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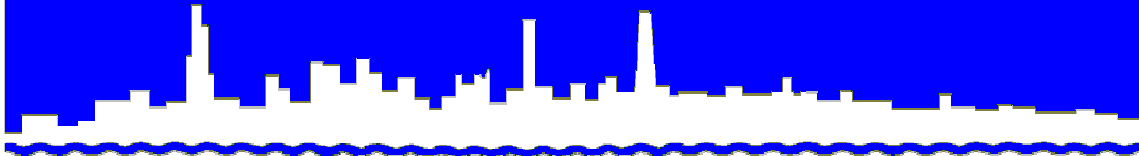
Metropolitan Water Reclamation District of Greater Chicago

RESEARCH AND DEVELOPMENT DEPARTMENT

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CONTROL, REDUCTION, AND UTILIZATION OF GREENHOUSE

GASES IN WASTEWATER TREATMENT:

METHANE AND NITROUS OXIDE

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METHANE AND NITROUS OXIDE

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GENERAL OBJECTIVE

A literature review was conducted to examine the sources of methane and nitrous oxide in wastewater treatment and collection. An evaluation of control, reduction, and/or utilization of these fugitive gases is also included. This literature review does not include gas emissions from stationary fossil fuel combustion which provides power to the Metropolitan Water Reclamation District of Greater Chicago (District) water reclamation plants (WRPs) and facilities or mobile fossil fuel combustion from District vehicles. General wastewater treatment and emerging technologies were examined with emphasis on District processes.

Summary and Conclusions

According to a recent United States Environmental Protection Agency (USEPA) report, wastewater treatment and human sewage are considered major sources of the greenhouse gases, particularly methane and nitrous oxide, in the atmosphere (USEPA, 2006). Below are brief synopses of our findings for both gases followed by a detailed literature review.

Methane. Methane emissions are largely produced from anaerobic processes. According to the International Panel of Climate Change (IPCC), the only major source of methane at the District is the WRP anaerobic digesters. The main factor in determining the extent of methane production in anaerobic processes is the amount of degradable organic fraction in the wastewater, i.e. methane (CH_4) yield increases with higher biochemical oxygen demand (BOD). Environmental factors that influence CH_4 production include temperature, pH, retention time, wastewater treatment efficiency, competition between methanogens and sulfate reducing bacteria, and toxicants. Neutral pH and higher temperature promote methane production. Additionally, anaerobic systems are sensitive to oxygen.

Anaerobic conditions can also occur in District collection systems, primary clarifiers, concentration tanks, low oxygen pockets in aeration basins, drying beds, and facultative lagoons. However, methane release from these sources are considered to be minimal. Methane will also be produced in the pelletizer facility that is currently under construction at the Stickney WRP. Appropriate control technologies, such as regenerative thermal oxidation, are expected to prevent methane release to the atmosphere.

Methane gas is produced by design in District anaerobic digesters. However, processes must be in place to prevent fugitive emissions of methane. Currently, the District uses methane for heating and limited flaring. Flaring is the simplest method to convert methane into carbon dioxide, therefore reducing the heat-trapping power of methane. However, cogeneration using the energy from methane is the most efficient use of methane.

Soluble methane may be present in the secondary effluent and anaerobic digester centrate. Air stripping of aqueous methane can be used to remove methane from effluent. However, the recovered methane gas must be utilized or thermally oxidized to prevent methane emissions.

Methane may also be produced in low oxygen pockets in aeration basins. Methane production in aeration tanks is often an indicator of poor aeration efficiencies. Reducing rumen protozoa supply to the aeration system may help control methane production. Many methanogens adhere to protozoa, which have been observed to support the methanogenic activity of the attached bacteria; however, this is more relevant with respect to animal waste processing. Additionally, supplying microbial inhibitors will suppress methanogenic activity without compromising removal of BOD and suspended solids (SS).

Nitrous Oxide. In wastewater treatment, collection, and effluent discharge, nitrous oxide production and emission can occur through both incomplete nitrification and denitrification. Understanding the controlling parameters and optimization of nitrification and denitrification should prevent the production of nitrous oxide.

The District nitrifies influent ammonia during secondary aeration. Nitrification occurs most prevalently in District WRP activated sludge aeration tanks. The wastewater ammonia concentration, BOD concentration, alkalinity, temperature, and potential for toxic compounds are major issues in the design of biological nitrification processes. Nitrifying bacteria need carbon and phosphorus as well as trace elements for cell growth. The growth kinetics of the ammonia-oxidation is rate limited below temperatures of 28°C and longer solids retention times (SRTs) are needed. Typical design SRT values may range from 10 to 20 days at 10°C to 4 to 7 days at 20°C. Above 28°C, the relative kinetics of ammonia and nitrite oxidation change, whereby nitrite will accumulate at lower SRTs.

Additionally, nitrification rates increase up to DO concentrations of 3 to 4 mg/L. Larger suspended floc size inhibits nitrification as DO diffusion into the floc is reduced, and nitrifying bacteria within the floc do not receive adequate DO. Dissolved oxygen concentrations below 0.50 mg/L greatly inhibit nitrification. Nitrification is also pH-sensitive and rates decline significantly at pH values below 6.8. Compounds that are toxic to nitrifying organisms include solvent organic chemicals, amines, proteins, tannins, phenolic compounds, alcohols, cyanates, ethers, carbonates, benzene, heavy metals, and un-ionized ammonia (NH_3) (Tchobanoglous et al., 2003).

