# REAL TIME MONITORING OF NITROUS OXIDE EMISSIONS FROM WASTEWATER TREATMENT PROCESSES BY MEMBRANE INTRODUCTION MASS SPECTROMETRY

By

ALEXANDER (SANDY) THOMPSON
B.Sc., Vancouver Island University, 2005

A thesis submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
in
ENVIRONMENT AND MANAGEMENT

We accept this thesis as conforming
to the required standard

……

Dr. Chris Gill, Professor, Department of Chemistry,
Co-Director, Applied Environmental Research Laboratories
Vancouver Island University, Nanaimo, BC

……

Dr. Lenore Newman, MEM Program Head
School of Environment and Sustainability

……..

Dr. Anthony Boydell, Director
School of Environment and Sustainability

ROYAL ROADS UNIVERSITY
June 2010

# ABSTRACT

This project investigated membrane introduction mass spectrometry (MIMS) as a real time (on-line) analytical monitoring technique for nitrous oxide gas emissions from processes within a full-scale biological nutrient removal wastewater treatment plant. Experiments have shown that treatment processes including nitrification (aerobic - ammonia to nitrate) and denitrification (anoxic - nitrate to nitrogen gas) can become disrupted resulting in unintended nitrous oxide emissions ($N_2O$). A limited number of studies have been conducted that monitor real time $N_2O$ emissions from full-scale treatment bioreactors and there remains significant uncertainty in true emissions. Two real time monitoring experiments (22 hours each) are shown where MIMS was able to track nitrous oxide emissions from the aerobic and anoxic zones of the bioreactor. Concentrations were calculated from response factors obtained using an internal standard. Estimated quantities of nitrous oxide emissions under various scenarios and recommendations for future investigations are also provided.

ACKNOWLEDGEMENTS

The author would like to thank Dr. Chris Gill from the Applied Environmental Research Laboratories (Vancouver Island University, Nanaimo, BC) for support in all aspects of this project. Dr. Gill was instrumental in providing use and transport of a MIMS instrument, troubleshooting, experiment setup and above all, years of dedicated mentorship. The assistance of many members of the Applied Environmental Laboratories Research Group is gratefully acknowledged, as well as Andrew Tucker and Ron Sander for sponsoring the project (supervisor and manager respectively, wastewater treatment plant).

TABLE OF CONTENTS

## LIST OF FIGURES

## LIST OF TABLES



## CHAPTER 1 - INTRODUCTION AND LITERATURE REVIEW

*Research Question and Objectives*

The primary objective of this research project was achieved by answering the following research question:

1) Can the nitrous oxide emissions from a full-scale biological nutrient removal wastewater treatment plant be monitored in real time by membrane introduction mass spectrometry (MIMS)?

This was accomplished by demonstrating that MIMS was able to track real time nitrous oxide emissions from the aerobic and anoxic zones of the bioreactor over extended periods.

Secondary objectives included:

- Determining if the results are consistent with those obtained during other wastewater treatment research
- Propose improvements for future investigations of wastewater emissions by MIMS
- Development of estimated yearly emissions based on various treatment plant and analytical monitoring scenarios
- Development of recommendations for organizations operating wastewater treatment plants to assist with monitoring and mitigation of nitrous oxide emissions

*Biological Nutrient Removal Wastewater Treatment*

Biological nutrient removal (BNR) for wastewater treatment is a well-established process used to remove nutrients including ammonia ($NH_3$), ortho-phosphate ($PO_4^{3-}$), and nitrate ($NO_3^-$) from municipal and industrial liquid-waste streams (Oldham & Rabinowitz, 2001). The processes for nutrient removal hinge on optimizing chemical and physical conditions (dissolved oxygen, solids retention time, carbon source addition, internal recycle rates, chemical additions, etc) within bioreactors that favor specific and beneficial bacterial communities. Under acceptable operating conditions, these bacterial communities can efficiently uptake and remove dissolved nutrients from the wastewater. The masses of bacteria are mechanically separated from the water-phase resulting in improved overall water quality. There are many different bioreactor designs; a common variation in western Canada is a version of a suspended growth system which is divided into fixed zones that include anaerobic, anoxic, and aerobic zones (Oldham & Rabinowitz, 2001). An example of a bioreactor design is given in Figure 1.

The biological removal of influent ammonia nitrogen involves nitrification followed by denitrification (Paredes, Kuschk, Mbwette, Strange, Muller, & Koser, 2007). During nitrification, bacteria oxidize ammonia to nitrite ($NO_2^-$), then to nitrate under aerobic conditions ($NH_3 \rightarrow NO_2^- \rightarrow NO_3^-$). This is followed by bacterial denitrification where nitrate is converted to nitrogen gas ($N_2$) through nitrite, nitric oxide (NO), and nitrous oxide ($N_2O$) intermediates ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$) (Tallec, Garnier, Billen, & Gousailles, 2008). Research has indicated, however, that the microbial pathways utilized during this conversion of ammonia to nitrogen gas can become 'modified'. These modifications have been correlated with the production and emission of nitrous oxide gas during the wastewater treatment processes (Tallec et al., 2008; Shiskowski & Mavinic, 2006; Burgess, Colliver, Stuetz, & Stephenson, 2002; Czepiel, Crill, & Harriss, 1995).

### *Nitrous Oxide and Wastewater Treatment*

There are a number of reasons that we should be concerned with nitrous oxide emissions. Nitrous oxide is a potent greenhouse gas with a global warming potential about 310 times that of carbon dioxide and a residence time in the atmosphere of approximately 120 years (IPCC, 2000). It has also been shown to be involved in the degradation of stratospheric ozone (Barton & Atwater, 2002).

It has been found by numerous groups that many of the bacterial processes used in the treatment of wastewater nitrogen (nitrification, denitrification and nitrate ammonification) are indeed responsible for $N_2O$ production (Tallec et al., 2008; Shiskowski & Mavinic, 2006; Burgees et al., 2002; Czepiel et al., 1995). Researchers have been working to determine the physical, chemical, and biological conditions that cause increased nitrous oxide production but

progress is challenged by the sheer complexity of microbial activities (Paredes et al., 2007). Laboratory and full-scale wastewater treatment monitoring experiments have gained some insight to the operational and chemical conditions that can lead to elevated nitrous oxide emission rates. These can include ammonia shock (Burgess et al., 2002), nitrite build up and pH (Shiskowski & Mavinic, 2006), along with temperature and low free oxygen within certain zones of bioreactors (Tallec et al., 2008).

According to the 2006 Intergovernmental Panel on Climate Change (IPCC) report chapter six "Nitrous Oxide Emissions From Wastewater" very limited data is available (pertaining to wastewater emissions) and it is important to develop a better understanding of the quantities of nitrous oxide emitted from wastewater treatment plants (Doorn et al., 2006). A recent, and thorough, review of nitrous oxide from wastewater processes research found an extremely wide variation in $N_2O$ emissions as a percentage of total nitrogen loading from 0.005% to 90% (Kampschreur, Temmink, Kleerebezem, Jetten, & van Loosdrecht, 2009). Similar to the IPCC document, these researchers explicitly highlight the need for additional research and new analytical techniques for monitoring wastewater treatment processes for nitrous oxide emissions.

