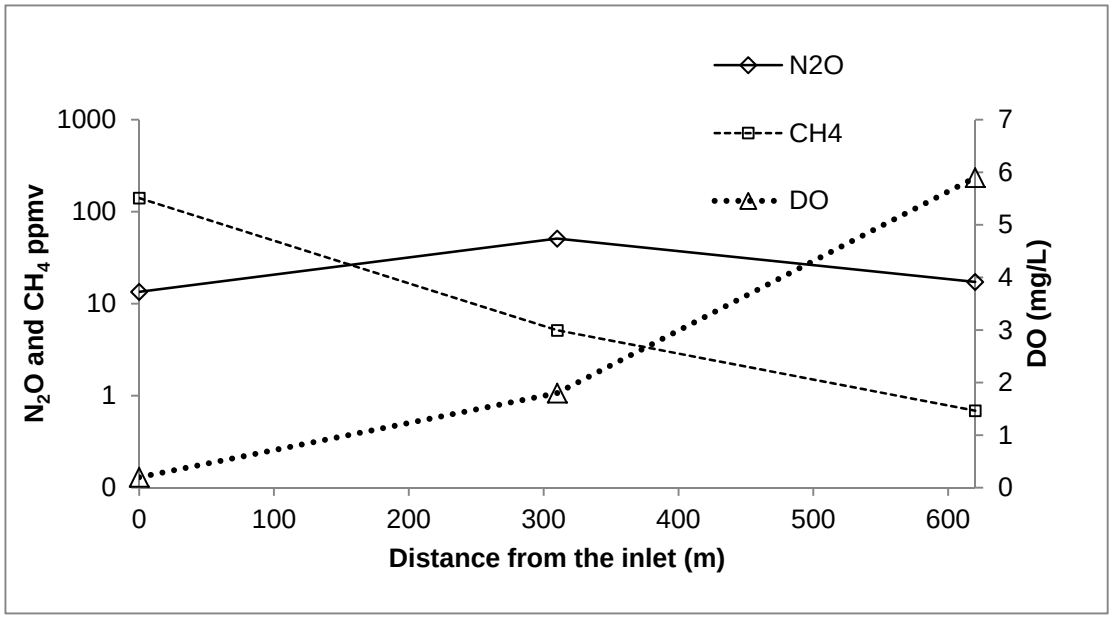

Figure 18. Average daily headspace N_2O and CH_4 concentrations and DO at Stickney aeration basin B, tank 1.

However, when the closed chamber method was used (Rolston, 1986), no significant fluxes were measured from the biosolid piles. Overall (Figure 20), aeration basins constitute the main source of N_2O (5.1 x 105 kg/y), followed by grit chambers (7.5 x 104 kg/y). The main source of CH_4 are the Imhoff tanks (2.2 x 106 kg/y), followed by the plant exhausts (2.8x105 kg/y), the aeration basins (2.0 x 105 kg/y), the anaerobic digesters and the grit chamber (1.4 x 105 and 1.3 x 105 kg/y respectively). The calculated cummulative fluxes from the Stickney WWTP were 5.9 x 105 ± 22% kg N_2O/y, equivalent to 204 g/Pe/y, and 2.8 x 106 ± 17% kg CH_4/y or 1122 g/Pe/y.

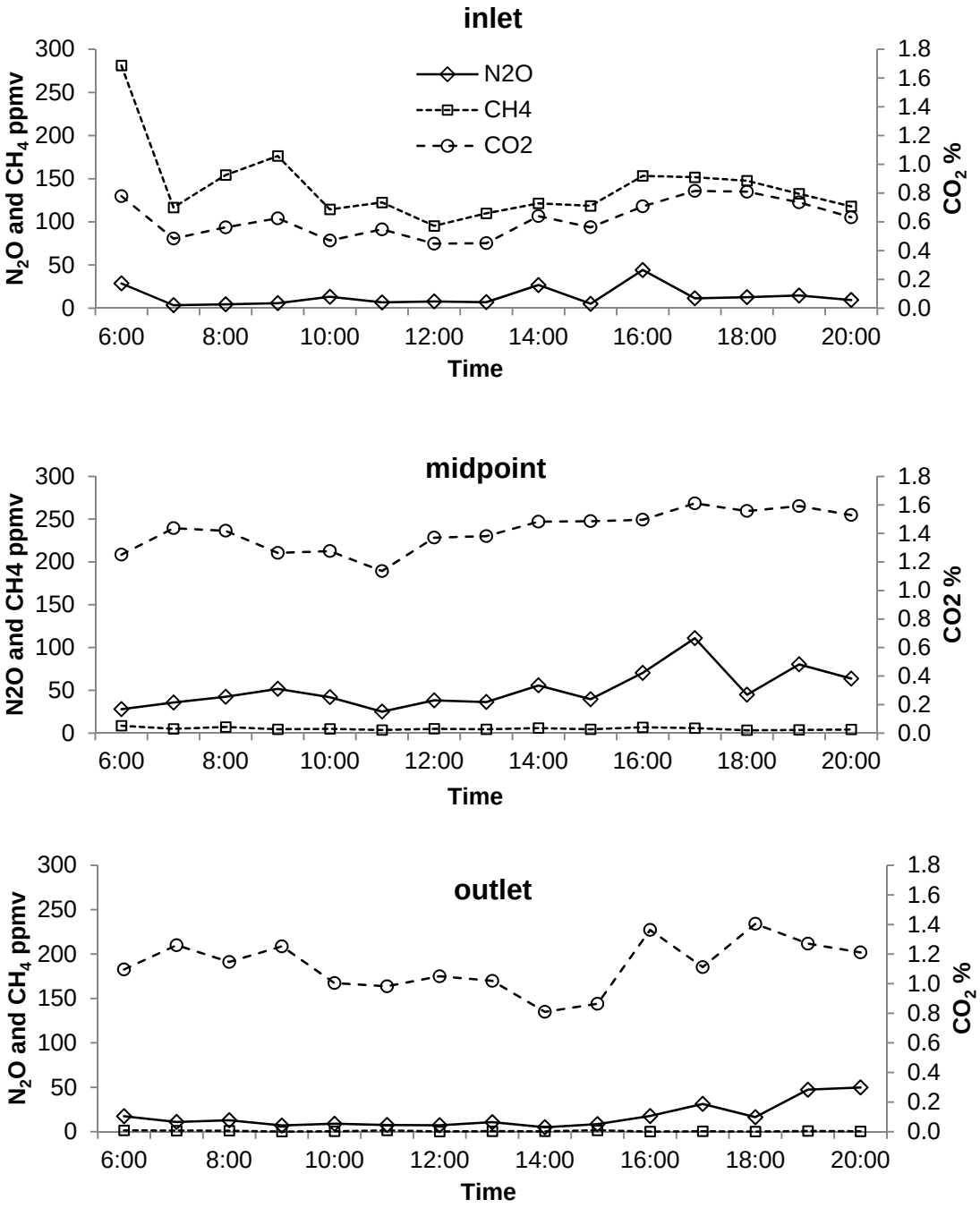

Figure 19. Average concentrations of fugitive N_2O, CH_4, and CO_2 throughout the day for Stickney aeration basin B at inlet, midpoint, and outlet of a single tank.

4.4.2 North Side

The primary settling tanks at North Side WWTP showed N_2O concentrations ranging from 0.1 to 0.5 ppmv, and CH_4 concentrations from below detection to 264 ppmv. The aeration basins showed low N_2O concentrations (0.6-20 ppmv) and CH_4 concentrations ranging from 1 to 205 ppmv. Variations of N_2O concentrations did not appear to be systematic along the flow path, while CH_4 concentrations were higher in proximity of the inlets, and decreased rapidly as in the Stickney plant. The final settling tanks showed low N_2O emission rates (0.1-1.9 ppmv) and CH_4 concentrations ranging from 2 to 264 ppmv. Fluxes calculated for North Side were 1.4×10^4 kg/y N_2O and 6.4×10^4 kg/y CH_4 from the aeration basins. The second highest contributors to fugitive emissions are the plant exhausts, with 1.7×10^4 kg/y N_2O and 8.6×10^4 kg/y CH_4. Greenhouse gas emissions from the primary settling tanks presented high temporal variability; N_2O emissions were negligible, while a great uncertainty remains for CH_4 emissions. Total fluxes were 1.7×10^4 kg/y N_2O (12 g/Pe/y) and 8.6×10^4 kg/y CH_4 (61 g/Pe/y).

4.4.3 Egan

The primary settling tanks were sampled with a closed chamber method (Rolston et al., 1986) and calculated fluxes were negligible for N_2O and 3.4×10^4 kg/y for CH_4, the largest CH_4 flux at Egan. The north aeration basin, equipped with full plate air diffusers, showed N_2O concentrations from 6 to 80 ppmv, and CH_4 concentrations from 1

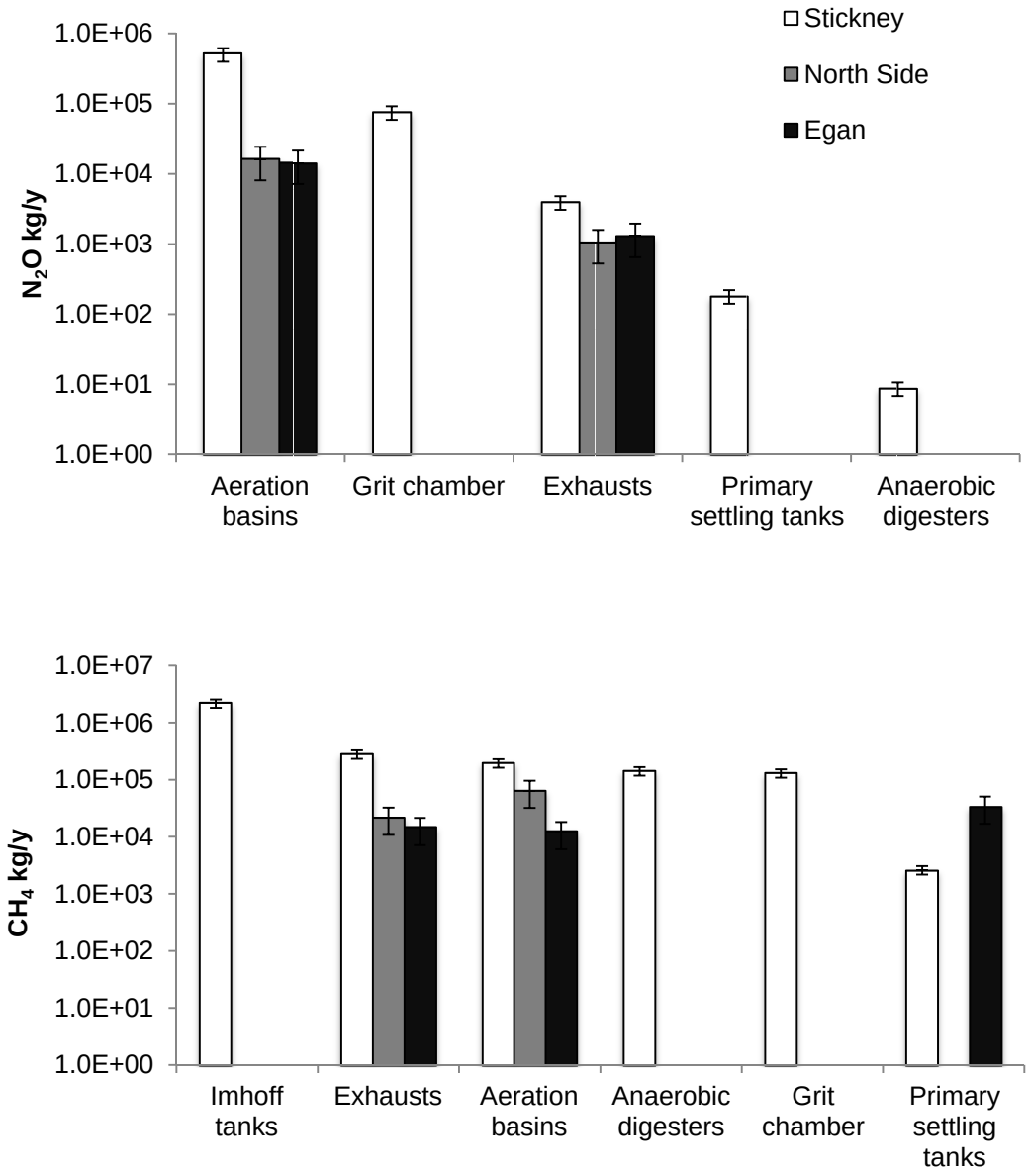

Figure 20. Significant sources of N_2O (top) and CH_4 (bottom) for the three WWTPs investigated. Error bars are calculated for the 95% confidence interval for Stickney. For North Side and Egan the error bars represent a 50% error; actual error could not be calculated.

to 34 ppmv. The south aeration basin, equipped with spiral-roll diffusers, showed N_2O values ranging from 4 to 46 ppmv and CH_4 from 5 to 241 ppmv. In aeration basins N_2O emissions increased along the flow path to decrease toward the outlet of the tanks. One exception is the very last sampling point of the north aeration basin, located near the outlet, where 55 ppmv of N_2O were measured. As seen in the other WWTPs, concentrations of CH_4 are high near the inlet, to decrease along the flow path. However, 208 ppmv of CH_4 were measured about 2/3 down the flow path in proximity of the second baffle. The N_2O fluxes for north and south basin were 1.1×10^4 kg/y and 2.9×10^3 kg/y respectively, for a total of 1.4×10^4 kg/y N_2O. Fluxes for CH_4 were 7.9×10^3 and 4.2×10^3 kg/y for north and south basin respectively, for a total of 1.2×10^4 kg/y CH_4. The exhausts accounted for 1.3×10^4 kg/y N_2O and 1.4×10^4 kg/y CH_4. Total fluxes were 1.6×10^4 kg/y N_2O (91.8 g/Pe/y) and 6.0×10^4 CH_4 (353.6 g/Pe/y).

4.5 DISCUSSION

Variable amounts of GHG emissions were observed from all the treatment steps and exhausts that were sampled. Emissions from treatment tanks can also be enhanced by the aeration. For example, the high concentrations of N_2O and CH_4 observed at the inlet of the grit chamber, in combination with the short residence time of the water in this tank (< 2 hr) suggest that greenhouse gas might be produce upstream in the sewer system and

consequently released in the aerated grit chamber through an air-stripping effect. Similarly, the high CH_4 concentrations observed at the inlet of the aeration basins could be either produced in situ through methanogenesis, due to the low dissolved oxygen levels (< 0.2 mg/L), or could be carried over from the anaerobic primary settling tanks.