Given the necessary environmental parameters, nitrification and denitrification to produce nitrous oxide (N_2O) can occur in the District collection system (sewers, TARP tunnels and reservoirs, combined sewer overflows) and many WRP processes (aeration basin, anaerobic digesters, sludge conditioning and thickening, lagoons, drying beds, and receiving streams). However according to the IPCC, the aeration tanks, anaerobic digesters, and the receiving streams may be considered the major sources of N_2O from nitrification and denitrification. Additionally, low-temperature thermal heating of sludge may result in nitrous oxide emissions if emission controls are not in place.

Beyond process optimization, a number of studies examined intermittent aeration reactor technology with varying periods of oxic and anoxic conditions as a way to achieve maximum nitrogen removal with limited nitrous oxide production. It was observed that most nitrous oxide emissions occurred during the aerobic period when oxygen levels were still low. This is more likely due to nitrifying bacteria producing nitrite under the low DO conditions, where nitrous oxide is an intermediate. Additionally, nitrous oxide can be produced by incomplete nitrification

by nitrifiers. In both low DO aerobic and anoxic conditions, higher nitrate concentrations resulted in higher nitrous oxide emissions.

It was observed that nitrous oxide production decreased as pH increased and increased as redox potential increased. However, no significant temperature effects were observed. Finally, filling the reactors under anoxic conditions produced more N_2O than under aerobic conditions. It appeared that anoxic fill could increase N_2O production at the initial stage of the aerobic phase due to the accumulated ammonia during the anoxic phase.

Nitrifying bacteria genus can also affect the magnitude of nitrous oxide emissions. The N_2O production of *Alcaligenes faecalis*, a typical heterotrophic nitrifier, *Nitrosomonas europea,* a typical autotrophic ammonia oxidizer, and *Nitrobacter winogradskyi,* a typical nitrite oxidizer, were compared under oxic conditions. *Nitrosomonas europea* produced approximately 280-540 times the N_2O compared to *N. winogradskyi* and approximately 20-50 times the N_2O compared to *A. faecalis*. However, due to its heterotrophic nature and potential for dense population, it was suggested that *A. faecalis* can play an important role in N_2O generation under oxic conditions.

BACKGROUND

The Earth's surface and atmosphere are kept warm primarily by energy from the Sun. Half of the incoming solar radiation is visible light (0.40-0.75 μm), and the other half is infrared (0.8-3.0 μm). Due to filtration, absorption, and other mechanisms in the atmosphere, only half of the incoming radiation reaches the Earth's surface. Some of this incoming radiation is reflected, and the remainder is absorbed by the Earth's surface. Like any warm body, the Earth emits energy. Therefore the amount of energy that the planet absorbs and the amount that is released must be equal if its temperature is to remain constant.

The outgoing radiated heat energy from the Earth is in the thermal infrared (IR) region of the light spectrum (4-50 μm). Some atmospheric gases can temporarily absorb infrared light of specific wavelengths preventing the light from escaping from the Earth's atmosphere. Shortly after absorption, the IR light is remitted in all directions, and a fraction is directed towards the Earth. This re-radiated energy is absorbed by the Earth and consequently heats the surface and surrounding air. This phenomenon is known as the greenhouse effect, and the gases responsible are known as greenhouse gases (GHGs). The most prevalent GHGs include water vapor (H_2O), CO_2, CH_4, and N_2O (Baird, 2000).

According to a recent USEPA report, domestic and industrial wastewater treatment is the sixth highest contributor to atmospheric CH_4, and human sewage is the fourth highest contributor to atmospheric N_2O. Both gases have shown a significant increase in their atmospheric concentrations from these respective sources from years 1990 to 2003. Methane has increased from 23.8 to 36.8 Tg CO_2 Equivalents (48% increase), and N_2O has increased from 13.0 to 15.9 Tg CO_2 Equivalents (21.9% increase). These GHGs are of concern as their ability to trap heat in the atmosphere is markedly greater than CO_2. Methane and N_2O, respectively, are 21 and 300 times more powerful than CO_2 in trapping outgoing radiation (USEPA, 2006).

Once in the atmosphere, methane can be chemically reduced. The dominant CH_4 sink, accounting for 90% of its loss from air, is the reaction with the hydroxyl free radical ($OH^\bullet$) producing $CH_3^\bullet$ and water vapor ultimately being oxidized to CO_2. Other sinks for methane involve reactions with soil and loss to the stratosphere. The average atmospheric lifetime of methane is 10-15 years. Conversely, there are no sinks for nitrous oxide in the troposphere. Instead, all N_2O eventually rises to the stratosphere where it decomposes to diatomic oxygen and nitrogen or reacts with atomic oxygen (Baird, 2000).

GREENHOUSE GAS SOURCES

Methane

According to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, wastewater can be a source of methane when treated or disposed of anaerobically. Wastewater in closed underground sewers is not believed to be a significant source of CH_4. According to the IPCC, the most significant CH_4 emission potentials for wastewater and sludge treatment and discharge systems are summarized in Table 1 (Doorn and Irving, 2006).