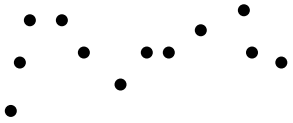
### *Monitoring Nitrous Oxide Emissions*

The complexities of wastewater treatment processes originate from the fact they are carried out by masses of bacteria under a host of variable chemical and physical conditions including, but not limited to: diurnal flow patterns, nutrient loading concentrations, seasonality, dissolved oxygen content and a myriad of chemical additions. The analytical techniques selected by researches define the amount, quality and certainty of data collected during experiments.

There are three general categories into which analytical monitoring techniques can be divided (Table 1).

Table 1:

Categories of analytical monitoring techniques and their relationship to sampling, delay in results and depiction of data.

| Monitoring Technique | Sampling Type | Delay in Results | Depiction of Data |
|---|---|---|---|
| | | | |
| On-Line and Real Time | Continuous sample flow introduced directly to instrument | Seconds to minutes |  |
| At-Line | Individually collected and prepared samples transferred to on-site instrument for analysis | Minutes to hours |  |
| Off-Line | Individually collected samples preserved and transported to off-site laboratory for preparation and analysis | Hours to days to weeks |  |

(Source: Callis, Illman, & Kowalski, 1987)

Table 1 illustrates that the resolution of information collected during experiments varies directly with the selection of analytical monitoring techniques. A number of at-line and off-line analytical techniques were used to measure nitrous oxide during lab scale and full-scale experiments (Kampschreur et al., 2009). Gas chromatography (GC) with electron capture detection (ECD) has been applied extensively to analyze nitrous oxide emissions from bench scale experiments (Shiskowski, Simm, & Mavinic, 2004; Czepiel et al., 1995) and full-scale operational treatment plant experiments (Foley, de Haas, Yuan, & Lant, 2010; Czepiel et al., 1995). A method with greater sensitivity for nitrous oxide detection involves the use of solid

phase microextraction (SPME) as a pre-concentration step followed by gas chromatography with mass spectrometry detection (GC-MS) (Silva, Rocha-Stantos, & Duarte, 2009). Unfortunately, these (at-line and off-line) methods are less able to provide highly detailed information because of time delay due to the chromatography step. Also, they tend to be time consuming and resource intensive to implement because of individual sample collection.

Ideally, to resolve the dynamic conditions and emissions observed during biological wastewater treatment, real time (on-line) analysis should be implemented. Real time analysis offers the advantage of continuously collecting data so that detailed, temporally resolved measurements can be obtained (Table 1, depiction of data). This level of detailed information is essential during process, reaction, kinetic and biological production based experiments (Milagre, Milagre, Rodrigues, Rocha, Santos, & Eberlin, 2005; Hayward, Lister, Kotiaho, Cooks, Austin, Natayan, & Tsao, 1988). Infrared (IR) gas analyzers and portable $N_2O$ gas monitors have been used to provide real time data in laboratory and outdoor experiments (Tallec et al., 2008; Shiskowski & Mavinic, 2006; Strom, Lamppa, & Christensen, 2007). Although these instruments have an advantage over chromatography based systems by facilitating real time monitoring they tend to be less sensitive and can be prone to interferences. More recent advances in IR technology, however, have seen the development of microsensors and optical fiber analyzers that are able to provide real time monitoring of nitrous oxide along with greater sensitivity (Foley, et al., 2010; Meyer, Allen, & Schmidt, 2008; Silva et al., 2009). High quality research has been conducted with the above mentioned analytical techniques. There is, however, a need for new analytical techniques for investigating nitrous oxide emissions from biological systems. Membrane introduction mass spectrometry is presented as analytical technique to

bridge this technological gap by coupling the sensitivity of mass spectrometry detection with a real time, continuous, on-line, membrane based, sampling technique.

### *Membrane Introduction Mass Spectrometry*

Membrane introduction mass spectrometry is a real time monitoring technique that uses a polydimethylsiloxane (PDMS or Silicone$^{TM}$) semi-permeable membrane as the sampling device (Johnson, Cooks, Allen, Cisper, & Hemberger, 2000; Wong, Cooks, Cisper, & Hemberger 1995). This hollow fiber (tubular shaped) membrane is typically about 10 centimeters long and 1 millimeter in diameter and functions as an interface between the sample (bioreactor gas emissions during this research) and the mass spectrometer detector (Thompson, Creba, Ferguson, Krogh, & Gill, 2006). The composition of the membrane is such that volatile compounds (including nitrous oxide) contained within a sample that is flowed over the exterior of the membrane, can pass through, while the bulk sample matrix is excluded. The volatile compounds that pass through the membrane are transferred directly to the mass spectrometer for detection. There are many designs and membrane geometries possible (Ketola, Kotiaho, Cisper, & Allen, 2002). For this work, the hollow fiber membrane was housed within a stainless steel (¼ inch tubing) flow through cell (membrane interface) allowing the sample to be continuously introduced to the membrane with a small air pump (Figure 2) (Etzkorn, Davey, Thompson, Creba, LeBlanc, Simpson, Krogh, & Gill, 2009). The membrane interface is generally mounted inside a GC oven for temperature control. This MIMS setup allows the use of a permeation tube of an internal standard (eg. deuterated toluene) in an on-line flow cell that facilitates instrument calibration, the production of response factors and tracking of instrument drift during extended real time operation (Mendes, Sparrapan, & Eberlin, 2000).

MIMS expands on the utility of chromatography systems (GC-ECD, GC-MS) by continuously sorting ions of molecules (that have passed through the membrane) based on their masses then quantifying their relative concentrations in the original sample stream. This operation facilitates simultaneous monitoring of multiple compounds. The direct sampling strategy means that no sample preparation is required. Other advantages include elegantly simple construction, operation and maintenance, relatively low costs for development, and greatly expand research and process monitoring capabilities compared to the aforementioned techniques. Membrane interface systems are not commercially available; however, their in-house construction is relatively straightforward (Johnson et al., 2000). Numerous research groups continue to exploit the capabilities of MIMS as a real time, efficient and sensitive analytical detection system (Thompson, Etzkorn, Van Pel, Krogh, Drakeford, & Gill, 2008; Short, Toler, Kibelka, Rueda Roa, Bell, & Byrne, 2006; Boscaini, Alexander, Prazeller, & Mark, 2004; Mendes, Sparrapan, & Eberlin, 2000). Technological advances in MIMS systems are on-going and include utility in challenging environments such as mobile applications (Etzkorn et al., 2009) and underwater (Short et al., 2006). Further advances also capitalize on the selective nature of enzyme based reactions for even greater analysis capabilities (Creba, Weissfloch, Krogh, & Gill, 2007). Reviews of the MIMS technique and its applications have been published (Ketola, Kotiaho, Cisper, & Allen, 2002; Johnson et al., 2000). The dynacalibrator (Model 450, VICI Metronics, Poulsbo, WA) provided precise metering and dilution of gas standards from permeation tubes and was utilized for the development of the project calibration curve and response factors (see methodology section). Membrane cleaning is carried out after each experiment by flushing with a flow of zero air or nitrogen gas.

# CHAPTER 2 - RESEARCH METHODOLOGY

The methodology used to execute this project was divided into four sections: instrumental, sample train apparatus, data analysis and nitrous oxide monitoring by SUMMA canister. Each section is described below.