A hot spot for N_2O emissions is constituted by the aeration basins as pointed out elsewhere (Czepiel et al., 1995; Kampschreur et al., 2008; Ahn et al., 2010). The aeration basins contribute ~85-95% of N_2O. Nitrous oxide is mainly produced in the middle portion of the tanks, where DO levels are > 1 mg/L. This is consistent with other studies (Kimochi et al., 1998; Ahn et al., 2010), where the highest N_2O emissions were also seen in the aerobic portion of the tanks. The high N_2O concentrations observed at the overaerated battery D at Stickney suggest that overaeration, and in general terms a fast rate of variation of DO levels, has a significant impact on N_2O emission (Kimochi et al., 1998). The grit chamber at Stickney also accounts for 13% of the total N_2O. Another important contribution of N_2O is the exhausts, which accounted for 0.7%, 6%, and 8% of the total N_2O flux at Stickney, North Side, and Egan respectively although North Side and Egan values are likely overstimated as grit chamber N_2O emissions could not be measured at those plants.

The exact biological source of N_2O emissions from the aerated tanks has not yet been unequivocally determined. Several biological pathways can be responsible for N_2O production, including incomplete denitrification due to oxygen inhibition, nitrification under variable DO levels, and nitrifier denitrification (Ritchie and Nicholas, 1972;

Knowles, 1982; Anderson and Levine, 1986; Kester et al., 1997; Zumft, 1997; Kampshreur et al., 2008). The NO_2-N showed good positive correlation with N_2O emissions at the aeration basins at Stickney ($R^2 = 0.7$), followed by a moderate positive correlation between N_2O and DO ($R^2 = 0.38$). This could be interpreted in two ways: (1) N_2O is correlated to NO_2^- and DO because it is produced during nitrification of ammonia; (2) N_2O is produced by oxygen-inhibited incomplete denitrification, which is more prominent at higher NO_2^- concentrations.

The N_2O emission factor values calculated for North Side (12.3 g/Pe/y) and Egan (91.8 g/Pe/y) are in good agreement with similar values calculated for other undisclosed US WWTPs (Ahn et al., 2010), while the emission factor value for Stickney (204 g/Pe/y) is higher. Part of this discrepancy can be explained by the fact that the present study also includes emissions from sources other than the ammonia nitrification treatment. Given the average TKN values of 33, 20, and 28 mg/L, our calculations show that about 0.94%, 0.16%, and 0.97% of the incoming TKN is emitted as N_2O at Stickney, North Side, and Egan respectively; this is within the range found in previous studies (0.01 to 1.8%; Ahn et al., 2010). N_2O emissions at North Side, normalized to the average TKN, are low compared to the other two plants, resulting in only 12 g/Pe/y N_2O emitted, compared to the 204 g/Pe/y for Stickney and the 92 g/Pe/y for Egan. While several reasons can account for this low value, including specific wastewater characteristics at the time of sampling, the distinct aeration technique employed at North Side (tapered), and the lack of industrial wastewater in the effluent might explain the difference with the other plants

studied. Further studies are required to identify the biological source(s) of the N_2O being emitted to the atmosphere.

The distribution of CH_4 emissions followed a different pattern than N_2O. At Stickney, the most significant contribution to fugitive CH_4 is given by the Imhoff tanks, which account for 74% of the total CH_4 flux. Other contributions include exhausts (10%), aeration basins (7%), anaerobic digesters (5%), and the grit chamber (4%). The Stickney WWTP also employs facultative lagoons for sludge treatment, which were not sampled during this study, but are expected to be significant sources of CH_4, which might significantly increase the estimated CH_4 total flux. Additionally, roughly 2.6×10^8 kg/y of CH_4 are re-captured from the anaerobic digesters gas (60-65% CH_4) for beneficial use. Of this, about 80-85% is used at the plant, while the remaining 15-20% is flared. The flares are not 100% efficient; therefore some unburned CH_4 is also released to the atmosphere during combustion. This contribution has not been included in this study. At North Side, the aeration basins and exhausts contributed to 75% of and 25% of the CH_4 emissions respectively. The amount of CH_4 released from the aeration basins at this plant is higher than N_2O; this might indicate that the tapered aeration system at North Side plays a role in both decreasing the amount of N_2O produced, and limiting the oxygenation of the tanks, leading to a higher CH_4 production. At the Egan plant CH_4 emissions are dominated by the primary settling tanks contribution (56%), followed by exhausts (24%) and aeration basins (20%). Addittional CH_4 is likely to be emitted from the primary settling tanks at this plant. Additionally, significant concentrations of CH_4 were observed

in aeration basin North within the second baffle. The reason for the observed CH_4 production could be related to local anaerobic conditions depending on accumulation of organic matter or bacterial flock in this specific area of the tank, which is not aerated.

In general, the presence of CH_4 in the aeration basins off-gas suggests the presence of anaerobic pockets and/or micro-sites within the microbial floc. Furthermore, anaerobic activity still persists in the secondary clarifiers, as suggested by the buildup of significant CH_4 concentrations within the sampling hood when this was attached to the tank scraper. It is uncertain whether or not the biosolid piles constitute a significant source of N_2O (dry piles) or CH_4 (wet piles) to the atmosphere. The accumulation of these gases was significant only when the piles were disturbed upon insertion of the sampling hood, so an actual flux was not observed. It is likely, however, that N_2O and CH_4 accumulate in the pore space of the biosolids and diffuse out at a small rate, unless the piles are disturbed (for example when they are turned over to facilitate the drying) or when the pore gas is displaced by rainwater.

The amount of CH_4 (kg/y) released by the plants is in general larger than the amount of N_2O and the emission ratio CH_4/N_2O in kg/kg is 4.8, 5.0, and 3.8 for Stickney, North Side, and Egan respectively. It will be of further interest to investigate the conservatism in CH_4/N_2O flux ratios ratios within and across plants based on similar technologies or effluent characteristics. The CO_2 emissions are associated with a variety of processes, since CO_2 is produced both through aerobic respiration, anoxic

fermentation, and methanotrophy; however, this greenhouse gas is assumed to be C-neutral in wastewater treatment (Keller and Hartley, 2003).

Due to the fact that during cold periods the aeration basin receives warm air to maintain the wastewater temperature in an optimum range to facilitate microbiological activity, the temperature of the wastewater varied by only ~7°C. However, we did not observe any correlation between temperature of the wastewater and GHG emissions from the aeration basins from the three plants. Additionally, no correlation was observed between precipitation data, obtained from the monthly operating data from the MWRDGC, and GHG emissions. It is important, however, to notice two limitations of this study: (1) our data are limited to specific days and times of the day, and no samples were collected at night time (between 20:00 and 6:00); (2) our data are limited to the months June-December, therefore we have no constraints on any changes in GHG emissions that might take place during the coldest months of the year (December through March).

When applied to the Stickney WWTP, the IPCC model adopted by USEPA predicts emissions of 1.6×10^4 kg/y of N_2O and 1.03×10^7 kg/y of CH_4 (not including the CH_4 recaptured). Our CH_4 estimates are lower than predicted, as CH_4 contributions from the facultative lagoon were not accounted for. However, our N_2O estimates of 5.9×10^5 kg/y are substantially higher than those predicted by the model. Smaller contributions to emissions of N_2O, and CH_4 in particular, come from generally overlooked sources such as grit chambers, plant exhausts, as leaks from anaerobic digesters, and from currently

employed obsolete technology (e.g. Imhoff tanks), that is being replaced with new and more efficient designs. This suggests that full-scale studies of greenhouse gas emissions from WWTPs are a key factor in determining correct emission factor values on a plant basis. If these estimates for N_2O emissions prove to be correct, and representative of a large number of US WWTPs, the USEPA estimates for N_2O emissions from WWTPs could be largely underestimated (up to 1.5 orders of magnitude). This also implies that the global N_2O budget should be revised to accommodate these higher antrophogenic emissions. At the moment, there is great uncertainty concerning the amount of N_2O released through the use of both synthetic and natural fertilizers in agricultural soils (Davidson, 2009), and the role of soils as sinks of N_2O (Mosier et al., 1998). Furthermore, the IPCC methodology used to estimate N_2O emissions (De Klein et al., 2006) is based on mean emission factors that need to be extrapolated across vaste regions, resulting in large errors for the source estimates. It is likely that these increased anthropogenic emissions from WWTPs can be accommodated within the N_2O global budget as our ability to constraint each source increases.

4.6 CONCLUSIONS

At the Stickney, North Side, and Egan WWTPs, total fluxes of N_2O, CH_4, and CO_2 (Stickney only) were determined. The calculated cummulative fluxes from the

Stickney WWTP were $5.1x10^5$ kg N_2O/y, or 204 g/Pe/y, and 2.8×10^6 kgCH_4/y or 1122 g/Pe/y. The calculated cumulative fluxes for the North Side WWTP were 1.7×10^4 kg/y N_2O, or 12.3 g/Pe/y, and 8.6×10^4 kg/y CH_4, or 61.1 g/Pe/y. The calculated cummulative fluxes from the Egan WWTP were 1.6×10^4 kg/y N_2O, or 91.8 g/Pe/y, and 6.0×10^4 CH_4, or 353.6 g/Pe/y. About 0.94%, 0.16%, and 0.97% of the incoming TKN is emitted as N_2O at Stickney, North Side, and Egan respectively. The aeration basins invariably constitute the main source of N_2O (>85%). Main sources of CH_4 are primary tanks (particularly Imhoff), anaerobic digesters, plant exhausts, and aeration basins. The IPCC model used by USEPA to estimate N_2O and CH_4 emissions appears to underestimate the former by up to t1.5 orders of magnitude.

CHAPTER 5

STABLE ISOTOPE AND ISOTOPOMERIC CONSTRAINTS ON NITROUS OXIDE PRODUCTION IN THE STICKNEY AERATION BASINS AND CARBON ISOTOPE ANALYSIS OF OFF-GAS AND SUSPENDED SOLIDS

5.1 INTRODUCTION

A detailed study on N_2O, CH_4, and CO_2 emissions from aeration battery B was conducted at the Stickney WWTP between June and November 2010. The main objective of this study was to use concentrations, and bulk and site-specific N stable isotope data on $N_2O(g)$ and aqueous nitrogen species (NH_3-N and NO_3-N) to determine: (1) distribution of the aqueous N species along the flow path of the wastewater in a single aeration basin tank; (2) stable isotope trends in the aqueous N species along the wastewater flow path that could be related to nitrification and/or denitrification processes; (3) production mechanism of N_2O based on the site preference (SP) data; and (4) a N isotope mass balance for a representative tank of the aeration basin. An additional objective was to use ^{14}C and ^{13}C isotope data for CH_4 and CO_2 emissions from the aeration basin, the anaerobic digesters, and the Imhoff tanks, to characterize their C sources. Additionally, off-gas emission samples were collected 15 times during the period June-November 2010 to obtain a better constraint on the variability of off-gas

emissions through time. Samples were collected from five Type II hoods (Section 2.2) placed along the wastewater flow path. A total of 150 off-gas samples for N_2O, CH_4, and CO_2 concentrations and isotopic analysis, 30 aqueous samples for N stable isotope analysis in NH_4^+ and NO_3^-, 10 off-gas samples for N_2O bulk isotopic and isotopomeric analysis, and related aqueous samples for water quality analyses were collected. Additionally, 15 samples of suspended solids were collected for $\delta^{15}N$ and $\delta^{13}C$ analysis.

5.2 SAMPLING COVERAGE AND METHODS

During this phase, all gas samples were collected using Type II hoods and Method 1 (see sections 2.1 and 2.2). The Stickney WWTP utilizes four aeration basins for biological nitrification of ammonia; a single aeration basin includes eight tanks, each one consisting of four passes; five hoods were placed in a single tank (tank #1) of the aeration basin B. Depending on the wastewater flow, the residence time in the tank is approximately 8 to 10 hours. Three hoods were placed in the first pass, starting from the tank inlet, one hood was placed halfway between passes 2 and 3, and the last hood was placed at the outlet (**Figure 21**). When summed together, the total length of the four passes, which corresponds to the total flow path length of the wastewater, is approximately 520 m. The distances of the hoods from the *inlet* of the tank were therefore 2, 65, 130, 260, and 520 m, respectively. After placement, the hoods were allowed to

equilibrate for three days before the first sample collection. Off-gas samples from the five hoods were collected on seven different days over the sampling period June-November 2010. During four of these days samples were collected at 10:00am, 2:00pm, and 6:00pm, for a total of 15 sets of samples. Associated water quality samples were collected as described in section 2.1 and analyzed at the Stickney WWTP laboratories as described in section 2.2. Temperature, DO, and pH were measured in situ with dedicated probes. All gas samples were analyzed using the SRI Greenhouse Gas GC as described in section 2.3. During 6 different days a total of 12 off-gas sample sets from hoods 1 to 5 were collected for $\delta^{13}CO_2$. During one aeration basin sampling event (July 6th, 2010) additional samples were collected: (1) water aliquots for stable isotope analysis of N aqueous species (NH_4^+ and NO_3^-); (2) additional off-gas samples for $\delta^{13}C$ and ^{14}C analysis of CO_2, $\delta^{13}C$ analysis of CH_4, and N_2O bulk isotopic and isotopomeric analysis; and (3) suspended solid samples for $\delta^{15}N$ and $\delta^{13}C$ analysis. In addition: (4) Imhoff tank off-gas was collected from three different tanks for $\delta^{13}CO_2$ analysis from the tail and the central vent of a single tank; (5) anaerobic digester off-gas was collected for stable isotope analysis of CO_2, CH_4, and ^{14}C; this latter set of samples included grab samples from five digesters and a time series set of 4 samples collected every 15 minutes from digester 18. The additional off-gas samples were collected with methods 1 or 2 (Section 2.1). The analytical methods employed are described in section 2.2 (off-gas GC analysis), section 2.5 (stable isotopic and isotopomeric analyses of NH_4^+, NO_3^-, and N_2O) and section 2.6 ($\delta^{13}C$ analysis of CO_2 and CH_4, and ^{14}C analysis of CO_2).

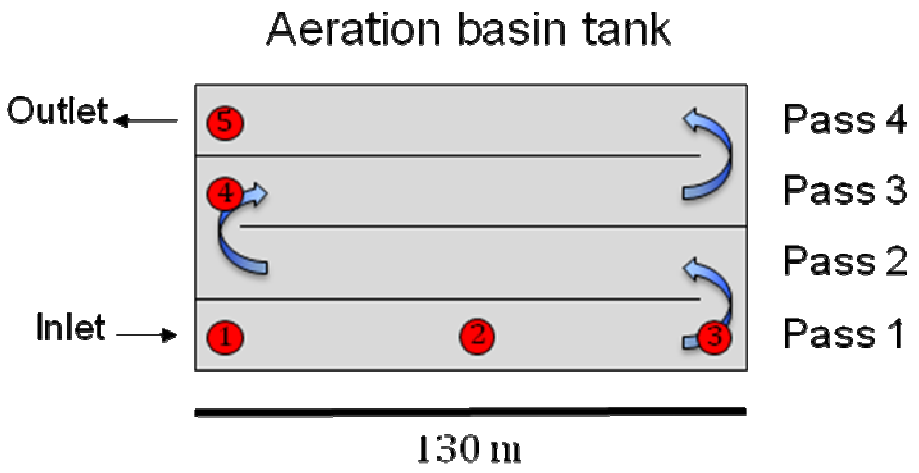

Figure 21. Representation of a single tank for the aeration basins at Stickney. The tank includes four passes. Blue arrows represent the wastewater flow path between passes going from the inlet to the outlet of the tank. Each pass (L x W x D) is 130 x 10 x 4.5 m. Red dots represent the position of the five sampling hoods used.