Anaerobic Processes. In the District WRPs, anaerobic fermentation processes are used for the treatment of waste sludge in anaerobic digesters. The District's processes are operated in the mesophilic temperature range (30-35°C). In anaerobic treatment complex wastes are stabilized in three basic steps: hydrolysis, acid fermentation, and methanogenesis (Tchobanoglous et al., 2003). In hydrolysis particulate material is converted to soluble compounds that can then be hydrolyzed to simple monomers (amino acids, sugars, and fatty acids) that are used by bacteria. During fermentation, these simpler monomers are degraded further. These organic substrates serve as both the electron donors and acceptors. The principal products of fermentation are acetate hydrogen, CO_2, propionate, and butyrate. The latter two compounds are further fermented to hydrogen, CO_2, and acetate. Acetate, hydrogen, and CO_2 are the precursors of methane formation carried out by methanogens. Two groups of methanogens are involved. *Aceticlastic methanogens* split acetate into CH_4 and CO_2; hydrogen-utilizing methanogens use hydrogen as the electron donor and CO_2 as the electron acceptor to produce methane. Other bacteria in the anaerobic process, *actogens*, use CO_2 to oxidize hydrogen and form acetic acid, which is eventually converted to methane (Tchobanoglous et al., 2003).

Before the anaerobic digestion process, the District thickens wasted sludge using gravity belt thickeners or concentration tanks. Sludge in concentration tanks thicken via gravity settling. Anaerobic digestion causes biogas production in these concentration units. Although the tanks are covered, the H_2S produced during the digestion may corrode the fixed cover and seals. This corrosion may open pathways for methane to escape the concentration tanks and into the surrounding air. Upon anaerobic digestion, the digested sludge is placed in concrete holding tanks which provide less opportunity for fugitive methane emissions.

The main factor in determining the extent of methane production in any of these processes is the amount of degradable organic fraction in the wastewater; this is commonly expressed in BOD. Under the same conditions, CH_4 yield increases with higher BOD. Environmental factors that influence CH_4 production include temperature, pH, retention time, degree of wastewater treatment, competition between methanogens and sulfate reducing bacteria, and toxicants (El-Fadel and Massoud, 2001).

Anaerobic digestion can occur wherever the optimal conditions are present. However, the District WRPs have a number of unit processes and areas where anaerobic activity is most prevalent: Anaerobic sludge digesters, Imhoff Tanks, and storage lagoons. Additionally, sludge

TABLE 1: CH$_4$ EMISSION POTENTIALS FOR WASTEWATER AND SLUDGE TREAT-
MENT AND DISCHARGE SYSTEMS

Untreated	Surface water discharge	Stagnant, oxygen-deficient rivers and lakes may allow for anaerobic decomposition to produce CH$_4$ (includes reservoirs and CSOs)
	Closed, underground sewers	Not a source of CH$_4$
Treated	Aerobic treatment processes	May produce limited CH$_4$ from anaerobic pockets
		Poorly designed/managed aerobic treatment systems produce CH$_4$
	Anaerobic sludge treatment	Sludge may be a significant source of CH$_4$ if emitted CH$_4$ is not recovered or flared
	Anaerobic lagoons	Likely source of CH$_4$

drying beds, concentration tanks, storm water reservoirs, and collection systems can be viewed as minimal sources of methane; the IPCC does not consider these major sources. And although the IPCC does not consider closed sewers a source (Table 1), limited methane emissions can occur through sewer caps and manholes, sewer cracks, and junctures.

Finally, thermal treatment of biosolids can produce CH_4. A Segher Hardpelletiser is currently under construction at the Stickney WRP. This is a convective thermal drying technology to convert sludge into pathogen-free pellets. Once in operation, the self-contained unit will be an oxygen-free environment, and dust control technology via bag filters and zero emission controls such as regenerative thermal oxidation will most likely be in place. Regenerative thermal oxidation involves heating and promoting complete combustion. Prior to complete evaluation of the pelletizer technology, it is premature to consider it a source of CH_4 and N_2O. However, the pelletizer could be a concern should the control technology not work efficiently.

Based on the IPCC's suggested sources and their methodology for determining methane emissions, the methane production from the District has two main sources: aerobic treatment of wastewater and anaerobic treatment of sludge. The methane emissions from the District can be estimated as follows: (Doorn, 2006),

$$CH_4 = \left[\sum_{i,j} (U_i \cdot T_{i,j} \cdot EF_j) \right] (TOW - S) - R \qquad (1)$$

CH_4 = Total methane emissions from domestic wastewater (kg/year)

i = Income group (rural, urban high income, urban low income)

j = Each treatment/discharge pathway or system, i.e. aerobic and anaerobic treatment

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

EF_j = Emission factor (kg CH_4/kg BOD)

TOW = Total organics in wastewater in inventory year (kg BOD/year)

S = Organic component removed as sludge in inventory year (kg BOD/yr)

R = Amount of CH_4 recovered in inventory year (kg CH_4/yr)

Considering the 2006 IPCC guidelines, the District service area would be considered as having a high-income urban population with all sewer discharge being delivered to the District plants via covered sewer collection systems. Therefore, U_i = 1.0 and $T_{i,j}$ = 1.0. Additionally the two pathways considered are j = *centralized, aerobic treatment of wastewater* and j = *anaerobic digestion of sludge*.