## *Instrumental*

Briefly, an ion trap mass spectrometer (Thermo-Fisher GCQ, San Jose, CA) with a gas chromatograph was modified according to Etzkorn et al. (2009) and operated under similar instrumental parameters with the exception that tandem (MS/MS) mass spectrometry was not used for the project. It was anticipated that MS/MS would allow resolution of nitrous oxide from the direct (isobaric) interference of carbon dioxide because both molecules have the same mass (44 atomic mass units). Preliminary investigations found that MS/MS was not suitable due to inadequate fragmentation of the nitrous oxide ion within the ion trap of the mass spectrometer (nitrous oxide was expected to fragment from its parent mass of 44 to mass 30 allowing us to differentiate it from carbon dioxide which fragments to mass 28). To overcome this issue, selective ion monitoring (SIM) was used for mass 30. Information that assisted with determining these instrument operating parameters was derived from the NIST chemistry webbook library (NIST, 2008) (Figure 3). These operating parameters were similar to those used during another study of nitrous oxide and other intermediates during denitrification by mass spectrometry (Thomsen, Geest, & Cox, 1994). It should be noted that mass 30 also corresponds to the mass of nitric oxide (Figure 3). The presence of nitric oxide in the emissions sampled could cause a direct isobaric interference with the measurement of nitrous oxide (see discussion section).

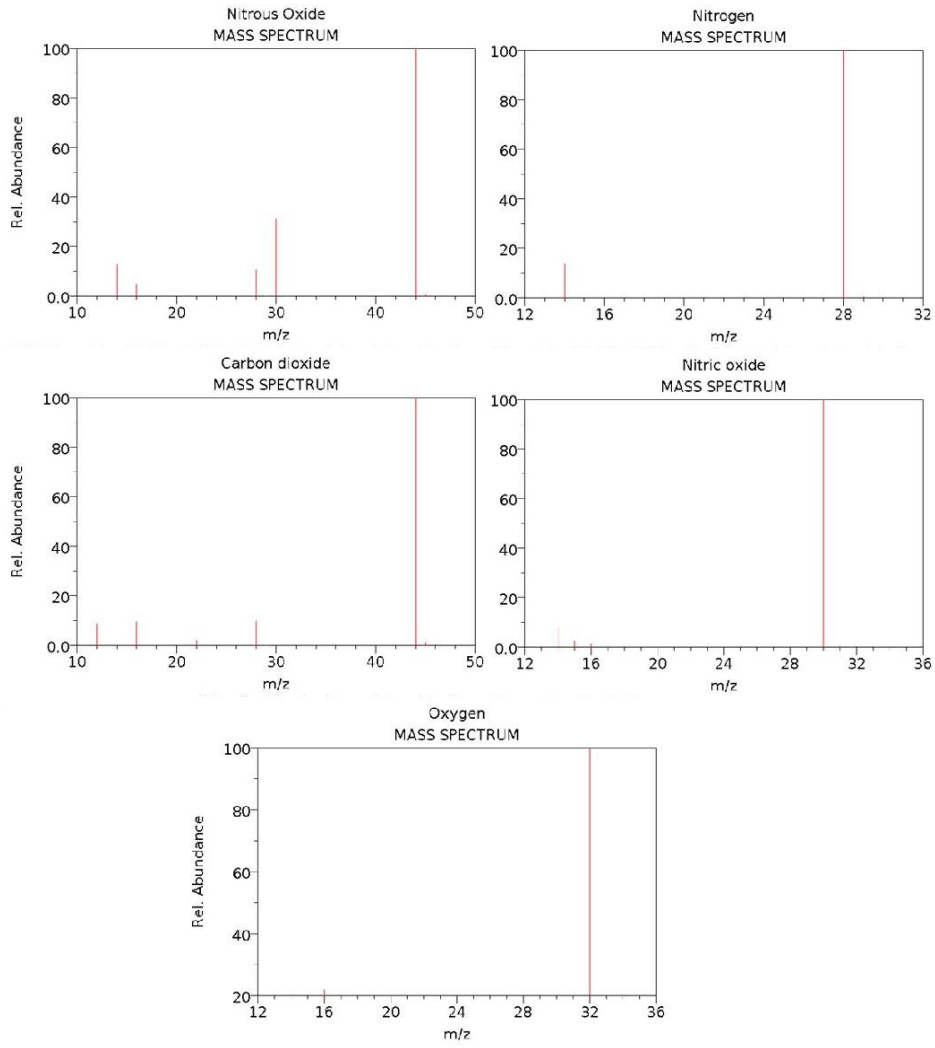



Figure 3. Electron impact ionization mass spectra of atmospheric gas molecules. In these examples, parent ions are at 100% relative abundance and fragmentation ions are of lesser abundance (NIST, 2008).

*Sample Train Apparatus*

A headspace ranging from approximately 0.1 m – 1.0 m in height was created above the bioreactor sampling zone using a standard department store nylon reinforced polyethylene tarp. An estimated 95% coverage was achieved. An air blower with an eight inch outlet (AIR Systems International, #SVB-E8EC, Chesapeake, VA) was suspended about 0.5 m above the

bioreactor liquid surface. A flange was adapted to the blower so that four inch 'dryer ducting' could be attached to the outlet. The maximum listed flow rate of this blower was 1390 cubic feet per minute (cfm) at the eight inch outlet and measured at approximately 40 cfm at the exit of the dryer ducting during a typical experiment (on-site aerometer measurement). It was expected that construction of the new on-site wastewater treatment plant laboratory (located about 40 m from the bioreactor) would be complete before the experimental stages of this project; however, such was not the case. Because the new lab was still under construction an additional 80 m of ducting was required to transfer the bioreactor emissions approximately 120 m to the instrument location. A continuous air sample was drawn from the exit of the dryer ducting via 10 m of ¼ inch Teflon tubing using a diaphragm air pump into the membrane interface at a rate of 4.4 liters per minute. An inline particulate filter was used to pre-filter the air upstream of the membrane interface. Experiments were ended with a back flush of nitrogen gas that served to both clean the membrane and allow a baseline measurement in the absence of nitrous oxide.

### *Data Analysis*

The nitrous oxide calibration curve (Figure 4) and deuterated-toluene internal standard instrumental response factor (RF) was determined at the Applied Environmental Research Laboratories (Vancouver Island University, Nanaimo, BC). The internal standard was introduced continuously during experiments by a permeation tube mounted in-line with membrane interface (Figure 2). Gas phase concentrations were calculated according to VICI Metronics Inc, Generating Calibration Gas Standards, Technical Note 1001 (available at www.vici.com/support/tn/tnmenu.php).