The total N_2O flux from the tank was calculated assuming that the averaged N_2O concentrations of hoods 1-2-3 is representative of the emissions of pass 1, that concentrations measured from hood 4 are representative of passes 2-3, and that concentrations measured from hood 5 are representative of pass 4. The total flux was calculated based on the amount of air pumped into the tank using equation 2.1. The air usage for the single tank was 4.3 x 10^6 m^3/day for the day of July 6th, and overall 1.2 x 10^9 m^3/year were used for entire aeration basin B in 2010. Stable isotopic compositions of N, C, O, and H are reported using the delta notation (Equation 2.6) with atmospheric N_2,

Vienna Pee Dee Belemnite (VPBD), and Vienna Standard Mean Ocean Water (VSMOW) as the isotopic references for N, C, and O and H, respectively.

5.3 RESULTS

5.3.1 Off-gas concentrations and wastewater quality

Off-gas and wastewater quality analysis results are presented in **Table XIII**. The temperature of the tank varied between 22.3 and 23.7ºC with an average of 22.9ºC; the pH of the water varied from 6.7 to 7.2 and averaged 7.0. The DO varied between 0 and 7.6 mg/L and increases from inlet to outlet.

Overall, off-gas N_2O, CH_4, and CO_2 concentrations present high variability. The N_2O concentrations vary between 0.3 and 99 ppmv with an average of 24 ppmv; CH_4 concentrations vary between 0.0 and 820 ppmv with an average of 160 ppmv; CO_2 concentrations vary between 7,100 and 26,400 ppmv with an average of 15,700. As observed for the 2009 study (Chapter 4), the distribution of the off-gas concentrations follows specific patterns. The N_2O concentrations are generally low toward the inlet and increase along the flow path, reaching a maximum at hood 4, and then decrease again toward the outlet (**Figure 22**). The CH_4 concentrations are higher in proximity of the tank inlet, and rapidly decrease toward the outlet of the tank (**Figure 23**). A pattern similar to N_2O is followed by CO_2 (**Figure 24**). Assuming that tank 1 is representative of the eight

TABLE XIII.

ANALYTICAL RESULTS FOR OFF-GAS EMISSIONS AND WATER QUALITY PARAMETERS.

Hood	Collection		CH_4	CO_2	N_2O	NH_3-N	NO_2-N	NO_3-N	TOC	TKN	COD	SS	pH	DO	T
#	day	time	ppmv	ppmv	ppmv	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L			mg/L	ºC
Off-gas and water quality samples															
1	7/5/2006	10AM	460	12,600	6.6	9.4	0.3	2.9	33.4	100	1,820	2,550	7.1	0.2	22.4
2	7/5/2006	10AM	130	11,950	8.9	8.3	0.5	3.8	26.9	97	141	1,470	6.9	0.1	23.1
3	7/5/2006	10AM	16	14,850	94	6	0.8	5.7	22.7	79	885	1,430	6.8	0.2	22.9
4	7/5/2006	10AM	98	2,500	99	1.4	0.7	9.4	35.5	121	1,842	1,240	6.7	1.8	23.3
5	7/5/2006	10AM	13	15,250	14	1.1	0.2	11.4	20.3	98	977	960	6.9	5.9	23.3
1	7/5/2006	2PM	490	12,250	9	8.2	0.4	1.6	37.8	114	947	2,540	7.1	0.1	22.7
2	7/5/2006	2PM	104	16,200	47	8.9	0.6	2.9	30.7	95	1,626	2,000	7	0.1	23
3	7/5/2006	2PM	12	14,200	80	7	0.8	4.2	33.1	133	1,842	1,500	6.8	0.8	23.5
4	7/5/2006	2PM	53	23,200	89	1.5	1.6	8.4	20.5	56	1,431	1,330	6.8	3.9	23.1
5	7/5/2006	2PM	16	18,050	-	1	0.1	11.2	32.2	115	1,561	1,480	7	7.6	23.3
1	7/5/2006	6PM	820	12,300	13	12.9	0.5	0.6	56.3	117	1,907	2,070	7.2	0.0	22.3
2	7/5/2006	6PM	310	12,400	12	12.8	0.2	1.4	36.2	107	1,950	1,900	7.1	0.6	22.8
3	7/5/2006	6PM	76	16,050	26	11.7	0.3	2.1	34.2	95	1,215	980	7	0.5	22.7
4	7/5/2006	6PM	80	21,500	78	5.6	1	4.8	34.8	109	1,539	920	6.9	2.1	22.5
5	7/5/2006	6PM	17	12,400	17	0.6	0.2	9.6	36.5	117	2,123	2,700	7	6.9	22.9
1	8/16/2006	11AM	520	14,500	31	12	0.2	0.1	43.2	107	1,534	3,280	7.1	0.1	23.7
2	8/16/2006	11AM	260	14,050	1.3	11.6	0.1	0	43.3	119	1,576	2,840	7	0.1	23.5
3	8/16/2006	11AM	37	18,900	2.5	8.9	0.1	0.5	49	151	2,065	2,920	7	0.2	23.2
4	8/16/2006	12PM	23	24,200	55	2.6	0.3	3.3	36.3	107	1,598	3,810	7	0.1	23.1
5	8/16/2006	12PM	12	17,250	11	1.6	0.1	4.1	60	184	2,914	3,690	7.1	4.8	23.3
1	8/16/2006	2PM	270	10,300	23	9.9	0.1	0.1	59.4	167	2,638	3,190	7.1	0.0	23
2	8/16/2006	1PM	106	-	0.3	9.3	0	0.1	26	77	1,003	3,500	7	0.1	22.9
3	8/16/2006	2PM	26	19,500	1.4	8.8	0	0.1	29.2	78	1,131	3,400	6.9	0.04	22.8
4	8/16/2006	2PM	17	24,200	47	5.6	0.3	2.2	32.8	103	1,343	3,580	7	0.04	23.3
5	8/16/2006	2PM	11	17,100	27	1.4	0.1	4.9	58.5	182	2,893	3,660	7.1	5.02	23.1
1	8/16/2006	6PM	341	12,200	38	11.8	0.2	0.2	47.6	128	1,959	2,260	7	0.03	22.6
2	8/16/2006	6PM	127	14,000	0.3	10.5	0	0	39	100	1,364	3,180	7	0.05	22.7
3	8/16/2006	6PM	119	18,550	1.7	9.2	0.1	0.2	44.6	145	2,022	3,530	6.9	0.05	22.8
4	8/16/2006	6PM	0	23,300	60	3.2	0.3	3	42	130	1,959	3,630	6.8	0.03	22.7

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TABLE XIII (Continued)

Hood #	Collection day	time	CH_4 ppmv	CO_2 ppmv	N_2O ppmv	NH_3-N mg/L	NO_2-N mg/L	NO_3-N mg/L	TOC mg/L	TKN mg/L	COD mg/L	SS	pH	DO mg/L	T °C
Off-gas and water quality samples															
5	8/16/2006	6PM	17	17,650	29	0.8	0.1	5.2	38.5	121	1,576	3,980	6.9	4.43	22.8
1	9/6/2006	10AM	688	9,400	21	10.9	0.2	1.3	58.5	130	2,147	2,470	7	0.28	22.5
2	9/6/2006	10AM	280	12,000	3.6	10.5	0.1	1.4	52.5	141	1,945	2,500	7	0.71	22.8
3	9/6/2006	10AM	65	16,600	1.1	9.6	0.1	2.1	46.6	124	1,807	2,480	7	1.03	22.5
4	9/6/2006	10AM	21	23,450	64	4.3	0.4	6	36.7	94	1,489	2,470	6.9	2.28	22.7
5	9/6/2006	10AM	3	13,350	13	0.9	0.1	10	49.3	127	1,977	2,480	6.8	6.84	22.6
1	9/6/2006	2PM	617	9,650	9	10.7	0.3	0.9	39.8	95	1,351	2,400	7.1	0.19	22.9
2	9/6/2006	2PM	314	12,350	3.2	10.6	0.2	1.7	45.4	113	1,627	2,430	7.1	0.79	22.8
3	9/6/2006	2PM	1	-	0.9	10.1	0.1	2.5	38.6	113	1,669	2,350	7	1.05	22.9
4	9/6/2006	2PM	22	23,660	73	5.1	0.5	6.7	39.9	104	1,616	2,430	6.8	2.57	23
5	9/6/2006	2PM	3	15,950	26	1.7	0.1	10.2	34.8	110	1,510	2,480	7.1	6.97	22.9
1	9/6/2006	6PM	553	8,800	8.3	13.7	0.4	1.2	46.9	123	2,210	2,410	7.1	0.24	22.6
2	9/6/2006	6PM	307	13,250	4.3	12.9	0.2	1.2	51.3	138	2,019	2,500	7	0.79	22.4
3	9/6/2006	6PM	62	15,050	0.8	11.4	0.1	1.4	39.1	102	1,499	2,350	6.9	1.13	22.4
4	9/6/2006	6PM	21	23,950	64	5.5	0.4	5.2	39.1	108	1,860	2,340	6.9	2.41	22.5
5	9/6/2006	6PM	4	14,400	20	1.3	0.1	10.1	45.9	133	1,945	2,560	6.9	6.32	22.6
Off-gas samples only															
1	7/8/2006	3PM	707	11,250	6	-	-	-	-	-	-	-	-	-	-
2	7/8/2006	3PM	149	10,450	3.4	-	-	-	-	-	-	-	-	-	-
3	7/8/2006	3PM	35	13,950	7.9	-	-	-	-	-	-	-	-	-	-
4	7/8/2006	3PM	50	16,750	29	-	-	-	-	-	-	-	-	-	-
5	7/8/2006	3PM	22	12,300	3.6	-	-	-	-	-	-	-	-	-	-
1	8/6/2006	12PM	706	18,000	7.4	-	-	-	-	-	-	-	-	-	-
2	8/6/2006	12PM	282	20,400	1.9	-	-	-	-	-	-	-	-	-	-
3	8/6/2006	12PM	47	18,350	1.6	-	-	-	-	-	-	-	-	-	-
4	8/6/2006	12PM	54	24,000	47	-	-	-	-	-	-	-	-	-	-
5	8/6/2006	12PM	24	19,150	9.1	-	-	-	-	-	-	-	-	-	-
1	6/28/2006	10AM	651	-	5.6	-	-	-	-	-	-	-	-	-	-

- datum not available

TABLE XIII (Continued)

Hood #	Collection day	time	CH_4 ppmv	CO_2 ppmv	N_2O ppmv	NH_3-N mg/L	NO_2-N mg/L	NO_3-N mg/L	TOC mg/L	TKN mg/L	COD mg/L	SS	pH	DO mg/L	T ºC
Off-gas samples only															
2	6/28/2006	10AM	381	14,300	1.7	-	-	-	-	-	-	-	-	-	-
3	6/28/2006	10AM	140	-	5.3	-	-	-	-	-	-	-	-	-	-
4	6/28/2006	10AM	103	26,350	23	-	-	-	-	-	-	-	-	-	-
5	6/28/2006	10AM	13	16,400	3.7	-	-	-	-	-	-	-	-	-	-
1	11/9/2011	10AM	140	8,000	56	-	-	-	-	-	-	-	-	-	-
2	11/9/2011	10AM	18	11,200	65	-	-	-	-	-	-	-	-	-	-
3	11/9/2011	10AM	4	16,900	17	-	-	-	-	-	-	-	-	-	-
4	11/9/2011	10AM	43	19,950	27	-	-	-	-	-	-	-	-	-	-
5	11/9/2011	10AM	5	16,700	40	-	-	-	-	-	-	-	-	-	-
1	11/9/2011	2PM	191	7,900	26	-	-	-	-	-	-	-	-	-	-
2	11/9/2011	2PM	40	9,200	25	-	-	-	-	-	-	-	-	-	-
3	11/9/2011	2PM	12	13,950	10	-	-	-	-	-	-	-	-	-	-
4	11/9/2011	2PM	50	21,300	30	-	-	-	-	-	-	-	-	-	-
5	11/9/2011	2PM	5	13,150	16	-	-	-	-	-	-	-	-	-	-
1	11/9/2011	6PM	328	7,100	19	-	-	-	-	-	-	-	-	-	-
2	11/9/2011	6PM	111	7,750	27	-	-	-	-	-	-	-	-	-	-
3	11/9/2011	6PM	39	12,500	6.7	-	-	-	-	-	-	-	-	-	-
4	11/9/2011	6PM	65	20,550	21	-	-	-	-	-	-	-	-	-	-
5	11/9/2011	6PM	4	12,300	11	-	-	-	-	-	-	-	-	-	-
	Average		159	15,700	24	7.2	0.3	3.7	40.1	116	1,690	2,493	7	1.8	22.9
	Stdev		210	4,800	25	4.3	0.3	3.5	10.1	25	504	815	0.1	2.4	0.3
	mean		54	14,850	15	8.8	0.2	2.5	39	113	1,627	2,480	7	0.6	22.8
	Max		819	25,350	99	13.7	1.6	11.4	60	184	2,914	3,980	7.2	7.6	23.7
	Min		0	7,100	0	0.6	0	0	20.3	56	141	920	6.7	0	22.3

- datum not available

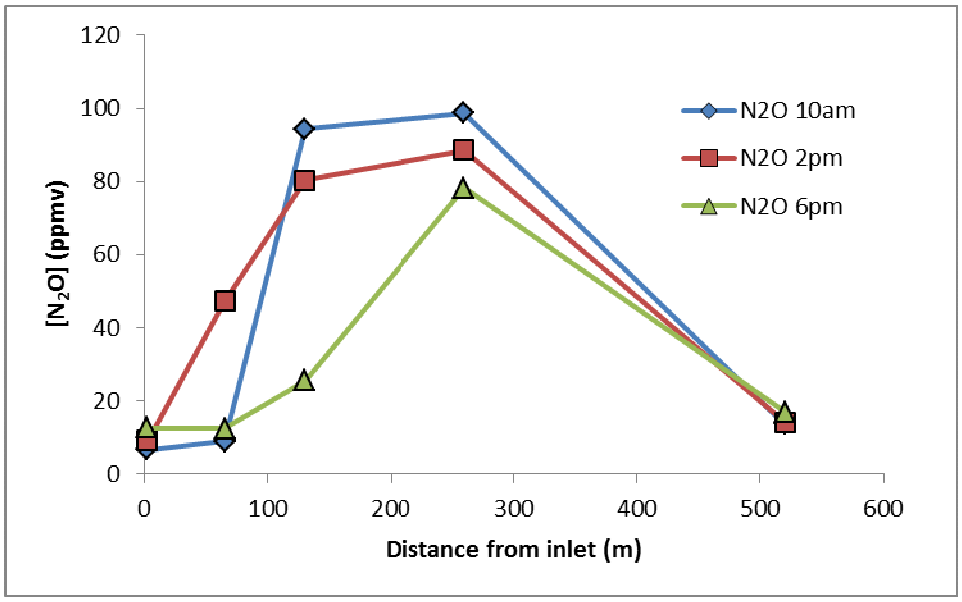

Figure 22. Representative N_2O trends as observed along the wastewater flow path in the aeration basin at different times of the day (data for July 6th, 2010).