The IPCC estimates EF_j as follows (Doorn and Irving, 2006):

$$EF_j = B_0 \cdot MCF_j \tag{2}$$

B_0 = Maximum CH_4 producing capacity (kg CH_4 /kg BOD)

MCF_j = Methane correction factor

The IPCC default value for B_0 is 0.6 kg CH_4/kg BOD. However, a recent National Association of Clean Water Agencies (NACWA) review of the USEPA Report considered this B_0 value as conservative and suggested a value of 0.4 kg CH_4/kg BOD (Hockstad, 2007). According to the IPCC, the MCF_j ranges from 0–0.1 for centralized aerobic treatment plants, such as those employed by the District. Taking a conservative approach and using a MCF_j value of 0.1, the IPCC EF_j is 0.06 kg CH_4/kg BOD, and the NACWA-amended EF_j is 0.04 kg CH_4/kg BOD for the aerobic treatment wastewater. Additionally, the IPCC considers a MCF_j range from 0.8–1.0 for the anaerobic digestion of sludge. Again using a conservative value of 1.0 for MCF_j, this gives an IPCC EF_j value of 0.6 kg CH_4/kg BOD and a NACWA-amended EF_j value of 0.4 kg CH_4/kg BOD for the anaerobic treatment of sludge.

The *TOW* can be calculated as follows (Doorn and Irving, 2006):

$$TOW = TOW_D \cdot I \tag{3}$$

TOW_D = Total organics in wastewater in inventory year from domestic sources (kg BOD/year)

I = Correction factor for additional industrial BOD discharged into sewers

The 2000 TOW_D from all District plants using BOD_5 operational data gives an estimated load of 377.0 x 10^6 kg BOD_5/year. The IPCC suggests a default value for I as 1.0 giving a *TOW* of 377.0 x 10^6 kg BOD/year.

The organic component removed in the primary (S_p) and secondary (S_s) sludge was determined from plant operational data. The primary sludge organic component was estimated as follows:

$$S_p = \frac{(BOD_5^{raw} - BOD_5^{primary})}{BOD_5^{raw}} \cdot TOW \tag{4}$$

No oxidation or respiration of the incoming BOD_5 was considered. It is assumed that all BOD removed by the primary settling tanks was found in the residual sludge. Thus the load received by the aeration tanks (TOW_s) is

$$TOW_s = TOW - S_p \tag{5}$$

$$BOD_5^{raw} = \text{BOD}_5 \text{ in incoming wastewater}$$

$$BOD_5^{primary} = \text{BOD}_5 \text{ in wastewater after primary treatment}$$

The organic component of the wasted sludge from the secondary treatment was estimated as follows:

$$S_s = TOW_s \cdot Y \tag{6}$$

where Y is the biomass yield and can be calculated as

$$Y = \frac{\dfrac{VSS_s}{BOD_{5\ removed}}}{1 + (SRT)(k_d)} \tag{7}$$

$$VSS_s = \text{Volatile suspended solids in wasted sludge (kg)}$$

$$BOD_{5\ removed} = \text{Organic load removed during secondary treatment (kg BOD}_5)$$

$$SRT = \text{Solids retention time in aeration tanks (days)}$$

$$k_d = \text{Endogenous decay coefficient (0.10 day}^{-1}\text{) (Tchobanoglous et al., 2003)}$$

From all seven plants the total organic component in the sludge for 2000 was estimated by

$$S = S_p + S_s \tag{8}$$

giving 286.1 x 10^6 kg/yr.

The methane recovered (R) in 2000 from flaring, boiler use, or cogeneration was estimated for all seven plants from the digester gas produced in the anaerobic digesters. Only the Calumet, Egan, Hanover Park, and Stickney WRPs employ anaerobic digesters. It was assumed that 60.0% of the digester gas produced was composed of methane. Using the molecular weight ($MW_{methane}$ = 18 g/mol, or 0.018 kg/mol) and the ideal gas law, the mass of methane recovered was estimated as follows:

$$R = \frac{PV}{R_{IGC}T} \, MW_{CH_4}$$ (9)

P = Gas pressure (atm)

V = Volume of gas produced (L)

R_{IGC} = Ideal gas constant (L·atm/mol·K)

T = Digester temperature (K)

The methane recovered in District plants for 2000 was estimated as 27.7×10^6 kg if atmospheric pressure (1 atm) is assumed. (It should be noted that gas production data may be unreliable due to poor metering equipment performance). Therefore, using Equation 1, the estimated 2000 District total methane emissions from both aerobic treatment of wastewater and anaerobic digestion of sludge was 32.37×10^6 kg CH_4/yr using the IPCC EF_j value and 12.35×10^6 kg CH_4/yr using the NACWA EF_j value. The mass emissions of methane can be converted to CO_2 equivalents by

$$CO_2 \; Equivalents = Mass \; CH_4 \times 21$$ (10)

giving 679.7×10^6 kg CO_2 equivalents using the IPCC EF_j value and 259.4×10^6 kg CO_2 Equivalents using the NACWA EF_j value.

Based on the USEPA's *Inventory of U.S. Greenhouse Gas Emissions and Sinks 1990-2004*, the total 2000 U.S. methane emissions from wastewater treatment was estimated to be 34.3×10^9 kg CO_2 Equivalents. Based on the District estimates, the IPCC methane emission estimate is 1.98% of the 2000 total, and the NACWA-amended estimate is 0.76% of the 2000 total. It should be considered that many assumptions and default values were used in this calculation. Additionally, the IPCC calculation was developed for countries and not individual plants. (Note: These estimates exclude the methane emissions from the Stickney WRP Imhoff Tanks.)