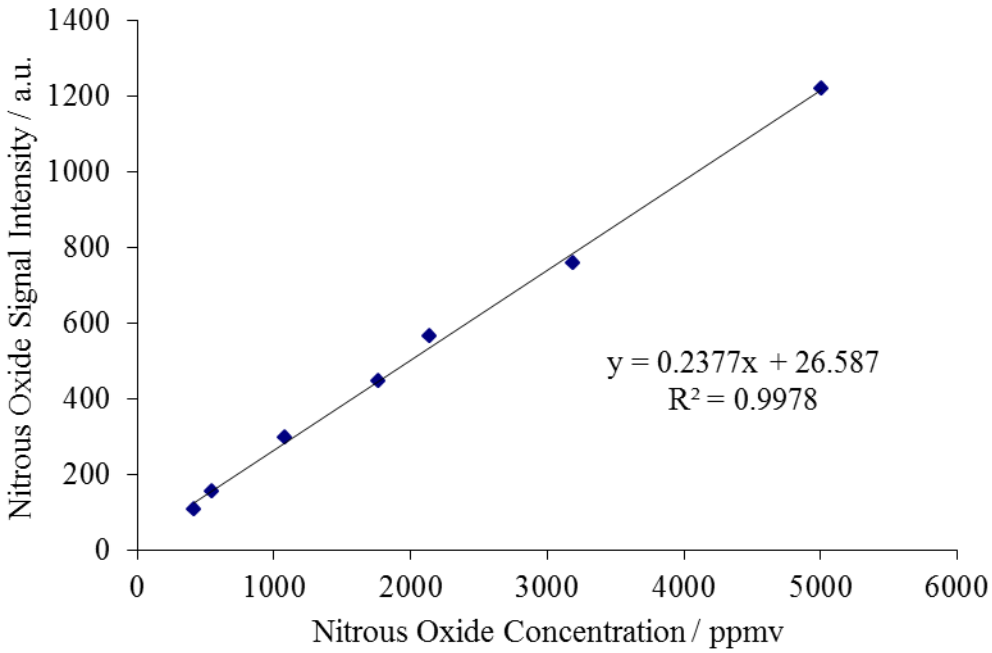



Figure 4. Experimentally determined direct calibration curve for nitrous oxide.

Nitrous oxide response factors relative to the internal standard were determined over a range of concentrations (Table 2). These were calculated from experimental measurements using Equation 1 (Etzkorn et al., 2009). The responses factors were averaged to develop a single response factor of 0.0012+/-0.0001. The real time data collected during experiments was exported to a Microsoft Excel spreadsheet for conversion of instrument signals to concentrations (parts-per-million-volume (ppmv)) using the response factor (Equation 2).

Table 2:

Experimentally determined response factor for nitrous oxide relative to deuterated toluene internal standard.

| $N_2O$/ ppmv | Response Factor (RF) |
|---|---|
| 5009 | 0.0011 |
| 3192 | 0.0011 |
| 2141 | 0.0012 |
| 1761 | 0.0012 |
| 1083 | 0.0013 |
| 543 | 0.0014 |
| 413 | 0.0013 |
| Average | **0.0012** |
| Std Dev. | **0.0001** |

Equation 1: $$RF = \frac{\text{Signal nitrous oxide / Concentration nitrous oxide}}{\text{Signal internal standard / Concentration internal standard}}$$

(Source: Etzkorn et al., 2009)

Equation 2: $$N_2O \text{ conc.} = \frac{\text{Signal nitrous oxide}}{RF} \text{ X } \frac{\text{Internal standard signal}}{\text{Internal standard conc.}}$$

*Nitrous oxide Monitoring by SUMMA Canister*

An additional nitrous oxide measurement was obtained during the MIMS aerobic zone monitoring on November 3, 2009. For this, a SUMMA canister (regulated air sampling vacuum chamber) was used to collect a 60 minute composite air sample directly adjacent to the emissions sample transfer blower. This was analyzed at an independent commercial laboratory by GC-ECD (Maxxam Analytics, Ottawa, Ontario).

# CHAPTER 3 - RESULTS

## *Aerobic Zone Monitoring*

The first aerobic (nitrification) zone of the bioreactor was monitored over a 22 hour period beginning November 3, 2009 (Figure 5). Response factors were applied to the raw signal data as described in the methodology chapter. During this MIMS monitoring experiment a SUMMA canister was also used to collect a composite emissions sample between hours four and five. The result was 0.86 ppmv nitrous oxide compared to the MIMS result of about 170 ppmv over the same time interval. From Figure 5, the MIMS results show an initial concentration of 100 ppmv that increases to about 170 ppmv between hours zero to five. The concentration dropped sharply to about 70 ppmv from hours five to six and fluctuated between 60 and 100 ppmv from hours six to 13. A long and gradual increase from hour 13 to 22 is depicted by a concentration increase from about 80 to 220 ppmv. The experiment was ended after 22 hours with a backflush of nitrogen gas.

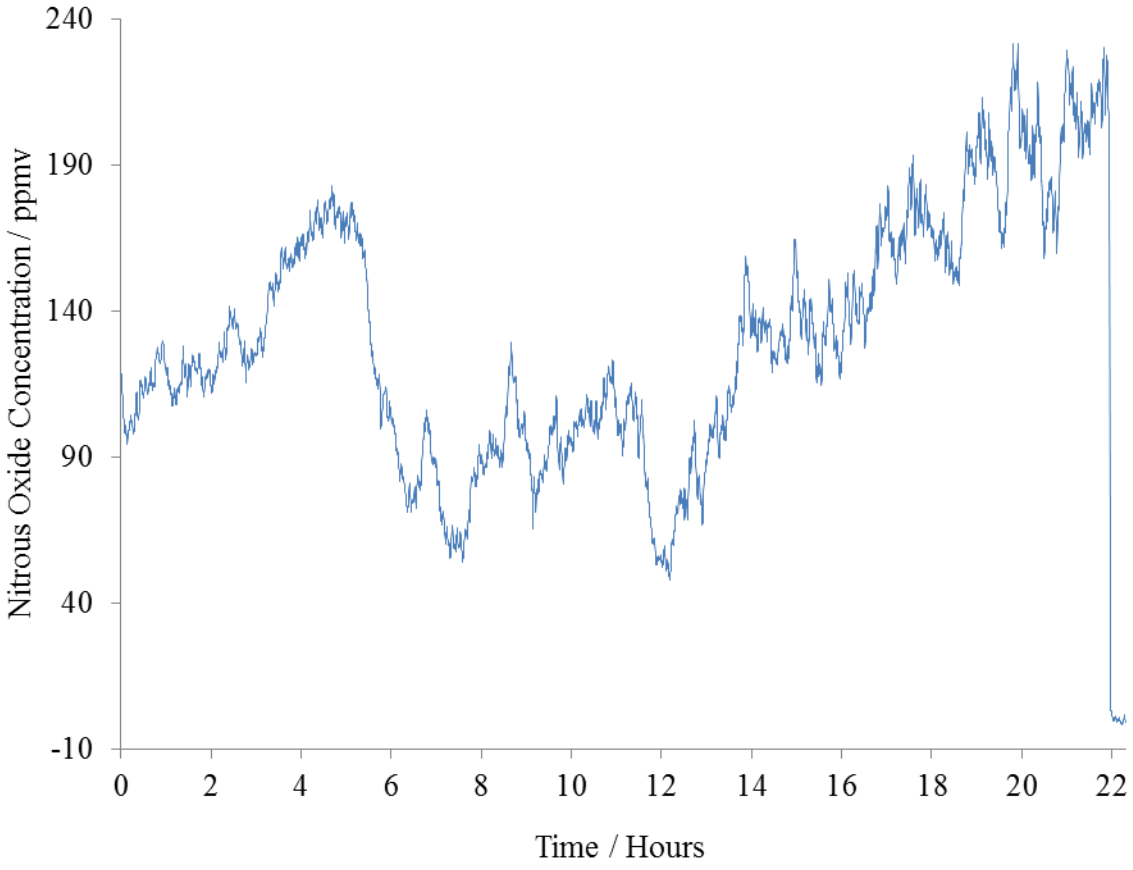



Figure 5. Aerobic zone monitoring results.