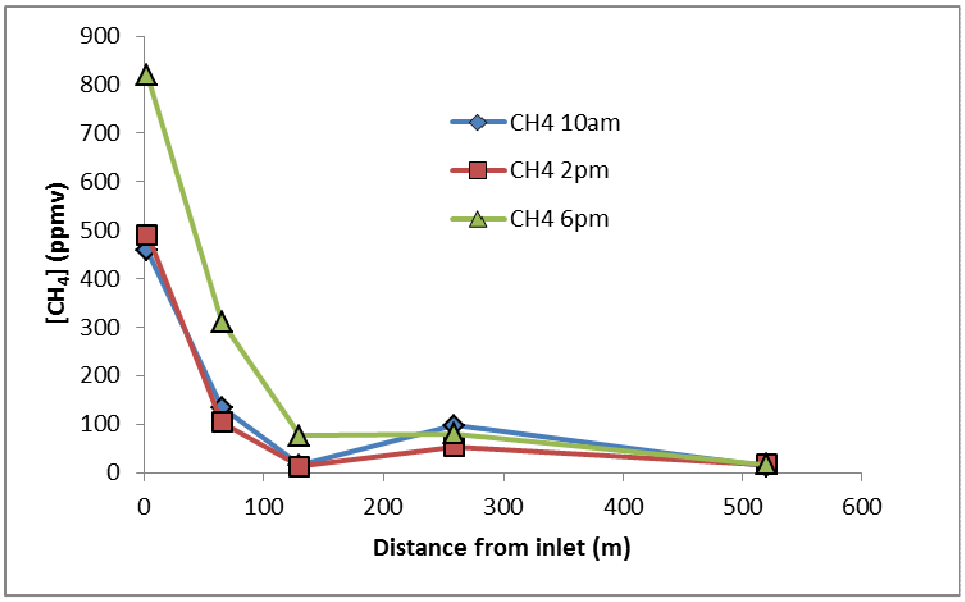

Figure 23. Representative CH_4 trends as observed along the wastewater flow path in the aeration basin at different times of the day (data for July 6th, 2010).

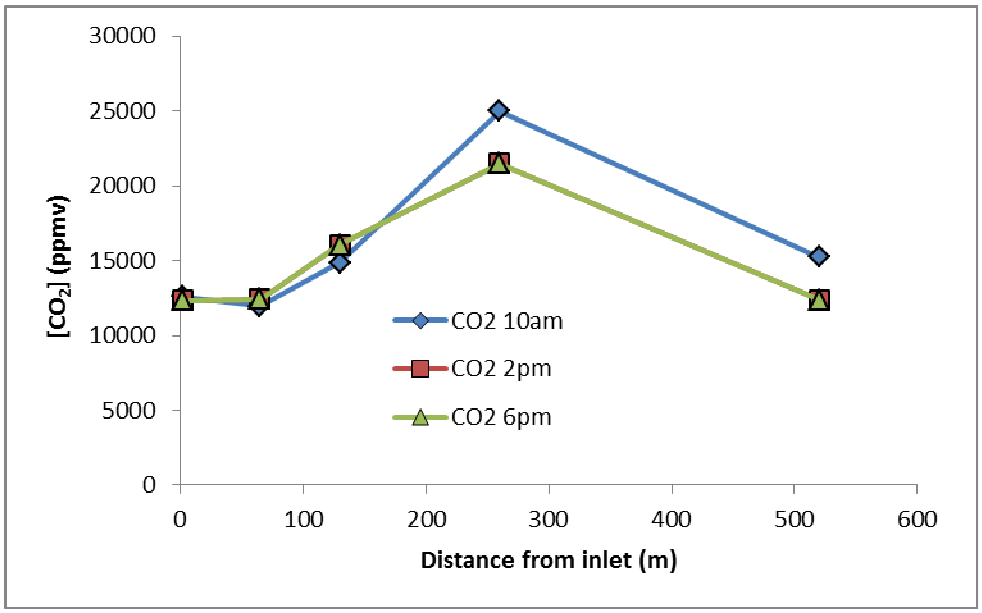

Figure 24. Representative CO_2 trends as observed along the wastewater flow path in the aeration basin B at different times of the day (data for July 6th, 2010).

tanks of aeration basin B, and given pumped air flux for the aeration basin of 1.2 x 10^9 m^3/y, the calculated N_2O, CH_4, and CO_2 fluxes for the aeration basin B were: 5.8 x 10^4, 7.2 x 10^4, and 3.4 x 10^7 kg/y for N_2O, CH_4, and CO_2 respectively. The N_2O flux, calculated for the single day of July 6th, is 390 kg/day, or 248 kg/day of N_2O-N. For the N aqueous species, NH_3-N varied between 0.6 and 13.6 mg/L with an average of 7.2 mg/L; NO_2-N varied between 0 and 1.6 mg/L with an average of 0.3 mg/L; NO_3-N varied between 0 and 11.4 mg/L with an average of 3.7 mg/L. The NH_3-N decreases from the inlet toward the outlet (**Figure 25**), while NO_3-N increases. The NO_2-N generally reaches a maximum at hood 4 and decreases again moving toward the outlet of the tank; however,

no systematic increase is observed from hood 1 to 3. Good correlation is generally observed between N_2O and NO_2^- (R^2 = 0.65, **Figure 26**). Given an average wastewater flow through aeration battery B of 6.2 x 10^8 L/day (datum relative to July 6th, 2010; Lanyon et al., 2010), and given an average NO_3-N concentration of 3.7mg/L, the total mass of NO_3^- flowing through the aeration basin in one day is 2,280 kg, resulting in 10.9% of the NO_3-N emitted as N_2O. Similar calculations for different sampling dates yield a range of 5-12% of NO_3-N converted to N_2O.

The suspended solids, which in first approximation are entirely constituted by the bacterial biomass in the aeration basin, varied between 920 and 3,980 mg/L, with an average of 2,493 mg/L. The COD varied between 141 and 2,914 mg/L averaging 1,690 mg/L. The Total Kjeldahl Nitrogen (TKN), which includes the organic nitrogen stored in the bacterial biomass, varied between 56 and 184 mg/L and averaged 116 mg/L. Finally, the Total Organic Carbon (TOC) varied between 20 and 60 mg/L, averaging 40 mg/L.

5.3.2 Stable isotope analysis of ammonium, nitrate, suspended solids, and nitrous oxide

Stable isotope rations of N and O in the aqueous N-species (NO_2^-/NO_3^- and NH_4^+) and N_2O were analyzed for the samples collected on July 6th, 2010. The bacterial method used to measure the $\delta^{15}N$ in the aqueous species (Section 2.5) does not distinguish between NO_3^- and NO_2^-, therefore the $\delta^{15}N$ values are inclusive of both aqueous species (**Table XIV**). Since the amount of NO_2^- remains generally low in the tank, the combined $\delta^{15}N$ of NO_2^- + NO_3^- will be referred to as $\delta^{15}N_{NO3}$ from here on. The $\delta^{15}N_{NO3}$ varied

between +5.3 and +20.4‰, while $\delta^{18}O_{NO3}$ varied between -1.6 and +8.0‰. A good linear correlation (R^2 = 0.89) is observed between $\delta^{18}O_{NO3}$ and $\delta^{15}N_{NO3}$ with a slope of 0.53 (**Figure 27**). The $\delta^{15}N_{NO3}$ initially decreases as the NO_3^- concentration increases, and it tends to increase again towards sampling hoods 4-5 (**Figure 28**).

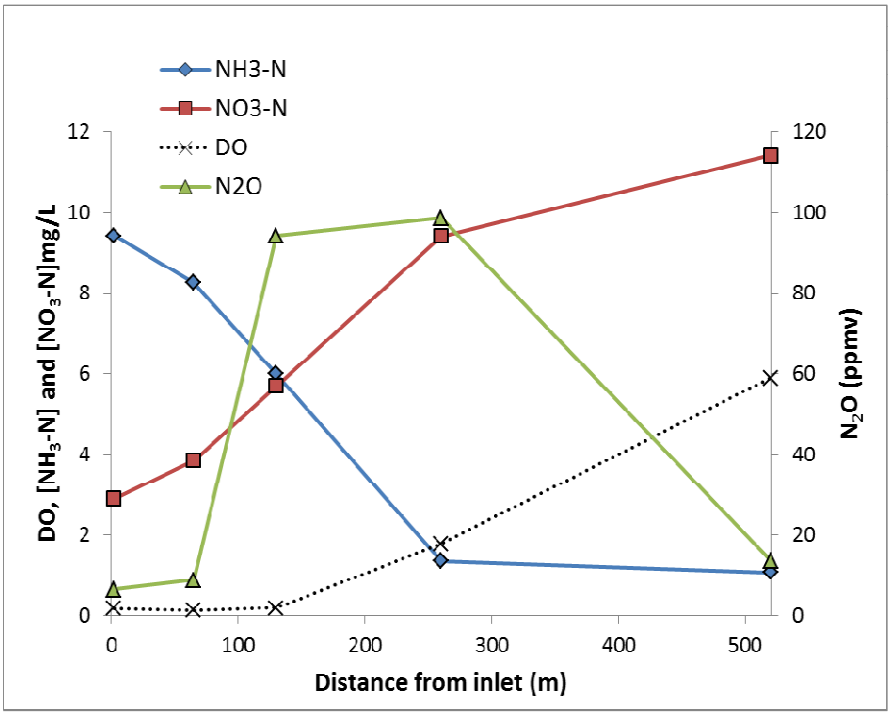

Figure 25. Representative concentration trends for the nitrogen aqueous species and dissolved oxygen along the flow path in aeration basin B at different times of the day (data for July 6th, 2010).

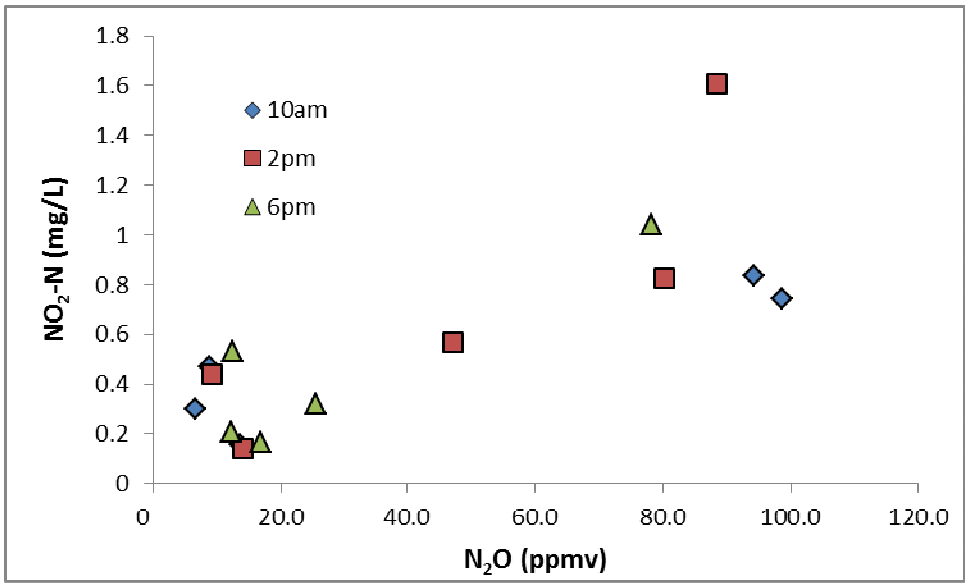

Figure 26. Measured N_2O(g) concentrations plotted against NO_2-N(aq) concentrations for aeration basin B at different times of the day. Data from July 6th, 2010. The R^2 value for the regression line (not shown) is 0.65.

The $\delta^{15}N$ of NH_3-N was determined on the ion NH_4^+ as at the pH range of the tank (6.7-7.2) NH_3 is present as NH_4^+, according to the reaction:

(5.1) $$NH_3 + H^+ \rightarrow NH_4^+$$

The $\delta^{15}N_{NH4}$ value varied between +6.1 and +49.4‰ and tends to increase with decreasing NH_4^+ concentration and decrease again towards hood 5 where NH_4^+ concentrations approach zero (**Figure 29**). The $\delta^{15}N$ value of the suspended solids was

almost constant throughout the tank, and averaged +6.8‰, with a range of +6.3 to +7.3‰ and a standard deviation of 0.2‰. Similarly, the $\delta^{13}C$ value of suspended solids was almost constant, averaging -20.2‰ (PDB), with a range of -19.9 to -20.5‰ and a standard deviation of 0.1‰.

The $\delta^{15}N_{N2O}$ (**Figure 30**) varies between +0.35 and -34.4‰ while $\delta^{18}O$ varies between +23.5 and +60.3‰. The highest $\delta^{15}N_{N2O}$ values are observed toward the inlet of the tank, where off-gas N_2O concentrations are low. As more N_2O is produced (hoods 3-4-5), the $\delta^{15}N_{N2O}$ values range from -20.5 to -34.4‰. Similarly, the highest $\delta^{18}O_{N2O}$ values (+49.4 to +60.3‰) are observed in the N_2O collected at hood 1, while for hoods 3-4-5 values range from +23.5 to +44.7‰. The N_2O SP values (**Figure 31**) range between +11.7 and -4.5‰ and average +2.7‰.

TABLE XIV.