Nitrous Oxide

According to the IPCC, N_2O is associated with the degradation of nitrogen compounds in wastewater (Doorn and Irving, 2006). Nitrous oxide is a stable gas that is produced as an intermediate during nitrification and denitrification. Though the predominant product of nitrification is nitrate (NO_3^-) and of denitrification is N_2, a portion of the nitrogen is emitted as nitrous oxide. In nitrification, ammonium (NH_4^+) is oxidized to NO_3^- by autotrophic bacteria under aerobic conditions. In denitrification, nitrate is reduced to N_2 by facultative heterotrophic bacteria under anoxic conditions (Barton and Atwater, 2002). According to the IPCC, the most significant N_2O emission potentials for wastewater, sludge treatment, and discharge systems are summarized in Table 2 (Doorn and Irving, 2006). Much like methane, closed sewers are not considered a source of nitrous oxide.

TABLE 2: N$_2$O EMISSION POTENTIALS FOR WASTEWATER AND SLUDGE
TREATMENT AND DISCHARGE SYSTEMS

|		
Untreated	Surface water discharge	Rivers and estuaries are likely sources of N$_2$O (Includes reservoirs, CSOs)
	Closed, underground sewers	Not a source of N$_2$O
Treated	Aerobic treatment processes	Advanced plants with nutrient removal are small but distinct sources of N$_2$O
	Anaerobic sludge treatment	Not a source of N$_2$O
	Anaerobic lagoons	Not a source of N$_2$O

Nitrification. The District uses extended aeration to oxidize ammonia in secondary aeration. Nitrification is a process that occurs in two steps in which ammonia is oxidized to nitrite (NO_2^-) followed by nitrite oxidation to nitrate. The District commonly achieves nitrification through suspended growth in aeration tanks. Because nitrifying bacteria grow much slower than heterotrophic bacteria, longer hydraulic and solids retention times are used (Tchobanoglous et al., 2003).

Aerobic autotrophic bacteria are responsible for nitrification in activated sludge. Generally, *Nitrosomonas* and *Nitrobacter* are responsible for the first (ammonium to nitrite) and second stages (nitrite to nitrate) of nitrification, respectively. The complete first stage reaction can be summarized as follows (Tchobanoglous et al., 2003)

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O \tag{11}$$
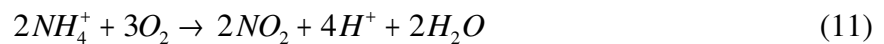
The theoretical intermediate reactions to complete the first stage nitrification reactions are shown in Figure 1 (Barton and Atwater, 2002), where N_2O is a minor product, analogous to the evolution of carbon monoxide during incomplete combustion.

The second stage of nitrification performed by *Nitrobacter* can be summarized as follows (Tchobanoglous et al., 2003),

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \tag{12}$$

No nitrous oxide is produced during the second stage.

The influent ammonia concentration, BOD concentration, alkalinity, temperature, and potential for toxic compounds are major issues in the design of biological nitrification processes. Optimal conditions for nitrification are critical as incomplete nitrification is a major source of nitrous oxide production in wastewater treatment.

Nitrifying bacteria need carbon and phosphorus as well as trace elements for cell growth. Under normal conditions, neither CO_2 nor phosphorus are limiting. The growth kinetics of the ammonia-oxidizing bacteria is rate limited below temperatures of 28°C. The maximum growth rates for nitrifying organisms are much lower than the heterotrophic organisms necessitating longer solids retention times (SRTs). Depending on typical aeration tank design, SRT values may range from 10 to 15 days. Above 28°C, the relative kinetics of ammonia and nitrite oxidation change, whereby nitrite will accumulate at lower SRTs.

Additionally, nitrification rates increase as DO concentrations increase up to 4 mg/L. Larger suspended floc size inhibits nitrification as DO diffusion into the floc is reduced, and nitrifying bacteria within the floc will not receive adequate DO. DO concentrations below 0.50 mg/L greatly inhibit nitrification. Compounds that are toxic to nitrifying organisms include solvent organic chemicals, amines, proteins, tannins, phenolic compounds, alcohols, cyanates, ethers, carbonates, benzene, heavy metals, and un-ionized ammonia (NH_3) (Tchobanoglous et al., 2003).

FIGURE 1: FIRST STAGE NITRIFICATION PATHWAY
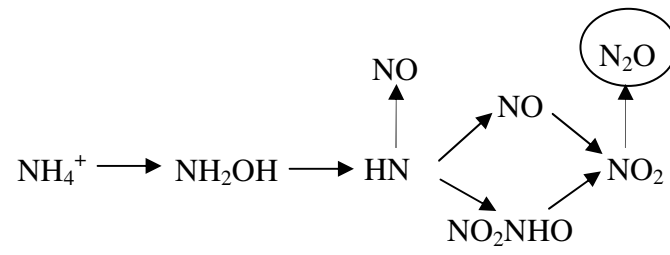
Sludge Thermal Drying Treatment. Thermal treatment of sludge produces nitrous oxide emissions, depending on the nitrogen content of the sludge. Werther et al. (1995) reported very high N_2O emissions, reaching concentrations as high as 350 ppm_v at lower temperatures of fluidized bed combustion (Werther, 1995). A Segher Hardpelletiser is currently under construction at the Stickney WRP. This is a convective thermal drying technology to convert sludge into pathogen-free pellets. Once in operation, the self-contained unit will be an oxygen-free environment, and dust control technology via bag filters and zero emission controls will be in place. As regenerative thermal oxidation is more than likely going to be used, N_2O emissions should be limited through complete combustion of the gases. However, a complete evaluation of the technology must be made before any assumptions/estimations can be made.