*Anoxic Zone Monitoring*

During this experiment the anoxic (denitrification) zone of the bioreactor was monitored with the MIMS system over a 22 hour period beginning November 1, 2009 (Figure 6). These results show an initial concentration of about 100 ppmv that fluctuates between about 100 and 140 ppmv from hour zero to hour nine. At hour nine the concentration increases from about 120 ppmv to about 250 ppmv by hour 15. The concentration gradually drops from 250 ppmv to 140 ppmv from hour 15 to hour 22 after which the experiment was ended with a backflush of nitrogen gas.

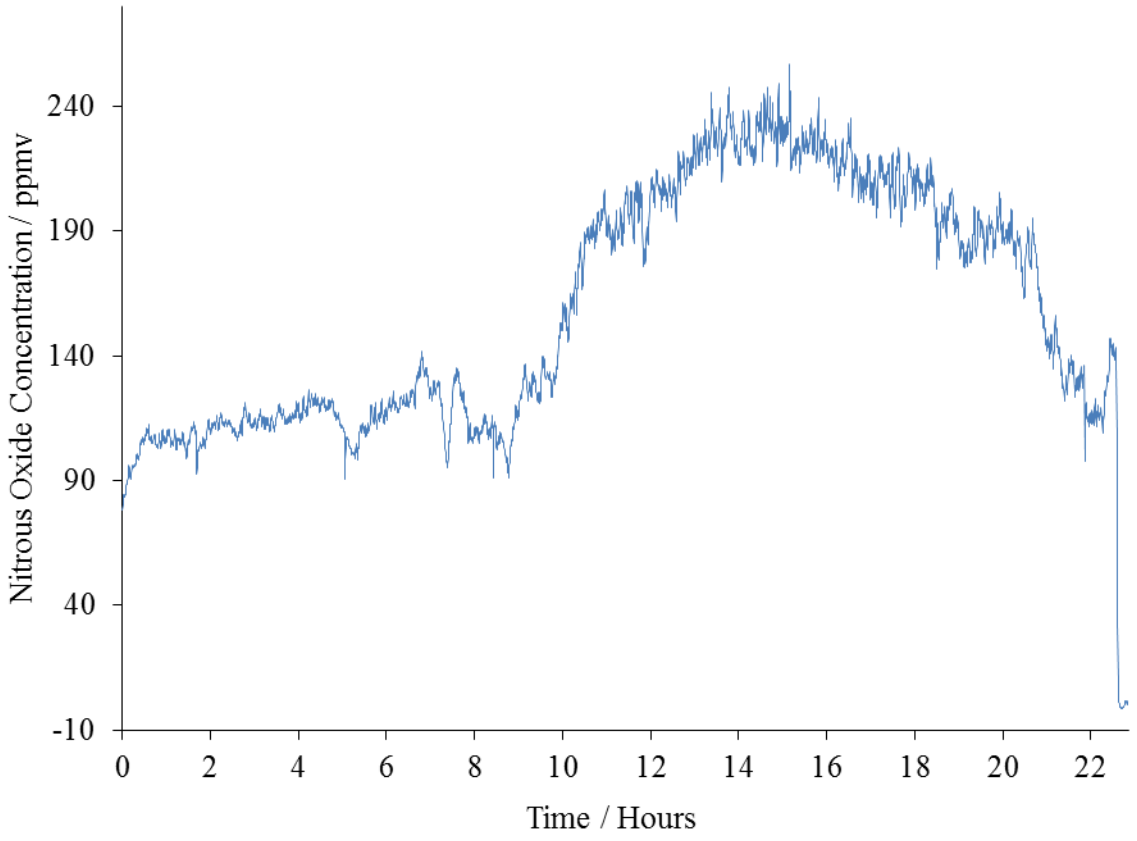



Figure 6. Anoxic zone monitoring results.

# CHAPTER 4 - DISCUSSION

This research project investigated membrane introduction mass spectrometry (MIMS) as a potential analytical method for real time monitoring of nitrous oxide emissions during wastewater treatment processes. The primary objective of this project was accomplished by demonstrating that MIMS was able to track real time nitrous oxide emissions from the aerobic and anoxic zones of the bioreactor over extended periods (Figures 5 and 6). Further work is required to develop this system for regular operation within wastewater treatment facilities and future efforts should be focused on improving the sample train apparatus, conducting long-term monitoring, and improving instrument parameters (eg: MS/MS) for nitrous oxide analysis.

## *Interpretation of Results*

The complexity of biological treatment processes, the myriad of wastewater treatment conditions and parameters, and potential uncertainty in measurements greatly increases the complexity of interpreting results. Although this research shows a relatively high level of nitrous oxide (compared to atmospheric background of about 0.315 parts-per-million-volume (ppmv)) produced by the bioreactor (50-220 ppmv in the aerobic zone; 100-250 ppmv in the anoxic zone), it appears to be consistent with previous studies (Foley et al., 2010; Kampschreur, van der Star, Wielders, Mulder, Jetten, & van Loosdrecht, 2008). A nitrification experiment by Kampschreur et al. (2008) revealed nitrous oxide emissions at 135 ppm during normal operation of their bioreactor. It is not fully understood why the microbial population in the bioreactor would be emitting such quantities of nitrous oxide. The literature suggests a number of conditions that can lead to elevated emissions including ammonia shock, nitrite build up and low

dissolved oxygen (see introduction section). Due to the limited data collected, it is difficult to be certain if such conditions were present during the MIMS experiment conducted for this work.

The main similarity in the two experiments (Figure 5 and 6) is the significant and gradual increase in emissions beginning around hour 12 of the aerobic experiment and hour 10 of anoxic experiment. Since both experiments began in the morning (about 8 am) these increases could coincide with the second and larger increase in diurnal wastewater flow to the bioreactor observed each day (the first flow increase begins around 9 am until noon, the second begins around 8 pm until midnight). This increased flow generally brings a large quantity of ammonia into the treatment plant that can overwhelm the nitrification process (observed as increasing ammonia discharge in plant effluent). Research has found that increased ammonia loading to biological treatment processes can result in increased nitrous oxide emissions (Burgess et al., 2002). It is also possible that increased nutrient loading during higher flows reduced dissolved oxygen concentrations within the bioreactor, another condition that can increase nitrous oxide emissions (Tallec et al., 2008). More detailed interpretations of the results become difficult due to the lack of additional information, an issue that could be addressed by future research (see additional sampling and analysis section).

## *Experimental Improvements for Future Investigations*

### *Sample Train Apparatus*

The sample train apparatus used for transferring the bioreactor emissions was not optimal for this work. The blower utilized was rated at approximately 1390 cubic feet per minute (cfm); however, the approximate flow rate from the end of the sample transfer ducting was only about 40 cfm. Increasing the transfer flow rate would reduce potential delays between emissions

events and measurement of those emissions. Further improvements in the sample transfer apparatus should be considered when the transfer distance is greater than about a few meters. It should be noted that this extended transfer distance (120m) was a result of the delayed completion date for the new laboratory facility. If extended transfer distance is unavoidable, improvements could see a more powerful blower and ducting with less internal air resistance. Others options could include capturing emissions with a hood placed directly on the liquid surface (Foley et al., 2010) or an apparatus where liquid sample is transferred followed by gas stripping (bubbling) in close proximity to the instrument. Ideally the sample train and emissions transfer would be eliminated all together by locating the MIMS system directly at the bioreactor. In theory this could solve sample transfer issues but would pose significant challenges in protecting the electronics of the instrument from damage by weather, etc.