STABLE N AND O ISOTOPE RESULTS FOR NITROGEN AQUEOUS SPECIES

Hood	time	T ℃	NH_4^+ µmol/L	NH_4^+ $\delta^{15}N$, ‰	$NO_3^- + NO_2^-$ $\delta^{15}N$, ‰	$NO_3^- + NO_2^-$ µmol/L	$NO_3^- + NO_2^-$ $\delta^{18}O$, ‰
1	10AM	22.4	601.2	+7.2	+11.9	403	+3.2
2	10AM	23.1	538.1	+11.3	+8.0	413	+1.6
3	10AM	22.9	374.3	+18.2	+5.3	610	+0.2
4	10AM	23.3	16.5	+17.6	+8.8	1011	+0.4
5	10AM	23.3	20.0	+7.4	+8.1	1002	-
1	2PM	22.7	702.5	+7.0	+20.4	207	+6.2
2	2PM	23	609.8	+10.6	+13.0	357	+3.8
3	2PM	23.5	-	-	+7.9	459	+1.5
4	2PM	23.1	56.3	+49.4	+7.4	900	-1.6
5	2PM	23.3	34.0	+8.3	+8.6	955	+1.5
1	6PM	22.3	917.7	+6.4	+18.8	248	+6.1
2	6PM	22.8	881.6	+8.3	+20.0	204	+8.0
3	6PM	22.7	781.2	+10.7	+13.6	280	+5.0
4	6PM	22.5	435.3	+19.9	+5.3	600	-1.5
5	6PM	22.9	7.0	+6.1	+10.2	991	+2.0

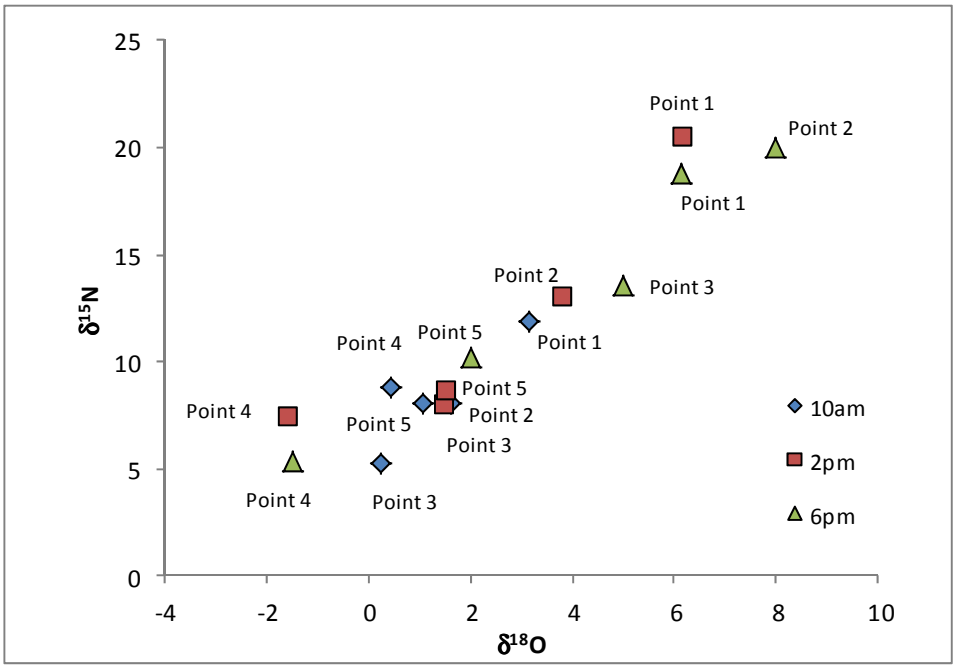

Figure 27. $\delta^{15}N$ (‰) and $\delta^{18}O$ (‰) values of NO_3^- along the flow path of the wastewater in aeration basin B at different times of the day. The sampling points correspond to hoods 1-5. The R^2 value of the regression line (not shown) is 0.89, with a slope of 0.53.

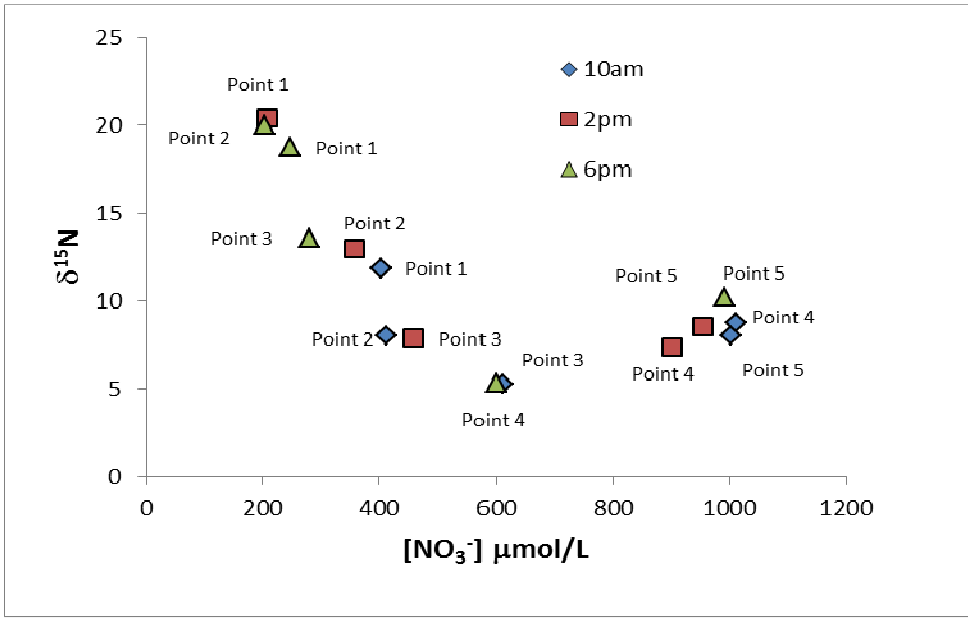

Figure 28. $\delta^{15}N$ values (‰) of nitrate versus nitrate concentration along the flow path of the wastewater in aeration basin B at different times of the day. The sampling points correspond to hoods 1-5.

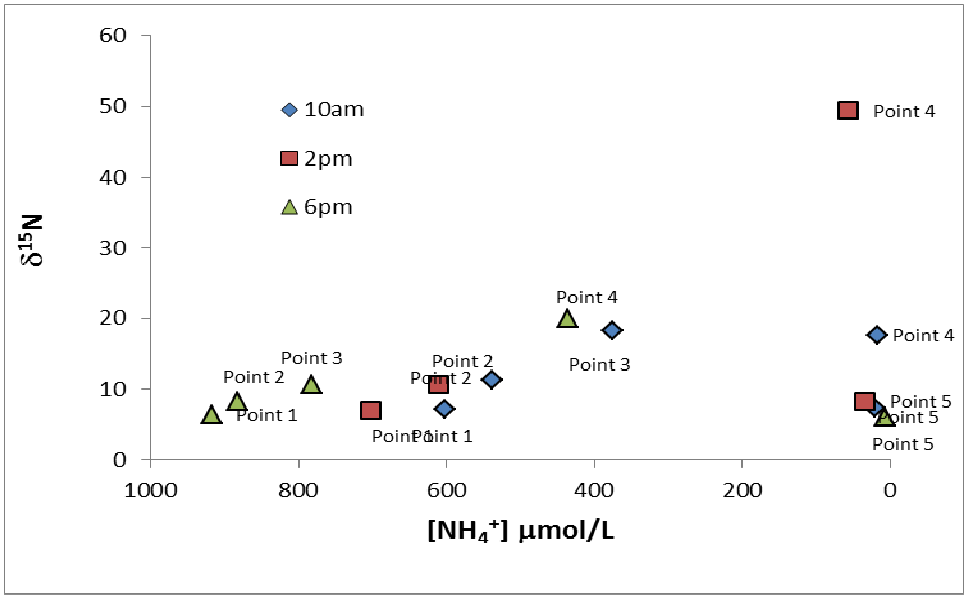

Figure 29. $\delta^{15}N$ value (‰) of ammonium versus ammonium concentration along the flow path of the wastewater in aeration basin B at different times of the day. The sampling points correspond to hoods 1-5.

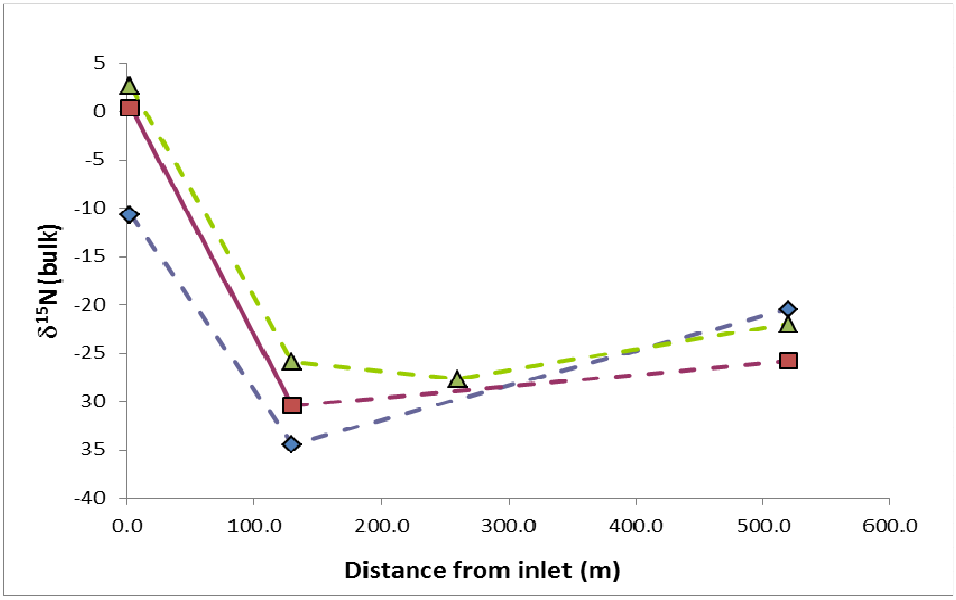

Figure 30. Bulk off-gas N_2O isotopic composition along the flow path of the wastewater in aeration basin B.

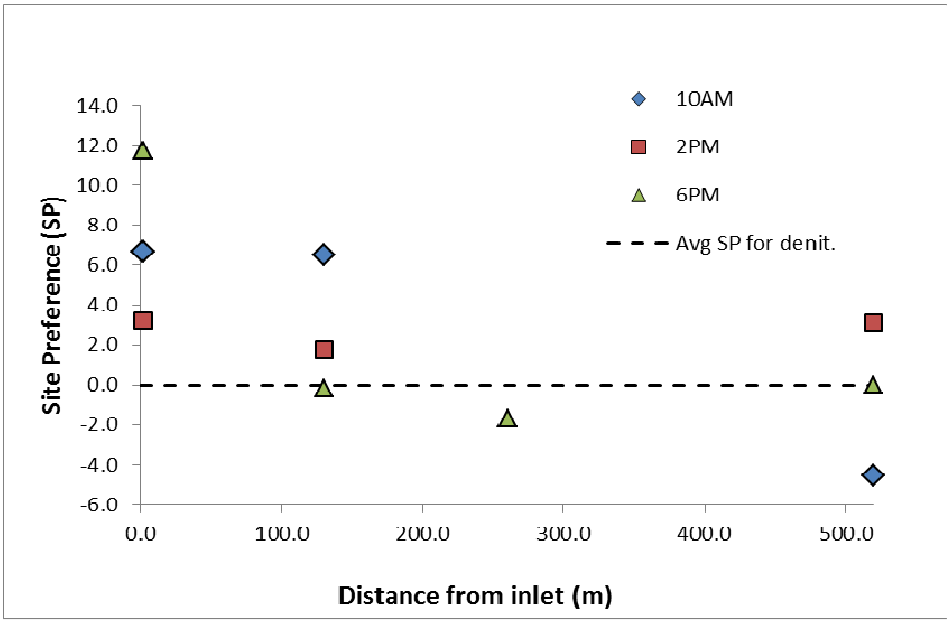

Figure 31. Site preference value (‰) in the off-gas N_2O along the flow path of the wastewater in aeration basin B. The dotted line indicates the average SP value associated with denitrification (~0‰).

5.3.3 Stable isotope analysis of CO_2 and CH_4, and ^{14}C analysis of CO_2.

The $\delta^{13}C$ and $\delta^{18}O$ values of CO_2 are reported in ‰ relative to VPDB (**Table XV**). In the aeration basin off-gas samples the $\delta^{13}C$ values varied between -14.1 and -18.7 with an average value of -16.3‰. No systematic variations were observed along the wastewater flow path, and the $\delta^{13}C$ values tend to remain constant throughout the day but varied on average 2‰ between sampling dates. The $\delta^{18}O$ varied between -2.1 and -11.9 with an average value of -7.9‰. The tail of the Imhoff tank $\delta^{13}C$ varied between -5.9 and -11 with an average value of -9.3‰. The $\delta^{18}O$ varied between -5.4 and -5.6 with average value of -5.5‰. The Imhoff tank central vents $\delta^{13}C$ varied between +6.6 and +6.3 with an average value of +6.4‰ and very little variability. The CO_2 from the anaerobic digesters also showed a very narrow range of $\delta^{13}C$ values (+6.8 to +5.6) averaging +6.1‰. The $\delta^{18}O$ values varied between -6.8 and -9.2 with average of -8.3‰. The time series results for $\delta^{13}C$ of anaerobic digester 18 are plotted as $\delta^{13}C$ and $\delta^{18}O$ versus $1/[CO_2]$ (**Figure 32**) to verify if any contamination from air CO_2 was present; the two regression lines suggest intercepts (x = 0) of +7.6 and -3.8 for $\delta^{13}C$ and $\delta^{18}O$, respectively, indicating minor sample contamination from air.

Only two of the aeration basin off-gas samples contained enough CH_4 to be analyzed for $\delta^{13}C$ after cryogenic enrichment. In these two samples (hoods 1-2), the $\delta^{13}C$ values of CH_4 were -33 and -44‰ (**Table XVI**). The two anaerobic digester samples

TABLE XV

$\delta^{13}C$ AND $\delta^{18}O$ VALUES FOR CO_2 FROM DIFFERENT SOURCES

	$\delta^{13}C$ (‰ PDB)				$\delta^{18}O$ (‰ PDB)			
Location	**Average**	**Max**	**Min**	**S**	**Average**	**Max**	**Min**	**S**
Aeration basin B	-16.3	-14.1	-18.7	0.9	-7.9	-2.1	-11.9	1.6
Imhoff tank (tail)	-9.3	-5.9	-11	2.9	-5.5	-5.4	-5.6	0.1
Imhoff tank (central vent)	6.4	6.6	6.3	0.1	-3.5	-3.4	-3.7	0.2
Anaerobic digesters 5,9,13,18,23	6.1	6.8	5.6	0.4	-8.3	-6.8	-9.2	1.0
Anaerobic digester 18								
1 (15 min)	5.7				-8.7			
2 (30 minutes)	6.3	6.8	5.7	0.5	-7.7	-6.8	-8.7	0.9
3 (45 minutes)	6.8				-6.9			
4 (60 minutes)	6.3				-6.8			

S = standard deviation

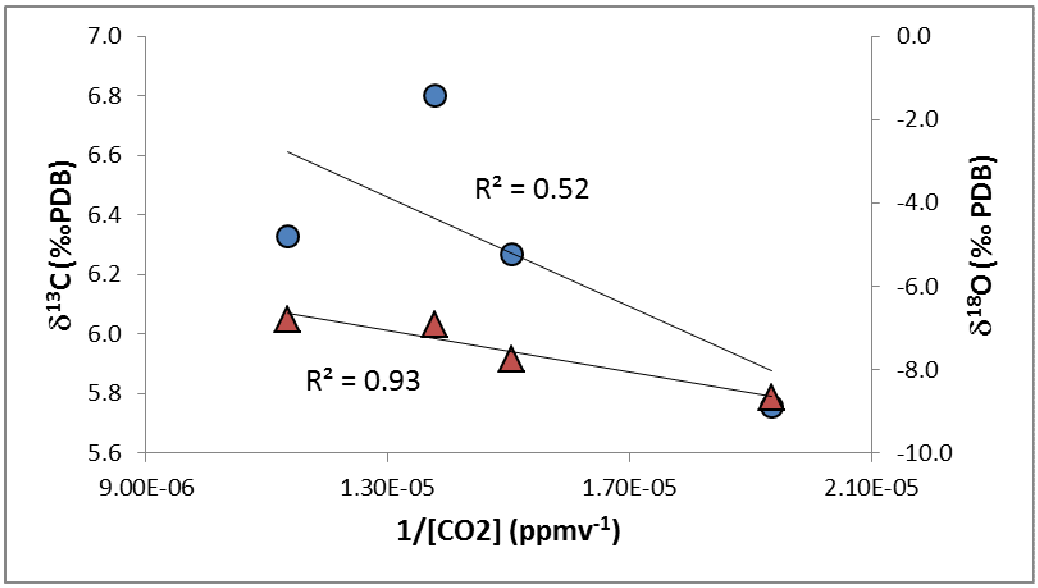

Figure 32. Anaerobic digester CO_2 $\delta^{13}C$ and $\delta^{18}O$ plot versus the inverse of the CO_2 concentration. The regression lines suggest $\delta^{13}C$ and $\delta^{18}O$ end members values for the degassed CO_2 of +7.6 and -3.8‰ PDB, respectively.

showed $\delta^{13}C$ values of -46.2 and -46.6‰ and a δD value of -329‰.