Summary. In wastewater collection, treatment, and effluent discharge, nitrous oxide production and emission can occur through both incomplete nitrification and denitrification. Nitrification occurs most prevalently in District WRP activated sludge aeration tanks. The influent wastewater ammonia concentration, BOD concentration, alkalinity, DO concentration, temperature, phosphorus, pH, and nitrifying bacteria genera are the major variables that control the extent of nitrification. The wastewater COD, nitrate concentration, denitrifying bacteria genera, floc size, DO concentration, and pH are the major variables that control the extent of denitrification. Incomplete nitrification and denitrification producing N_2O can occur in the District collection system (sewers, TARP, reservoirs, combined sewer overflows) and WRP processes (aeration basin, receiving streams, sludge conditioning and thickening, lagoons, drying beds, and anaerobic digestion). However, the secondary aeration tanks and the receiving stream are considered the major sources of N_2O from wastewater treatment. Incomplete nitrification leading to N_2O may be prevalent at the head of the aeration batteries due to low oxygen conditions. Additionally, low-temperature thermal heating of sludge may result in nitrous oxide emissions if emission controls are not in place.

The IPCC provides two methodologies for determining N_2O emissions from WRPs and the discharge from WRPs into the receiving stream; these methodologies do not consider a contribution from combined sewer overflows (CSOs). Nitrous oxide emissions from a centralized wastewater treatment process can be determined by (Doorn and Irving, 2006),

$$N_2O_{Plants} = P \cdot T_{Plant} \cdot F_{IND-COM} \cdot EF_{Plant} \tag{13}$$

N_2O_{Plants} = Total N_2O emissions from plants, kg N_2O/yr

P = Population, persons

T_{Plant} = Degree of use of wastewater treatment plants per capita, unitless

$F_{IND-COM}$ = Fraction of industrial and commercial co-discharged protein, unitless

EF_{Plant} = Emission factor, kg N_2O/person/year

Based on the 2000 District service population estimate of 5.29 Million and using a T_{Plant} value of 1.0, a default value of 1.25 for $F_{IND\text{-}COM}$ based on data from Tchobanoglous et al. (2003), and an IPCC default EF_{Plant} value of 0.0032 kg N_2O/person/year, the total N_2O_{Plants} from all seven District WRPS is 21,165 kg N_2O/yr. The mass emissions of N_2O can be converted to CO_2 Equivalents by,

$$CO_2\ Equivalents = Mass\ N_2O \times 300 \tag{14}$$

giving 6.35×10^6 kg CO_2 Equivalents (Doorn and Irving, 2006; Tchobanoglous et al., 2003). NACWA indicated that the IPCC default value for $F_{IND\text{-}COM}$ may be too conservative and suggested a value of 1.0; this would give a N_2O_{Plants} estimate of 16,932 kg N_2O/yr (5.08×10^6 kg CO_2 Equivalents).

Nitrous oxide emissions from the wastewater effluent can be determined by (Doorn and Irving, 2006),

$$N_2O_{Effluent} = N_{Effluent} \cdot EF_{Effluent} \cdot 44/28 \tag{15}$$

$N_2O_{Effluent}$ = Total N_2O emissions from effluents, kg N_2O/yr

$N_{Effluent}$ = Nitrogen in the effluent discharged to aquatic environments, kg N/yr

$EF_{Effluent}$ = Emission factor, kg N_2O-N/kg N

The factor 44/28 is the conversion of kg N_2O-N to kg N. Based on the total nitrogen released into receiving streams from the seven District WRPs of 3.59×10^6 kg N/yr based on total nitrogen effluent data and flow, and the IPCC default $EF_{Effluent}$ value of 0.005 kg N_2O-N/kg N, the total $N_2O_{Effluent}$ from all seven District WRPS is estimated as 2.82×10^4 kg N_2O/yr (8.46×10^6 kg CO_2 equivalents) (Doorn and Irving, 2006).

The total 2000 estimated nitrous oxide emission from the District are 49,353 kg N_2O/yr (14.81×10^6 kg CO_2 equivalents) using the IPCC input and 45,120 kg N_2O/yr (13.54×10^6 kg CO_2 equivalents) using the NACWA amendments. The U.S. 2000 N_2O emissions from wastewater and effluent were estimated to be 15.4×10^9 kg CO_2 Equivalents. Therefore, the District is estimated to have contributed 0.09-0.1% to U.S. N_2O emissions for 2000 from wastewater treatment and effluent. Again, it should be considered that many assumptions and default values were used in this calculation. Additionally, the IPCC calculation was developed for countries and not individual plants.