*Long- Term Monitoring*

The variations in emissions observed (50-220 ppmv in the aerobic zone; 100-250 ppmv in the anoxic zone) during the monitoring experiments is similar to observations made in previous studies (Kampschreur et al., 2008). At present it is difficult to determine if the variability observed was due to process conditions or uncertainty in instrumental measurements. Implementing a long-term monitoring program of at least several weeks would allow greater insight into typical bioreactor emissions and providing a seasonal ‘snapshot’ of background emissions. To obtain a true background of emissions a continuous monitoring program of 1 or 2 years should be initiated. This would capture seasonal variations over a wide range of operating conditions and would allow for determination of actual quantities of nitrous oxide emitted from the bioreactor rather than extrapolating based upon short sampling events.

*Additional Sampling and Analysis*

A limited amount of time and resources constrained the amount of additional sampling and chemical analysis that could be conducted for this study. Additional analytical data on the chemical conditions of the treatment plant during the experiments would have allowed a more thorough interpretation of the results. For example, nutrient analysis during the MIMS experiments may have facilitated estimates of influent nitrogen conversion rates to nitrous oxide gas. Additionally, tracking dissolved oxygen concentrations may have provided insight to bioreactor conditions leading to elevated nitrous oxide emissions.

The validation of MIMS using a SUMMA canister was unsuccessful. MIMS results show a sample nitrous oxide concentration of 170 ppmv versus 0.86 ppmv for the SUMMA canister. This discrepancy in sample concentrations could be attributed to large wind events observed during the hour long deployment of the SUMMA canister, or possibly a faulty SUMMA canister. Unfortunately, it was not possible to account for or quantify the potential of wind events to influence emissions concentrations in the sampling area of the canister. MIMS is less prone to such errors because of continuous sampling at a relatively higher flow rate, over an extended period. Operating MIMS in parallel with another real time monitoring technique such as an IR detector or nitrous oxide monitor would improve our ability to validate this method and reduce potential uncertainty in measurements.

*Challenges Associated with Monitoring Nitrous Oxide*

Using MIMS to monitor nitrous oxide posed a number of unexpected challenges. As previously stated, initial attempts at $N_2O$ measurements using tandem (MS/MS) mass spectrometry proved unsuccessful. The reasoning behind tandem mass spectrometric analysis

was to avoid interference that could be caused by carbon dioxide, which has the same atomic mass as nitrous oxide (see methodology section). Instead, we collected nitrous oxide data by monitoring mass 30, a fragment ion of nitrous oxide produced in the ion source of the mass spectrometer. Analyzing mass 30 during nitrous oxide research has been documented (Thomsen, Geest, & Cox, 1994). Collecting data for nitrous oxide by monitoring the presence of mass 30 eliminated the potential for interference from carbon dioxide, however, there remained the potential for interference from other ions of mass 30. It should be noted that nitric oxide (NO) that also has a mass 30 ion. In other work, analysis of wastewater for nitric oxide and nitrous oxide has shown the ratios (percent conversion of total influent nitrogen loading) of 0.2% NO versus 1.7% $N_2O$ and 0.003% NO versus 0.6% $N_2O$ depending on the wastewater treatment process investigated (Kampschreur et al., 2008). Using these ratios of NO to $N_2O$ an approximate contribution of nitric oxide to the total mass 30 signal could range between 0 and 12%. Additionally, Kampschreur et al. (2008) found nitric oxide concentrations as high as 50 ppm emitted during their treatment process experiments. The presence of nitric oxide as an interferent to our measurement of nitrous oxide was not confirmed due to limited resources. Future investigations should involve a more rigorous plan to identify and quantify these and other potential interferences.

### *Information Pertaining to Sustainability*

This project contains components that can be used to expand the scope of sustainability initiatives. To begin, the literature explicitly states that significantly more work is needed in the area of monitoring nitrous oxide (and other greenhouse gas) emissions from wastewater treatment processes (Foley et al., 2010; Kampschreur et al., 2009; Doorn et al., 2006). The lack

of emissions monitoring program may lead to treatment plants operating under conditions that emit unknown, and possibly significant, quantities of nitrous oxide gas. Monitoring and tracking nitrous oxide emissions is the first step in a strategic plan for reducing potential emissions and achieving certain sustainability objectives and policies. Presented below are calculations for three scenarios (based on actual field sampling and literature values) for the potential yearly discharge of nitrous oxide from the bioreactor studied during this project.

*Estimated Yearly Emissions Calculated From SUMMA Canister Analysis*

The aerobic zone bioreactor headspace was sampled with a SUMMA canister. This sampling device is a common technique used for collecting and transferring gas emission to analysis laboratories. SUMMA canisters are used when analytical instrumentation is not available on-site. This method is readily available and can be quickly implemented by untrained personnel with the disadvantages of long turn-around-time for results and high costs. The SUMMA canister collected a one hour composite sample that was analyzed at a commercial analytical laboratory (Maxxam Analytics) in Ottawa. A result of 0.86 ppmv was obtained. Based on this data, projections on the emissions from the aerobic zone monitoring are extrapolated for the all of the bioreactor aerobic zones (eight) for a one year period (Table 3).

Table 3:

Estimated yearly emissions calculated from SUMMA canister analysis.

| Item | Value |
|---|---|
| SUMMA Canister Analysis Result | 0.86 ppmv $N_2O$ |
| Atmospheric Background | 0.315 ppmv $N_2O$ |
| Corrected Aerobic Zone Emissions | 0.545 ppmv $N_2O$ |
| Conversion ppmv to milligrams per cubic meter ($mg/m^3$) | 1.07 $mg/m^3$ $N_2O$ |
| Total Aerobic Zone Air Volume (Ave Nov 1-Dec 1,2009) | 200 $m^3$/hour |
| $N_2O$ emission per hour based on 200$m^3$ air volume per hour | 214 mg/hr $N_2O$ |
| $N_2O$ emission per year (single aerobic zone) | 1.875 kg/year |
| $N_2O$ emissions per year (all eight aerobic zones) | 14.997 kg/year |
| $CO_2$ equivalents (eq) emitted per year | 4649 kg $CO_2$ eq/year |

*Estimated Yearly Emissions Calculated From Other Research*

The review by Kampschreur et al. (2009) shows seven groups that determined nitrous oxide emissions from full-scale wastewater treatment plants. The results range from 0.001% to 14.6% nitrous oxide as a percentage of the total nitrogen loading to the treatment plants examined. Based on this range estimates were made for approximate total nitrogen loading of 22.72 milligrams per liter (mg/L) (average of 16 samples over 3 months, Source: Andrew Tucker, 2009). This value was used to project emissions from the bioreactor based on the conversion of influent nitrogen to nitrous oxide (Table 4).