Data for ^{14}C in the CO_2 from the aeration basin (**Table XVII**) show that the fraction of modern carbon varies between 0.9078 and 0.9221 yielding $\Delta^{14}C$ values from -84.5 to -98.7‰ and apparent ages from 651 to 777 y. The anaerobic digester sample shows a fraction of modern carbon of 0.9645 yielding a $\Delta^{14}C$ value of -42.4‰ and an apparent age of 290 y. The calculations assume ^{14}C half-life = 5568 y (Libby, 1952), and follows the conventions by Stuiver and Polach (1977).

TABLE XVI

$\delta^{13}C$ AND δD VALUES FOR CH_4

Sample	Sampling date	$\delta^{13}C$ ‰	δD ‰
Hood 1	7/6/2010	-44	-
Hood 2	7/6/2010	-33	-
Hood 3	7/6/2010	-	-
Hood 4	7/6/2010	-	-
Hood 5	7/6/2010	-	-
Anaerobic digester 18	8/7/2010	-46.2	-329
Anaerobic digester 21	8/7/2010	-46.6	-329

TABLE XVII.

^{14}C DATA FOR CO_2 FROM THE AERATION BASIN (HOODS 1-3-4-5) AND ANAEROBIC DIGESTER 18.

Sample Name	$\delta^{13}C$	Activity dpm/g	fraction modern	±	$\Delta^{14}C$	±	^{14}C age y	±
Hood 1	-15	12.7309	0.9221	0.0033	-84.5	3	651	30
Hood 3	-15	12.5330	0.9078	0.0035	-98.7	4	777	35
Hood 4	-15	12.6483	0.9161	0.0033	-90.4	3	704	30
Hood 5	-15	12.5720	0.9106	0.0032	-95.9	3	752	30
An. dig. #18	+6.1	13.9157	0.9645	0.0036	-42.4	4	290	30

5.3.4 Stable N-isotope modeling

A fractionation model was developed to fit the NH_4^+ and NO_3^- stable N isotopes data. The model is based on the following assumptions: (1) NH_4^+ is quantitatively converted into NO_3^- through nitrification; (2) NO_2^- does not accumulate significantly, therefore reaction 1.3 is rate limiting, but not reaction 1.4; (3) 5-20% of the NO_3^- formed is denitrified. The initial fractionation factor for reaction 1.3 can be calculated for consumption of NH_4^+ between hoods 1 and 2 using the Rayleigh equation:

(5.2) $$\delta X = \delta_0 X + \varepsilon(X) \times \ln f$$

where $\varepsilon(X)$ is the enrichment factor for consumption with respect to species X, f is the concentration ratio C/C_0 for the species X, and subscript 0 signifies an initial value. For NH_4^+, an initial enrichment factor can be calculated as:

$$\varepsilon(NH_4^+) = \frac{\delta^{15}(NH_4^+) - \delta^{15}(NH_4^+)_0}{\ln f} \tag{5.3}$$

The calculated $\varepsilon(NH_4^+)$ values for 10:00am, 2:00pm, and 6:00pm are -37, -25, and -46‰ respectively; with the exception of -46‰, the other two values fall well within the range -38 to -5 of enrichment factors reported in literature for nitrification (Casciotti et al., 2003; Mariotti et al., 1980, 1981). The $\varepsilon(NH_4^+)$ values are expected to decrease along the wastewater flow path as less and less NH_4^+ is available for consumption (Mariotti, 1981). At each step of NH_4^+ consumption, the $\delta^{15}N$ of NO_3^- was recalculated using the following relationship (Toyoda et al., 2005):

$$\delta X_P = \delta X_S + \varepsilon(X)_P \tag{5.4}$$

where $\varepsilon(X)_P$ is the enrichment factor for production, and subscripts P and S indicate product and substrate, respectively.

Several studies have reported $\varepsilon(NO_3^-)$ values for denitrification (**Table XVIII**). The average $\varepsilon(NO_3^-)$ for bacteria of the species *Pseudomonas* and *Paracoccus*, which are the most diffuse species in wastewater treatment (Tchobanoglous, 2004), is -23‰. The $\varepsilon(NH_4^+)$ for consumption of NH_4^+ during production of NO_3^-, and the amount of newly formed NO_3^- reduced, with a constant $\varepsilon(NO_3^-)$ = -23‰, were chosen as fitting parameters. Good fits between the model and the data (**Figure 33, 34, and 35**) were obtained using $\varepsilon(NH_4^+)$ in the range between the initial calculated value and -10‰ and 0-12% of NO_3^- consumed by denitrification with a $\varepsilon(NO_3^-)$ = -23. For the 2:00pm data, up to 20% NO_3^- consumption was used. A fit between the model and the NH_4^+ stable isotope was also obtained from the model (**Figure 36**).

5.4 DISCUSSION

Given that the residence time in the aeration basin is 8-10 hours, and that a single set of samples from the five hoods was collected in ~1 hr, a single sample set does not represent a single parcel (volume) of water. However, temperature, flow rate through the aeration basin, amount of oxygen provided to the wastewater, and amount of SS are monitored and maintained nearly constant by the Management and Operation Department of the WWTP. Therefore, in first approximation, the aeration basin behaves as a system

TABLE XVIII.

NITROGEN AND OXYGEN FRACTIONATION FACTORS FOR DENITRIFICATION REPORTED IN THE LITERATURE.

Bacterium	$\delta^{15}N$ (‰)	$\delta^{18}O$ (‰)	Source
Unspecified NO_3^- consumption			
Pseudomonas stutzeri	-20 to -30		Wellman et al. 1968
Paracoccus denitrificans	-13 to -20		Delwiche and Steyn 1970
Unknown	-14 to -21		Miyake and Wada 1971
"	-2 to -12		Wada et al. 1975
"	-14 to -23		Blackmer and Bremner 1977
"	-29.4±2.4		Mariotti et al. 1981
"	-24.6±0.9		Mariotti et al. 1981
"	-30±6		Vogel et al. 1981
"	-15.9		Böttcher et al 1990
"	-22.9		Aravena and Robertson 1998
"	-20.7		Lehmann et al. 2003
"	-20 to -30		Brandes et al. 1998
"	-30		Voss et al. 2001
"	-22 to -25		Brandes et al. 1998
Ochrobactrum sp.	-29.6	-6.8 to -22.8	Granger et al. 2008
Pseudomonas chlororaphis	-16.9 to -23.0	-16.4 to -21.1	"
Paracoccus denitrificans	-17.6 to -26.6	-16.5 to -22.6	"
Pseudomonas stutzeri	-5.4 to -17.7	-4.8 to -17.7	"
Rhodobacter sphaeroides	-12.6 to -19.9	-7.9 to -13.1	"
$NO_3^- \rightarrow N_2$			
Paracoccus denitrificans	-24 to -33		Barford et al. 1999
Soil denitrifiers	-19 to -35		Snider et al. 2008
"	-38		Tilsner et al. 2003
$NO_3^- \rightarrow N_2O$			
Paracoccus denitrificans	-10 to -22		Toyoda et al. 2005
Pseudomonas aureofaciens	-37		Sutka et al. 2006
Pseudomonas chlororaphis	-13		Sutka et al. 2006
Pseudomonas fluorescens	-17 to -39		Toyoda et al. 2005
Pseudomonas fluorescens	-33 to -37		Yoshida 1984
Soil denitrifiers	-10 to -45		Perez et al. 2006
"	-27		Wada et al. 1991
"	-16		Schmidt and Voerkelius 1989
"	-24 to -32 and -11		Mariotti et al. 1981, 1982
Pseudomonas aeruginosa			Wahlen and Yoshinari, 1985
$N_2O \rightarrow N_2$			
Paracoccus denitrificans	-7 to -19		Barford et al. 1999
Pseudomonas fluorescens	-1 to -27		Yoshida 1984
Pseudomonas aeruginosa	-37 to -42		Wahlen and Yoshinari, 1985
Pseudomonas stutzeri	-4		Ostrom et al., 2007
Pseudomonas denitrificans	-7		Ostrom et al., 2007
Soil denitrifiers	-2 to -9		Ostrom et al., 2007
"	-9		Vieten et al. 2007
"	-2		Mandernack et al., 2000
"	-4		Schmidt and Voerkelius 1989

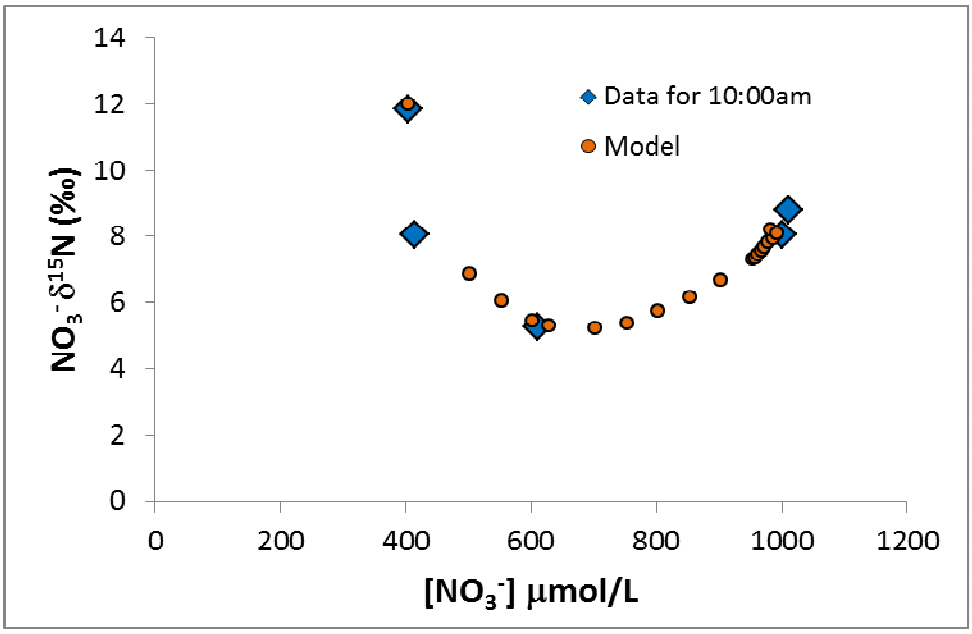

Figure 33. Fitting between the isotope fractionation model and the nitrogen stable isotope data (10:00am) for nitrate.

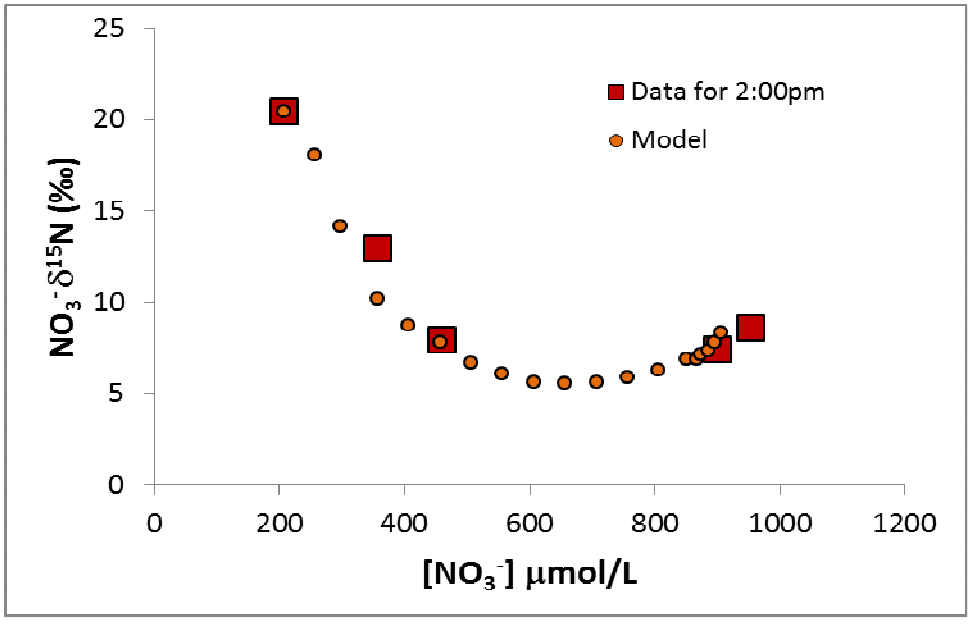

Figure 34. Fitting between the isotope fractionation model and the nitrogen stable isotope data (2:00pm) for nitrate.

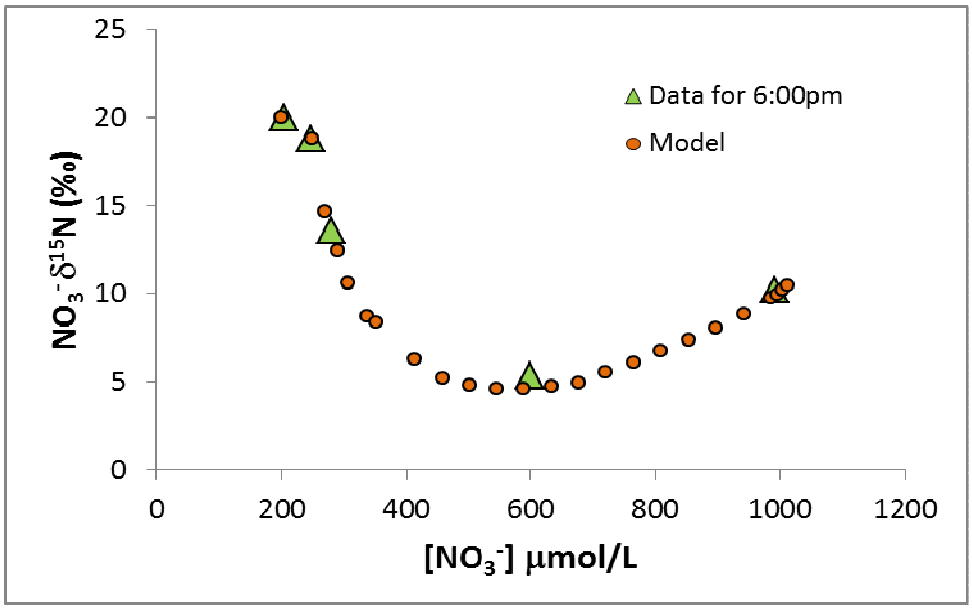

Figure 35. Fitting between the isotope fractionation model and the nitrogen stable isotope data (6:00pm) for nitrate.