CONTROL OF FUGITIVE GREENHOUSE GASES

Methane

Production and Use. A common practice in many wastewater treatment plants is the use of methane from anaerobic digesters as fuel. Theoretically, capture and use of digester gas prevents methane from being released to the atmosphere. Gas from anaerobic digestion contains 55-70% methane, 25-30% CO_2, and small amounts of nitrogen (N_2), hydrogen (H_2), hydrogen sulfide (H_2S), and water vapor. Typical values of digester gas vary from 0.75 to 1.12 m^3/kg of volatile solids destroyed. Once produced, the gas must be collected under the cover of the digester. Currently, the District employs cylindrical tanks with fixed covers (Egan WRP) and floating covers (Stickney and Calumet WRPs) (Tchobanoglous et al., 2003).

In large plants, digester gas may be used as fuel for boiler and internal-combustion engines which generate electricity. Hot water from heating boilers or from engine jackets and exhaust-heat boilers may be used for sludge heating and for building heating (Tchobanoglous et al., 2003). Digester gas can also be used in cogeneration, which is generally defined as a system for generating electricity and producing another form of energy. Digester gas can be used to power an engine to generate electricity (Tchobanoglous et al., 2003). Purification of the biogas may be required prior to combustion or power generation. The extent of this purification is a function of equipment selected and emission regulations.

Flaring. A simple method for reducing methane emissions from anaerobic digesters currently being employed at District plants is flaring. Flaring is used when there is not enough gas pressure for generator use or a need to heat the boilers. Flaring methane after capture can have significant emissions benefits; the combustion of methane converts it to carbon dioxide,

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2 \tag{16}$$

Because carbon dioxide has 21 times less the heat-trapping impact of methane, this is an easy and economic solution to reduce methane emissions (Energy Information Administration, 1997). However, it does not utilize the power generation potential of the emitted methane.

Controlling Methane in Aerobic Processes. Limited methanogenesis can occur in aerobic processes such as low DO pockets or inner floc in suspended systems where microenvironments of anaerobic conditions exist. While methane production is encouraged in anaerobic digesters for biogas use, it is an indicator of an inefficient aerobic process. Strategies for reducing methane emissions from aerobic processes include decreasing or eliminating rumen protozoa activity and adding methanogen inhibitors (Su et al., 2004).

Rumen protozoa are particularly important in ruminant methane production. Many methanogens adhere to protozoa, which have been observed to support the methanogenic activity

of the attached bacteria. Accordingly, removing protozoa can reduce methane production (Su et al., 2004).

Methanogen inhibitors can be divided into two groups: 1) polyhalogenated methane inhibitors such as the hemiacetal of chloral and starch and bromochloromethane (BCM); and 2) polyether ionophores such as monensin and lasalocid. Polyhalogenated methane inhibitors directly suppress methanogenic activity and reduce methane production by 20-80% (Su et al., 2004).

In one study, researchers investigated reducing GHG emissions, specifically methane, from anaerobically digested swine waste. Four different concentrations of BCM (0, 1, 5, and 10 mg/L) were added to wastewater before being pumped into an anaerobic digester. The COD, BOD, and SS concentrations for all four treatments were approximately 6100 mg/L, 1200 mg/L, and 2400 mg/L, respectively. After 120 hr, biogas was not produced in the 10 mg/L BCM treatment. The production of biogas decreased with the addition of 0, 1, and 5 mg/L BCM with 7975, 7760, and 6300 mL/day produced, respectively. The lower concentrations of BCM (1 and 5 mg/L) removed the highest percentage of COD, BOD, and SS; increasing BCM concentrations did not significantly improve percent removal of COD, BOD, and SS (Su et al., 2004). As methanogenesis is inhibited, much of the COD, BOD, and SS removal must be occurring in the first two steps of the anaerobic process, i.e. hydrolysis and fermentation. Because the District beneficially uses methane, this treatment is not attractive.

Removing Aqueous Methane from Wastewater. Not all methane produced in anaerobic digestion is converted to the gas phase for collection. Methane has a water solubility of 0.0014 M_{liq}/bar_{gas}. Therefore, the supernatant from dewater anaerobically digested sludge may have an observable methane concentration. Diffusion of methane is high, and it can be stripped relatively easily by either a stripping chamber after digestion or air diffusion (Greenfield and Batsone, 2005).

Nitrous Oxide

Intermittent Aeration Process. Although not directly applicable to District WRPs, a number of studies examining intermittent aeration were reviewed. These studies provide further insight into the sensitivity of the conditions and variables controlling nitrification, denitrification and the evolution of N_2O. Nitrous oxide can be produced through both nitrification and denitrification as well as during simultaneous nitrification and denitrification. An intermittent aeration process was examined by Kimochi et al. (1998) to investigate N_2O production (Kimochi et al., 1998). This process allows biological nitrogen removal in a single reactor via stirring with aeration to promote nitrification (aerobic) and without aeration (anoxic) to promote denitrification. The oxic and anoxic conditions were alternated for specific periods. Nitrous oxide reductase, responsible for reducing N_2O to N_2 during denitrification, becomes unstable in the presence of oxygen, thereby increasing N_2O emission (Kimochi et al., 1998).