Table 4:

Estimated yearly high (4%) and low (0.01%) range emissions based on percent of total nitrogen loading converted to nitrous oxide.

| Item | Value |
|---|---|
| Total Nitrogen Loading | 22.72 mg/L |
| Mass of Nitrogen Loading (10000$m^3$ flow/day) | 227.2 kg N/day |
| Low range $N_2O$ emitted (0.01% x 227.2 kg N/day) | 0.02272 kg $N_2O$/day |
| $N_2O$ emissions per year | 8.293 kg $N_2O$/year |
| Low range $CO_2$ equivalents per year | 2571 kg $CO_2$ eq/year |
| High range $N_2O$ emitted (4% x 227.2 kg N/day) | 9.088 kg $N_2O$/day |
| $N_2O$ emissions per year | 3317 kg $N_2O$/year |
| High range $CO_2$ equivalents (eq) per year | $1.03x10^6$ kg $CO_2$ eq/year |

*Estimated Yearly Emissions Calculated From Real Time MIMS Monitoring.*

The results from the analysis of the aerobic zone of the bioreactor by membrane introduction mass spectrometry were averaged over the entire sampling period. The emissions ranged from 50-220 ppmv with an overall average of about 78 ppmv. The concentration of 78 ppmv was used to estimate the yearly emissions from all of the aerobic zones of the bioreactor (Table 5). It should be noted that the 78 ppmv provides an average of emissions. In actuality, the emissions will vary according to treatment conditions and other parameters (see introduction and literature review section).

Table 5:

Estimated yearly bioreactor emissions based on MIMS aerobic zone analysis.

| Item | Value |
|---|---|
| Averaged $N_2O$ emissions MIMS Analysis Result | 78 ppmv $N_2O$ |
| Atmospheric Background | 0.315 ppmv $N_2O$ |
| Corrected Aerobic Zone Emissions | 77.7 ppmv $N_2O$ |
| Conversion ppmv to milligrams per cubic meter ($mg/m^3$) | 151 $mg/m^3$ $N_2O$ |
| Total Aerobic Zone Air Volume (Ave Nov 1-Dec 1,2009) | 200 $m^3$/hour |
| $N_2O$ emission per hour based on 200$m^3$ air volume per hour | 30200 mg/hr $N_2O$ |
| $N_2O$ emission per year (single aerobic zone) | 265 kg/year |
| $N_2O$ emissions per year (all eight aerobic zones) | 2120 kg/year |
| $CO_2$ equivalents (eq) emitted per year | $6.57x10^5$ kg $CO_2$ eq/year |

Additionally, the IPCC document contains calculations to determine nitrous oxide emissions from centralized wastewater treatment plants (Doorn et al., 2006). The document identifies uncertainty in these calculations and highlights numerous factors and discrepancies that should be determined by expert judgment. Using this document, an estimate of 72 kg of $N_2O$ per year (based on 3.2 grams $N_2O$/person/year and other factors) could be emitted from a population of 20 000 with centralized, advanced, wastewater treatment. This equals about 23 000 kg of $CO_2$ equivalents per year.

The reasoning behind these tables and calculations is to illustrate the range in nitrous oxide emissions estimates from wastewater treatment processes. These estimates vary depending not only on the rate of nitrogen loading conversion to nitrous oxide, which is a function of

treatment conditions, but can also vary depending on the selected analytical monitoring technique. Again, this information highlights the need for additional research into the emissions of nitrous oxide from wastewater treatment processes and the need for a long-term, real time monitoring program.

# CHAPTER 5 - RECOMMENDATIONS

## *Development of a Strategic Plan for Monitoring and Managing Nitrous Oxide Emissions*

A comprehensive strategic plan that outlines the intentions of on-site research and required experimental resources is essential. Research must be carefully synchronized with the general operation and maintenance of the facility and should be developed in conjunction with operations staff, management and other interested stakeholders including local sustainability coordinators. A key component of future work will focus on manipulating process parameters while monitoring potential emissions; this will require extensive organization. Stakeholders should collaborate to investigate a thorough benefit-cost analysis of nitrous oxide emissions from a local and regional perspective with the prime directive being the implementation of sustainability initiatives that account for all greenhouse gas emissions from wastewater treatment operations, and the goal of ultimately reducing these emissions.

## *Implementation of Long-Term Real Time Nitrous Oxide Monitoring*

This research project determined (by literature searches and experimental data) that an ongoing monitoring program for nitrous oxide emissions is essential. Currently, $N_2O$ emission estimates remain largely unknown. Implementing a real time, long-term, monitoring program (in a timely manner) will facilitate construction of an emissions database. The monitoring program should be expected to operate continuously for approximately 2 years in order to collect sufficient baseline nitrous oxide emissions information.

*Investigation of Bioreactor 'States' that Lead to Emissions*

In conjunction with emissions monitoring a data gathering program should begin that collects and logs information on bioreactor operating parameters and wastewater characteristics. The degree to which these additional measurements are taken should be determined in the strategic planning stages and will depend on available resources. It should be expected that certain operating conditions will lead to increased nitrous oxide emissions; with sufficient information, the bioreactor can be operated under parameters that minimize its nitrous oxide emissions.

# CHAPTER 6 - CONCLUSION

The idea of this research project stemmed from a number of observations. Anecdotally, it was observed that very few biological nutrient removal wastewater treatment plants account for the potential of their systems to produce potent nitrous oxide gas (either by calculations or by actual monitoring). An investigation of the literature revealed a limited body of information on actual nitrous oxide emissions from treatment processes and the existing information showed extreme variation and considerable uncertainty in results. It was also discovered that a limited number of analytical techniques are available for monitoring nitrous oxide gas and few that are able to operate in real time over long-term periods. Membrane introduction mass spectrometry was investigated for its ability to measure nitrous oxide emissions in real time thereby expanding the analytical techniques available to wastewater researchers. Experiments showed that MIMS was able to monitor nitrous oxide from treatment processes and provide detailed emissions information over extended periods (22 hours). A comparison between MIMS and a SUMMA canister (analyzed off-site by GC-ECD) showed considerable disparity in results; however, the MIMS results appear consistent with results observed in the literature. Additional work is required to optimize the sample train apparatus and several of the instrumental parameters. Future efforts should focus on manipulating various treatment parameters with the intent of discovering reasons for nitrous oxide emissions. As a sustainability component to this thesis an analysis of estimated yearly emissions based on various scenarios were developed. These estimates show that nitrous oxide emissions could range from 2511 kg $CO_2$ equivalent to $1.03 \times 10^6$ kg $CO_2$ equivalent per year from the aerobic zones of the bioreactor. The range in these values highlights the uncertainty in nitrous oxide emissions that may be present from the

complex biological processes present at wastewater treatment plants and the quality of monitoring techniques.

This project makes three recommendations that include:

1) Development of a Strategic Plan for Monitoring and Managing Nitrous Oxide
2) Implementation of Long-Term Real Time Nitrous Oxide Monitoring
3) Investigation of Bioreactor 'States' That Lead to Emissions

Future work focusing on these recommendations will contribute to the scope of sustainable practices in wastewater treatment and ensure that emissions of nitrous oxide are minimized.

# REFERENCES

Barton, P.K. & Atwater, J.W. (2002). Nitrous oxide emissions the antropogenic nitrogen in wastewater and solid waste. *Journal of Environmental Engineering*, 128, 137-150.

Boscaini, E., Alexander, M.L., Prazeller, P., & Mark, T.D. (2004). Membrane inlet proton transfer reaction mass spectrometry (MI-PTRMS) for direct measurements of VOCs in water. *International Journal of Mass Spectrometry*, 239, 171-177.