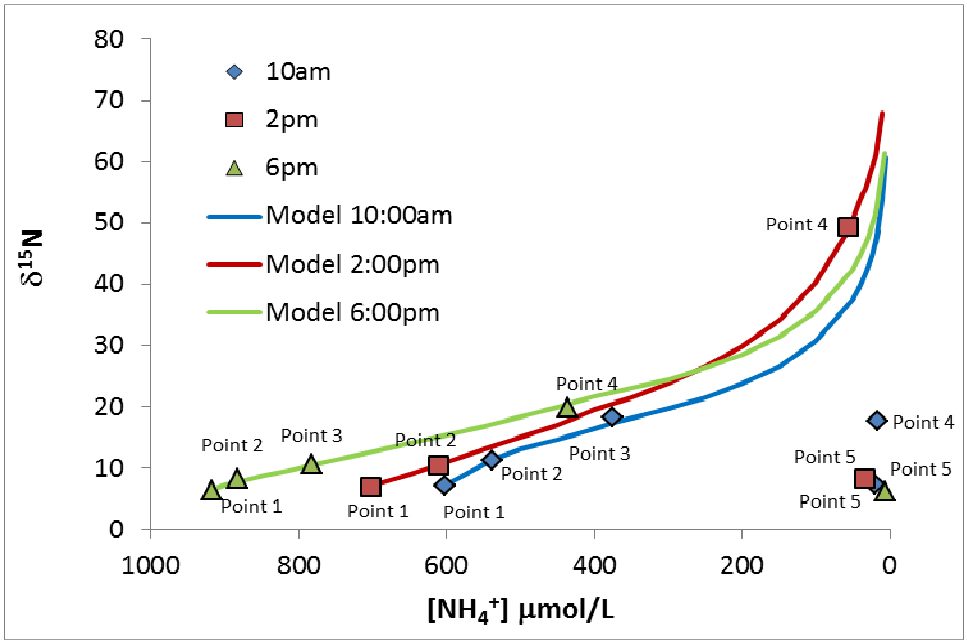

Figure 36. Fitting between the isotope fractionation model and the nitrogen stable isotope data (6:00pm) for ammonium.

at steady-state, the only unknown being the exact characteristics of incoming wastewater (TKN, aqueous N-species distribution, and COD). Off-gas N_2O, CH_4, and CO_2 present high variability, arguably due to two main factors: (1) changes in composition of the incoming wastewater; and (2) sampling position along the tank. However, the highest N_2O concentrations are systematically observed towards hoods 3-4, which does not seem to be consistent with production through nitrification. In fact, NH_3-N oxidation and nitrification arguably start at the inlet of the tank and proceed throughout the tank as shown by the rapid decrease of NH_3-N and increase of NO_3-N concentrations along the flow path of the wastewater. The specularity of the NH_3-N and NO_3-N trends seems to suggest that NH_3-N is nearly quantitatively oxidized to NO_3-N.This implies that organic nitrogen, generally present in the wastewater as proteins and amino-acids (Tchobanoglous, 2004), is the main source of nitrogen for the bacterial biomass assimilatory reactions in the aeration basin, rather than NH_3-N. The N_2O emissions are higher in the zone with DO between 0.2-2.5 mg/L, averaging 1.3 mg/L, which is consistent with previous studies on lab-scale batch reactors where the highest N_2O emissions mainly occurred through nitrifier denitrification at DO of ~1 mg/L (Tallec et al., 2006). There is poor correlation between DO and N_2O emissions; however, a generally good positive correlation between N_2O and NO_2-N might indicate that N_2O emissions increase either because of increased nitrification or because more nitrite is available for denitrification. The SP values for N_2O, averaging +2.6‰, strongly support this latter hypothesis when interpreted according to Sutka et al. (2006). Additionally,

there is a good linear correlation between $\delta^{15}N$ and $\delta^{18}O$ ($R^2 = 0.89$), with a slope of the regression line of 0.53, which is within the typical values observed for denitrification (0.5-1.0; Kim and Craig, 1990, 1993; Yoshinari et al., 1997; Granger et al., 2008). Despite the fact that denitrification is expected to be more predominant toward the inlet of the tank, where low DO favors denitrifiers, inhibition of the nitrous oxide reductase enzyme by increasing levels of DO might explain why N_2O emissions are higher at DO between 0.2 and 2.5 mg/L (Bell and Ferguson, 1991, Madigan et al., 2009;). Subsequently, N_2O emissions decrease again toward the outlet of the tank, possibly due to almost complete inhibition of denitrification at DO levels > 2.5 mg/L. Arguably, the denitrification process never completely stops, as low DO/anaerobic microenvironments likely persist within the bacterial floc. These micro-sites could also be exploited by methanogens, which would explain why CH_4 is still produced, in relatively minor amounts, at the outlet of the tank, where 2.7 to 24.1 ppmv of CH_4 was measured in the off-gas. The high concentrations of CH_4 measured at the inlet of the tank, on the other hand, could be either produced in situ through methanogenesis due to the low dissolved oxygen level (<0.2 mg/L) near the inlet, and/or could be carried over from the primary settling tanks. Finally, the rate of CO_2 emissions could depend on the DO available for respiration and oxidation, which is higher toward the outlet of the tank. The maximum in CO_2 emissions at hood 4 and subsequent decrease towards hood 5 could be due to consumption of utilizable substrate.

The observed $\delta^{15}NO_3^-$ values versus NO_3^- concentrations can be explained as the result of NH_4^+ nitrification with fractionation factor values ranging from -46 to -10‰, accompanied by variable amounts of denitrification in the range of 5-20% of the total NO_3^- present in the tank. The same model also explains the observed $\delta^{15}NH_4^+$ values versus NH_4^+ concentrations (Figure 35). In this latter case, however, generally the data for hood 5, and for hood 4 in one case, deviate from the model. The small concentrations of NH_4^+ (7-34 μmol/L) observed toward the outlet of the aeration basin might reflect NH_4^+ produced ex-novo through endogenous respiration of the biomass (Reaction 1.2). This hypothesis is supported by the fact that the $\delta^{15}NH_4^+$ is in the range +6.1 to +8.3‰, very similar to the $\delta^{15}N$ value of +6.8‰ obtained for the bacterial biomass.

The $\delta^{13}C$ of the aeration basin suspended solids, averaging -20.2‰, is in the range of similar values reported for dissolved and particulate organic matter (-20 to -26‰) from WWTP reported in other studies (Gearing et al., 1991; Vandover et al., 1992; Ramirez-Alvarez et al., 2007; Griffith et al., 2009), and about 4‰ lighter than the $\delta^{13}CO_2$ from the aeration basin (average = -16.3‰). The $\delta^{15}N$ for the suspended solids, averaging +6.8‰, is higher than previous values reported for WWTP organic matter but similar to those reported for sediments (Ramirez-Alvarez et al., 2007; **Figure 37**). The $\delta^{13}CO_2$ from the Imhoff tanks present higher values, averaging -9.3 and +6.4‰ for tank tail and central vent respectively. In particular, the positive value for the central vent is very similar to

$\delta^{13}CO_2$ values for anaerobic digesters (+6.1‰ average). This enrichment in ^{13}C might be due to the fact that in both these tanks methanogens produce but also metabolize CO_2 producing methane as a by-product. Preferential use of isotopically light CO_2 might passively enrich the residual CO_2 in the heavier carbon isotope. While this is the case for the entire anaerobic digester, the same effect is more prominent beneath the central vent of the Imhoff tanks were the settleable organic matter accumulates in significant amounts during primary treatment.

Generally, the fossil carbon in WWTP derives from any product that is made employing fossil fuels, such as motor oil, rubber, pharmaceuticals, surfactants, and personal care products. Only a small amount of fossil carbon is present in the aeration basin and anaerobic digesters off-gas CO_2, where the fraction of modern carbon is >0.9 in all cases, giving an apparent age of 290-777 y. This is a higher fraction of modern carbon compared to those reported for dissolved and particulate organic carbon from other WWTP studies (Griffith et al., 2009; **Figure 38**).

5.5 CONCLUSIONS

This study represents the first detailed stable isotope study on N aqueous species, off-gas N_2O, CO_2, and CH_4, and biomass for a full-scale single-stage nitrification metropolitan WWTP. The calculated N_2O, CH_4, and CO_2 fluxes for the entire aeration

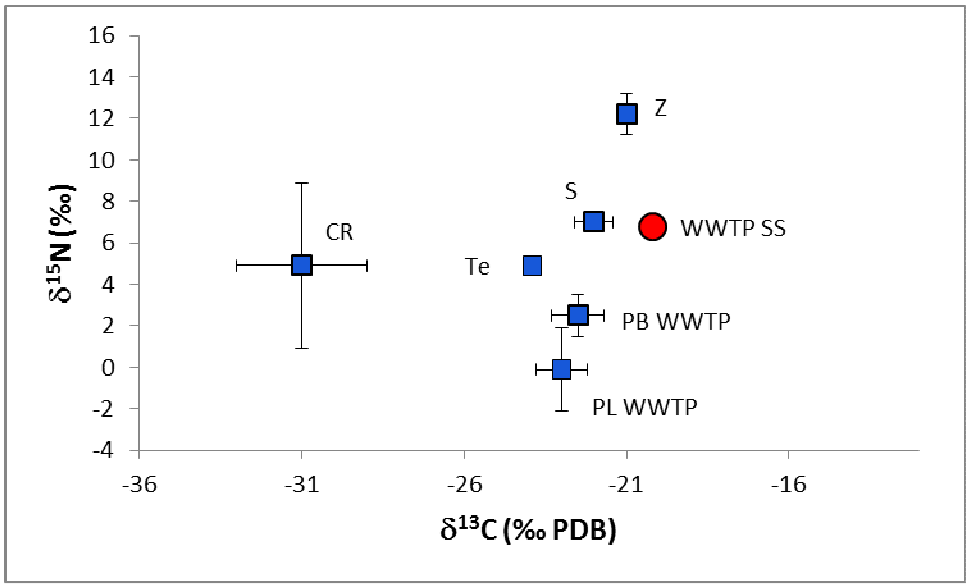

Figure 37. Comparison of $\delta^{13}C$ and $\delta^{15}N$ of various organic matter sources reported in literature (blue squares; Ramirez-Alvarez, 2007, and references therein) and for the suspended solids analyzed in this study (red dot). WWTP = wastewater treatment plant; PL = Point Loma; PB = Punta Bandera wastewater treatment plant; Te = Tijuana estuary; Z = zooplankton; CR = creeks and rivers; S = sediments; SS = suspended solids. For the Stickney WWTP SS point, the error is within the dot

basin B were: $5.8x10^4$, $7.2x10^4$, and $3.4x10^7$ kg/y for N_2O, CH_4, and CO_2, respectively. The stable N isotope and isotopomer data in conjunction with water quality data and off-gas N_2O emissions define several constraints on N_2O production: (1) N_2O is produced mainly by incomplete denitrification in the aeration basin tanks; (2) nitrification is the main pathway responsible of the ^{15}N distribution between NH_4^+ and NO_3^- in the aeration basin, followed by denitrification of about 5-20% of the NO_3^- produced; (3) inorganic NH_4^+ is mainly used in dissimilatory bacterial reactions (respiration) and nearly

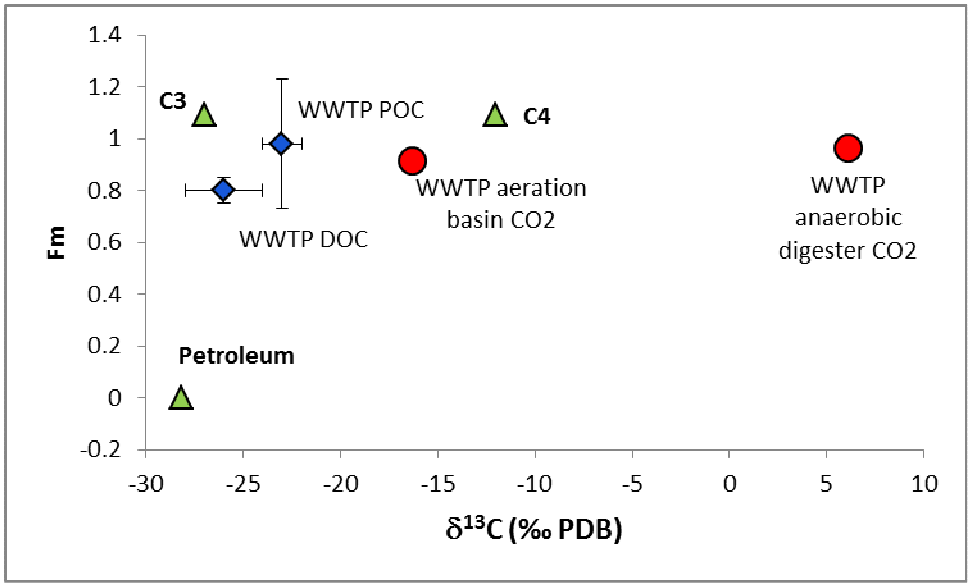

Figure 38. $\delta^{13}C$ isotopes of organic matter versus fraction of modern carbon (Fm). Wastewater treatment plant (WWTP) dissolved and particulate organic carbon (DOC and POC) data from Griffith et al., 2009, blue diamonds. Stickney WWTP off-gas CO_2 (red dots, this study) plotted with Petroleum and C3/C4 plants; error is within the red dots.

quantitatively converted into NO_3^-; (4) accumulation of NO_2^- in the tank results in higher N_2O emissions in the section of tank with DO ranging 0.2-2.5 mg/L. Additionally, CH_4 is present in the aeration basin tanks in significant amounts.

The $\delta^{13}C$ and $\delta^{15}N$ values for suspended solids are similar to the values reported in the literature for organic matter from WWTPs, while the $\delta^{13}C$ values of aeration basin and anaerobic digesters off-gas CO_2 tend to be higher than the values reported for dissolved and particulate organic carbon from WWTPs. Only a small fraction (<0.1) of fossil carbon is present in the off-gas CO_2.