The intermittent aeration process was examined at a full-scale wastewater treatment facility in Chiba, Japan. During the intermittent aeration, no pH adjustments were made, and emitted gas was collected in a gas collection chamber. The ammonia concentration decreased and nitrate concentration increased during the aeration periods; no nitrite was detected in the system. Different combinations of oxic/anoxic reaction times were examined: 30/30 minutes, 30/60 minutes, 30/90 minutes, and 120/0 minutes. The highest nitrogen removal was observed with the shorter anoxic periods. Most of the N_2O was emitted during aeration. The overall lowest emission was observed during the 30/90 minute run. However, this had the lowest overall nitrogen removal among the intermittent aeration runs. The 30/60 minute run was observed to have the best overall nitrogen removal and nitrous oxide emission control. Additionally, as nitrous oxide is relatively soluble, higher aqueous concentrations were observed during the anoxic periods (Kimochi et al., 1998).

In a similar study, two different reactor fill modes were examined: oxic and anoxic fill (Park et al., 2001). A relatively large fraction of influent nitrogen was converted to N_2O in the sequencing batch reactor (SBR) with the anoxic fill, whereas a small fraction of nitrogen was converted during the aerobic fill. It appeared that anoxic fill could increase N_2O production at the initial stage of the aerobic phase due to the accumulated ammonia during the anoxic phase. Park et al. (2001) suggested that since ammonia loadings are oxidized more rapidly at the initial stage of the aerobic phase, utilizing an aerobic stage fill could be an effective method of suppressing the N_2O production.

Thorn and Sorensson (1996) examined the effect that external factors such as pH and dissolved oxygen has on nitrous oxide reductase, the enzyme responsible for reducing nitrate to nitrogen gas. Inhibition of nitrous oxide reductase will increase nitrous oxide production. In this study, a pilot plant was used to test nitrogen removal using denitrification in an anoxic basin followed by sedimentation. A fraction of waste was recirculated back to the anoxic basin, and a nitrification step was simulated by addition of nitrate to the recirculated water (Thorn and Sorensson, 1996).

Temperature had no effect on the nitrous oxide production, and the addition of a carbon source provided only a slight enhancement of the denitrification rate with no effect on N_2O production. Nitrous oxide production decreased as pH increased and increased as redox potential increased. Adding nitrite or nitrate did not increase N_2O production rates (Thorn and Sorensson, 1996). Tallec et al. (2006) also tested the effect of oxygen concentration on the activated sludge process, because ammonia oxidizing bacteria can become nitrifying bacteria when oxygen is depleted; nitrite then plays the role of oxygen as the final electron acceptor. The highest N_2O emissions were observed at DO concentrations of 1 mg/L. This N_2O production increased with the addition of nitrite.

A study investigating intermittent aeration by Park et al. (2000) examined the accumulation of nitrate and its effect on N_2O production. In carbon-limiting conditions, nitrate is a better electron acceptor than N_2O. This leads to an accumulation of N_2O. In this study, an external carbon source was used with an intermittent aeration system during an anoxic period to reduce NO_3^- and N_2O emissions (Park et al., 2000).

An activated sludge reactor including both an aeration zone and a solid-liquid-gas separating zone was maintained in a 2.7-L volume. Four parallel reactors were operated to study the conditions controlling N_2O production. In two of the four reactors, biofilms were deployed using a cellulose media. The system was intermittently aerated to support alternating nitrification and denitrification processes. The operation cycle consisted of a 60-min aerobic phase and a 30-min anoxic phase, fed with domestic wastewater from Tsukuba City, Japan. Consistent with results reported by Kimochi et al. and Park et al., the highest N_2O emissions occurred during the aerobic phase. This increase in N_2O may be due to the lack of DO at the beginning of the aerobic stage (Park et al., 2000).

Residual nitrate can significantly contribute to N_2O production in the aerobic phase. Thus during denitrification, nitrous oxide emissions increased with an increase in nitrate concentration. When a carbon source (methanol), was supplied complete denitrification occurred during the anoxic period, thereby reducing N_2O emissions. The completeness of converting nitrate to nitrogen gas is done through coupling the denitrification reaction(s) with the oxidation of organic matter, in this case, methanol. Overall, the biofilm reactors reduced N_2O emissions and removed nitrogen relative to the suspended reactors (Park et al., 2000).

Bacteria Genera. The nitrifying bacteria genera can also affect the magnitude of nitrous oxide emissions. The N_2O production of *Alcaligenes faecalis*, a typical heterotrophic nitrifier, *Nitrosomonas europea*, a typical autotrophic ammonia oxidizer, and *Nitrobacter winogradskyi*, a typical nitrite oxidizer were compared (Inamori et al., 2003). Unit-*N. europaea* produced the most N_2O, approximately 280-540 times that of unit-*N. winogradskyi* and approximately 20-50 times that of unit-*A. faecalis*. However, due to its heterotrophic character and possible high population density, it was suggested that *A. faecalis* has a potential to play important roles in N_2O generation under oxic conditions (Inamori et al., 2003).

A. faecalis was introduced into an activated sludge process to examine its effect on N_2O production. Results showed that the system produced 5 times less nitrous oxide than the control. Moreover, the total nitrogen removal efficiency was 10% higher. Apparently, the introduction of *A. faecalis* was useful in reducing nitrous oxide emissions and increasing nitrogen removal efficiency (Inamori et al., 2003).

RECOMMENDATIONS

The District should survey one of the WRPs and survey CH_4 and N_2O emissions and identify the largest sources of fugitive emissions. The results of this survey should be used to formulate a strategy for reducing or eliminating fugitive emissions in the future.

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