Burgess, J.E., Colliver, B.B., Stuetz, R.M., & Stephenson, T. (2002). Dinitrogen oxide production by a mixed culture of nitrifying bacteria during ammonia shock loading and aeration failure. *Journal of Industrial Microbiology & Biotechnology*, 29, 309-313.

Callis, J. B., Illman, D.L., & Kowalski, B.R. (1987). Process Analytical. *Journal of Analytical Chemistry*, 59, 624a-637a.

Creba, A.S., Weissfloch, A.N.E., Krogh, E.T., & Gill, C.G. (2007). An Enzyme derivatized polydimethylsiloxane (PDMS) membrane for use in membrane introduction mass spectrometry. *Journal of American Society of Mass Spectrometry*, 18, 973-979.

Czepiel, P., Crill, P., & Harriss, R. (1995). Nitrous oxide emissions from municipal wastewater treatment. *Environmental Science and Technology*, 29, 2352-2356.

Doorn R.J., Towprayoon, S., Manso Vieira, S.M., Irving, W., Palmer, C., Pipatti, R., & Wang, C. (2006). Wastewater treatment and discharge. *IPCC Guidelines for National Greenhouse Gas Inventory*, Chapter 6.

Etzkorn, J.M., Davey, N.G., Thompson, A.J., Creba, A.S., LeBlanc, C.W., Simpson, C.D., Krogh, E.T., & Gill., C.G. (2009). The use of mims-ms–ms in field locations as an on-line quantitative environmental monitoring technique for trace contaminants in air and water. *Journal of Chromatographic Science*, 47, 57-66.

Foley, J., de Haas, D., Yuan, Z., & Lant, P. (2010). Nitrous oxide generation in full-scale biological nutrient removal wastewater treatment plants. *Water Reaserch*, 44, 831-844.

Hayward, M.J., Lister, A.K. Kotiaho, T., Cooks, R.G., Austin, G.D., Natayan, R., & Tsao, G.T. (1988). Tandem Mass Spectrometry for On-Line Fermentation Monitoring. *Biotechnology Techniques*, 3, 361-364.

Intergovernmental Panel on Climate Change (IPCC). (2000). Special Report on Emissions Scenarios, Cambridge University Press, Cambridge, UK.

Johnson, R.C., Cooks, R.G., Allen, T.M., Cisper, M.E., & Hemberger, P.H. (2000). Membrane introduction mass spectrometry: trends and applications. *Mass Spectrometry Reviews*, 19, 1-37.

Kampschreur, M.J., Temmink, H., Kleerebezem, R., Jetten, M.S.M., & van Loosdrecht, M.C.M. (2009). Nitrous oxide emission during wastewater treatment. *Water Research*, 43, 4093-4103.

Kampschreur, M.J., van der Star, W.R.L., Wielders, H.A., Mulder, J.W., Jetten, M.S.M., & van Loosdrecht, M.C.M. (2008). Dynamics of nitric oxide and nitrous oxide emission during full-scale reject water treatment. *Water Research*, 42, 812-826.

Ketola, R.A., Kotiaho, T., Cisper, M.E., & Allen, T.M. (2002). Environmental applications of membrane introduction mass spectrometry. *Journal of Mass Spectrometry*, 37, 457-476.

Mendes, M.A., Sparrapan, R., & Eberlin, M.N. (2000). Headspace membrane introduction mass spectrometry for trace level analysis of VOCs in soil and other solid matrixes, *Analytical Chemistry*, 72, 2166-2170.

Meyer, R.L., Allen, D.E., & Schmidt, S. (2008). Nitrification and denitrification as sources of sediment nitrous oxide production: A Microsensor approach. *Marine Chemistry*, 110, 68-76.

Milagre, C.D.F., Milagre, H.M.S., Rodrigues, J.A.R., Rocha, L.L., Santos, L.S., & Eberlin, M.N. (2005). On-Line monitoring of bioreductions via membrane introduction mass spectrometry, *Journal of Biotechnology and Bioengineering*, 90, 888-892.

National Institute of Standards and Technology (NIST). (2008). *Chemistry Workbook, Mass spectrum (electron ionization) Data.* Retrieved November 30, 2008, from http://webbook.nist.gov/chemistry/name-ser.html.

Paredes, D., Kuschk, P., Mbwette, T.S.A., Strange, F., Muller, R.A., & Koser, H. (2007). New aspects of microbial nitrogen transformations in the context of wastewater treatment – a review. *Engineering Life Sciences*, 7, 13-25.

Oldham, W.K. & Rabinowitz, B. (2001). Development of biological nutrient removal technology in western Canada. *Canadian Journal of Civil Engineering*, 28, 92-101.

Shiskowski, D.M., & Mavinic, D.S. (2006). The influence of nitrite and pH (nitrous acid) on aerobic-phase, autotrophic $N_20$ generation in a wastewater treatment bioreactor. *Journal of Environmental Engineering and Science*, 5, 273-283.

Shiskowski, D.M., Simm, R.A., & Mavinic, D.S. (2004). An experimental procedure for identifying the aerobic-phase biological source of nitrous oxide in anoxic-aerobic wastewater treatment systems, *Journal of Environmental Engineering and Science*, 3, 549-553.

Short, R.T., Toler, S.K., Kibelka, G.P.G., Rueda Roa, D.T., Bell, R.J., & Byrne, R.H. (2006). Detection and quantification of chemical plumes using a portable underwater membrane introduction mass spectrometer. *Trends in analytical Chemistry*, 25, 2006, 637-646.

Silva, L.I.B., Rocha-Santos, T.A.P., & Duarte, A.C. (2009). Optical Fiber Analyzer for in-situ Determination of nitrous oxide in workplace environments. *Journal of Environmental Monitoring*. Retrieved November 26, 2009, from www.rsc.org/jem.

Strom, L., Lamppa, A., & Christensen, T.R. (2007). Greenhouse gas emissions from a constructed wetland in southern Sweden. *Wetlands Ecology Management*, 15, 43-50.

Tallec, G., Garnier, J., Billen, G., & Gousailles, M. (2008). Nitrous oxide emissions from denitrifying activated sludge of urban wastewater treatment plants, under anoxia and low oxygenation. *Bioresource Technology*, 99, 2200-2209.

Thompson, A.J., Creba, A.S., Ferguson, R.M., Krogh, E.T., & Gill, C.G. (2006). A coaxially heated membrane introduction mass spectrometry interface for the rapid and sensitive on-line measurement of volatile and semi-volatile organic contaminants in air and water at parts-per-trillion levels. *Rapid communications in Mass Spectrometry*, 20, 2000-2008.

Thompson, A.J., Etzkorn, J.M., Van Pel, D.M., Krogh, E.T., Drakeford, D.R., & Gill, C.G. (2008). Membrane introduction tandem mass spectrometry (mims-ms/ms) as a real-time monitor for biogenic volatile organic compound (bvoc) emissions from plants. *Canadian Journal of Anaytical Science and Spectroscopy,* 53, 75-81.

Thomsen, J.K., Geest, T., & Cox, R.P. (1994). Mass spectrometric studies of the effect of pH on the accumulation of intermediates in denitrification by *Paracoccus denitrificans*, *Applied and Environmental Microbiology*, 60, 536-541.

Wong, P.S.H., Cooks, R.G., Cisper, M.E., & Hemberger, P.H. (1995). On-Line, in situ analysis with membrane introduction ms. *Environmental Science and Technology*, 29, 215A-218A.