CHAPTER 6

CONCLUSIVE REMARKS

The recent recognition of WWTPs as significant sources of N_2O and CH_4 has spurred an effort in the scientific community to identify their sources and quantify their emissions. Of these two gases, N_2O is of particular concern, given its long atmospheric residence time, high GWP value, and potential for stratospheric ozone destruction. The USEPA has adopted a methodology to estimate N_2O and CH_4 emissions that is derived from a methodology proposed by the IPCC in 2006. These estimates do not involve direct measurements and are based on fixed emission factors. For N_2O, the emission factors are 7.0 and 3.2 g N_2O produced per person per year in system, with and without biological nitrogen removal, respectively. For CH_4, a factor of 0.6 kg CH_4 per kg BOD5 is used unless CH_4 emissions are measured. The assumption that these factors can be extrapolated to all WWTP facilities within the US has been proven incorrect by recent studies. Many variables might be involved in controlling GHG emissions, including the quality of the incoming wastewater, treatment technologies used, and plant management. Methane emissions are generally seen as associated with anoxic treatment steps, while high N_2O emissions are generally observed in the aeration basins of activated-sludge WWTPs. However, there is debate on the main mechanism of N_2O production, as it can

be a by-product of both nitrification and incomplete denitrification. Identification of the source of N_2O is fundamental to design systems aimed to reduce these emissions. Previous studies mainly focused on the aeration basins as they have been shown to be the main source of N_2O.

The present study had three main objectives: (1) identify all sources of N_2O and CH_4 emissions from three large WWTPs in the Chicago metropolitan area; (2) determine total fluxes and emission factors for N_2O and CH_4; and (3) identify the biological reactions responsible for N_2O production. Additionally, we characterized the C sources for CH_4 and CO_2 using ^{13}C and ^{14}C isotopes.

In 2008, we conducted a pilot study at the activated-sludge WWTP of Stickney (See Chapter 3), managed by the MWRDGC, to define a methodology for measuring N_2O and CH_4 emissions from the various treatment steps. Emissions from grit chamber, primary tanks, aeration basins, concentration tanks, secondary clarifiers and anaerobic digesters were measured, as well as those from the plant exhausts. A total of 57 samples were collected. The samples were analyzed for N_2O and CH_4 at the UIC EIGL laboratory by gas chromatography. The total N_2O flux that we measured was higher than the flux calculated for Stickney using the USEPA method. The measured flux for CH_4 was instead lower than that predicted by the USEPA method. The aeration basins were confirmed to be the main source of N_2O, but also released significant amounts of CH_4. The grit chamber was a significant source of N_2O. The preliminary tanks (Imhoff type) dominated CH_4 emissions. We also measured significant N_2O and CH_4 fluxes from the

plant exhausts. A survey of the perimeter of the plant during a thermal inversion showed N_2O and CH_4 concentrations below detection limits, and the horizontal flux of these gases from the plant could not be quantified.

In 2009, we extended our survey on Stickney and we also sampled emissions from the North Side and Egan activated-sludge WWTPs (See Chapter 4), also managed by the MWRDGC. The three plants sampled are of different size and receive different amounts of wastewater (760, 245, and 27 MGD on average in 2010 for Stickney, North Side, and Egan respectively). Additionally, they employ different aeration techniques for the aeration basins. Stickney employs spiral-roll diffusers, and North Side employs spiral roll diffusers that were operated to obtain decreasing oxygen input moving away from the aeration basin inlet (tapered aeration). Egan employs two different aeration basins; the north one has full-plate diffusers, the south one has spiral-roll aeration similar to Stickney. A total of 494, 159, and 188 samples were collected from a variety of treatment steps and from the exhausts for Stickney, North Side, and Egan respectively. The samples were analyzed for N_2O, CH_4, and specific samples from Stickney were also analyzed for CO_2. Our results showed that in all three plants the aeration basins release > 85% of the total N_2O. Other significant contributions came from the grit chamber, the exhausts, and the anaerobic digesters, in this order. Methane follows a different pattern. At Stickney CH_4 is mainly (~86%) released by the primary (Imhoff type) tanks, followed by exhausts, aeration basins, as leaks from the floating-cover anaerobic digesters and from the grit chamber. At North Side we could not obtain a definite flux measurement from the

primary tanks, and therefore their contribution is not known. Significant contributions to CH_4 were measured from the aeration basin and exhausts. At Egan, the primary tanks emit most of the methane, followed by the exhausts and the aeration basins. The emission of significant amounts of CH_4 from the aeration basins suggested that methanogens are still active in these tanks, and that anaerobic micro-sites persist within the bacterial floc even in aerated conditions. These tanks had been generally overlooked when accounting for possible CH_4 sources within WWTPs. The total fluxes for N_2O were calculated to be 5.9×10^5, 1.7×10^4, and 1.6×10^4 kg/y for Stickney, North Side, and Egan respectively. The total fluxes for CH_4 were calculated to be 2.8×10^6, 8.6×10^4, and 6.0×10^4 kg/y for Stickney, North Side, and Egan respectively. The total CO_2 flux from Stickney was calculated to be 1.1×10^8 kg/y. An error on these emissions was calculated for Stickney, as the other two plants had a limited amount of data. The error for Stickney was calculated based on a 95% confidence interval, and was ± 22%, ± 17%, and ± 6% of the total flux for N_2O, CH_4, and CO_2 respectively. When applied to Stickney, the USEPA method yields fluxes of 1.6×10^4 kg/y of N_2O and 1.03×10^7 kg/y of CH_4 (not including the CH_4 recaptured). Our calculated N_2O flux is ~1.5 orders of magnitude higher than the USEPA prediction, while our calculation for CH_4 is only about 30% as large as the USEPA prediction. However, Stickney also employs facultative lagoons that were not sampled during the course of this study, and which are expected to greatly contribute to CH_4 emissions. Based on our data, the N_2O emission factors for Stickney, North Side, and Egan are 204, 12, and 92 g per person per year respectively, corresponding to 0.9,

0.2, and 1.0% of the average TKN of the plants emitted as N_2O respectively. These emission factors are much larger than those used by USEPA, and in agreement with N_2O emission factors from previous studies. Emission factors for CH_4 are 1122, 61, and 354 g per person per year for Stickney, North Side, and Egan respectively.

In 2010, the focus of this study was mainly to identify the biological pathway/pathways responsible for N_2O production in the aeration basins (See Chapter 5). To do so we used a novel stable isotope approach, taking advantage of the fact that bacterial enzymatic reactions cause N isotopic fractionation. We utilized bulk and site-specific (^{15}N site preference, SP) $\delta^{15}N$ data on N_2O, $\delta^{15}N$ data on aqueous NH_4^+ and NO_3^-, and water quality parameters to identify the metabolic pathways involved in N_2O production. The N_2O SP parameter has been shown to yield information on the N_2O source that is independent from the bulk $\delta^{15}N$. More specifically, SP values of ~ 0‰ have been associated with N_2O production by denitrification, and SP values of ~ +30‰ have been associated with N_2O produced by nitrification for a variety of nitrifying and denitrifying bacteria. Additionally, we monitored CH_4 trends along the wastewater flow path in the aeration basin, and used ^{13}C and ^{14}C isotope data to determine the C sources for CH_4 and CO_2 in the aeration basins and anaerobic digesters, and the fraction of fossil fuel carbon present. Sampling was conducted for fugitive emissions and associated wastewater samples at 5 locations in aeration basin B, tank 1, at Stickney. The sampling points were located at 3, 65, 130, 265, and 520 m from the inlet. Samples were collected from June to November 2010, at least once a month. Samples were generally collected at

10am, 2pm, and 6pm. Additional samples were collected for fugitive emissions only to assess the variability of these emissions through time.

We observed consistent trends along the wastewater flow path in the aeration basin. Methane emissions are high near the inlet, where CH_4 could be either produced in situ because of the low DO, or carried over from the primary treatment and released due to a stripping effect from the aeration, or likely a combination of both. Nitrous oxide emissions are low near the inlet, and reach their maximum between ¼ and the middle of the tank (0.2 < DO < 2.5 mg/L), and then decreasing toward the outlet of the tank. A similar pattern is followed by CO_2. The calculated N_2O, CH_4, and CO_2 fluxes for the aeration basin were: 5.8×10^4, 7.2×10^4, and 3.4×10^7 kg/y for N_2O, CH_4, and CO_2 respectively. The error (95% confidence interval) was calculated to be ± 28%, ± 23%, and ± 7% for N_2O, CH_4, and CO_2 fluxes respectively. These results are in good agreement with the fluxes calculated for the year 2009. Trends for NO_3-N and NH_3-N are specular, suggesting that NH_3 is quantitatively nitrified to NO_3^-. A good correlation was observed between N_2O emissions and NO_2^-; this correlation was inconclusive however, as it might be due to N_2O produced from NO_2^- through denitrification or could be a passive correlation due to increased production of both species through nitrification. The bulk $\delta^{15}N$ varied between approximately 0 and -35‰. The N_2O SP data, however, averaging ~ 0 for most of the samples, strongly suggest N_2O production through denitrification. Slightly positive values near the inlet (~ 3-11) might have suggested a small contribution (10-20%) from nitrification in this area of the tank. In addition, we

also found good linear correlation between $\delta^{15}N$ and $\delta^{18}O$ for NO_3^-, with a slope of ~0.5, which is typical of NO_3^- fractionation through denitrification.

The isotope data for NO_3^- and NH_4^+ could be fit with a Rayleigh-type fractionation due to nitrification of NH_3 (referred to as NH_4^+ due to the pH of the tank, which is ~7) and contemporaneous denitrification of the NO_3^-. The model assumed a NH_4^+ consumption fractionation factor for nitrification variable between -46 and -10‰ and a NO_3^- consumption fractionation factor for denitrification of -23‰. These fractionation factors for nitrification and denitrification were in agreement with those calculated from previous lab-scale and full-scale studies on numerous nitrifying and denitrifying microorganisms. Our results suggested that nitrification is the main biological pathway responsible for the ^{15}N distribution between NH_4^+ and NO_3^- in the aeration basin, followed by denitrification of about 5-20% of the NO_3^- produced. Denitrification of NO_3^- also seemed responsible for N_2O production, as suggested by the SP data.

Isotope data for C mainly showed that both suspended solids and CO_2 present similar $\delta^{13}C$ values as suspended solids and CO_2 in other WWTPs, and that the off-gas CO_2 stable isotope composition can be explained assuming an initial dissolved organic C composition of ~-20 to -30‰. Data for ^{14}C on CO_2 showed little (<10%) contribution from fossil carbon.

This is the first detailed study on N_2O and CH_4 emissions from each wastewater treatment step at activated-sludge WWTPs. Additionally, it constituted the first detailed

stable isotope study on N aqueous species, off-gas N_2O, CO_2, and CH_4, and biomass for a full-scale single-stage nitrification metropolitan WWTP.

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VITA

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Education

2011	Ph.D Earth and Environmental Sciences	University of Illinois at Chicago
2007	M.S. Earth and Environmental Sciences	University of Illinois at Chicago
2003	B.S. Geology (110/110)	University of Florence (Italy)

Research Interests

Environmental geochemistry, Isotope Geochemistry, Biogeochemistry, Environmental forensics, Renewable Energy.

Positions

2007-2011	Research Assistant	University of Illinois at Chicago
2005-2007	Teaching Assistant	University of Illinois at Chicago
2004	Co-researcher	Agency: Hydea (Florence, Italy)
2001-2004	Research Assistant	University of Florence (Italy)

Research and field experience

2008-2010	Greenhouse gas (N_2O, CH_4, and CO_2) emissions from wastewater treatment plants, Stickney, IL (USA)
2007-2009	Stable isotope (C, N) analysis of hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (RDX explosive)
2005-2007	Isotope Stratigraphy of the Travertine Deposits at Serre di Rapolano, Italy
2004	Monitoring of the suspended solid loads of the fluvial system of south-western Tuscany

1999-2004 Monitoring of the geochemical precursors of volcanic eruptions (Vulcano, Italy)

1999-2003 The Fumarolic Condensates of the Island of Vulcano (Italy). An extensive survey of the chemistry of fumarolic gases, and the emission of trace element to atmosphere through volcanic activity. Thesis submitted as partial fullfillment of the B.S. degree in Geology. Analysis were funded by the European Community and performed at the Southampton Oceanography Center (Southampton, England)

Laboratory Experience

Vast (> 2 years) experience in Gas Chromatography, Isotope Ratio Mass Spectrometry, and Elemental Analyzer techniques. Analysis performed include: determination of N_2O, CH_4, CO_2, and other gas concentrations in gaseous samples, C, N, and O stable isotope analysis of carbonates, wastewaters, biological samples, and CO_2 from various sources.

Good experience (> 1 year) in Liquid Chromatography on volcanic condensate gases and aqueous solutions and in several sample preparation techniques, including: Solid Phase Macro- and Micro-Extraction, Cryogenic Gas Purification (CO_2), U-Th separation and purification, perchlorate ion extraction and purification from water samples for ^{36}Cl and ^{37}Cl isotope analysis, and U-Th series dating with Multi-collector Inductively-Coupled Plasma Mass Spectrometry on travertine deposits.

Good experience (> 1 year) in RDX N-stable isotope GC-IRMS analysis for fingerprinting of explosives in natural environments.

Vast experience (> 2 year) in glassblowing techniques for maintenance and creation/modification of laboratory glassware.

Basic knowledge (> 6 months) of X-ray diffraction and fluorescence techniques, electron microprobe, and scanning electron microscopy on mineral and rock samples; graduate coursework on mineral-fluid interface processes and synchrotron radiation methods; graduate coursework on MATLAB® data modeling and processing.

Publications

- **Bellucci F**., Kozak J.A., Heraty L., Carbone J., Sturchio N.C., O'Connor C., Kollias L., and Lanyon R., 2010. *Greenhouse Gas Emissions from Three Chicago Wastewater Treatment Plants*. Oral presentation at WEFTEC 2010,

New Orleans, LA, Proceedings (In preparation for publication on Environmental Science and Technology)

- **Bellucci F**., Carbone J., Heraty, L., Sturchio N.C., Gonzalez-Meler M., Kozak J., and O'Connor C., 2010. *Greenhouse gas emissions from a large metropolitan water reclamation plant*. Oral presentation at Goldschmidt Conference 2010, Knoxville, TN, Abstracts.
- **Bellucci, F**., Heraty, L.J., Bowley, E., Sturchio, N.C., Jaraula, C., Kozak, J.A., Oksouie, A., and O'Connor, C., 2009. *Greenhouse gas (N_2O, CH_4, and CO_2) emissions from the Stickney Water Reclamation Plant, Stickney, IL (USA)*. GSA North-Central Section - 43rd Annual Meeting (2-3 April 2009), Abstracts.
- **Bellucci F**., Heraty, L.J., Sturchio, N.C., and Minissale, A.A., 2009. *Isotope and Pollen Stratigraphy of the Travertine Deposits at Serre di Rapolano, Italy*. GSA North-Central Section - 43rd Annual Meeting (2-3 April 2009), Abstracts. (In preparation for publication in Quaternary Science).

Recent Awards

- LAS Earth and Environmental Sciences Demar-Rodolfo Scholarship, Spring 2010

Recent activities

Sep 2011	Defense of Ph.D Dissertation
Aug 2011	Submitted abstract for poster presentation at AGU conference 2011
Dec 2010	Submitted abstract for oral presentation at WEFTEC 2011
Oct 2010	Present as speaker at WEFTEC 2010, New Orleans, LA
Sep 2010	Attended: International School of Fluid Geochemistry. Abbadia S. Salvatore (Si), Italy
Jun 2010	Present as speaker at Goldschmidt 2010 Conference, Knoxville, TN