Correlation between nitrous oxide (N$_2$O) emission and carbon to nitrogen (COD/N) ratio in denitrification process: a mitigation strategy to decrease greenhouse gas emission and cost of operation

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ABSTRACT

The reliability and accuracy of in-situ ion selective electrode and ultraviolet (NOx) probes have been investigated at four different treatment plants with different operational conditions. This study shows that the mentioned probes tend to compromise their accuracy and trending stability at lower NOx of <1.0 mg N/L, which if used as a measuring variable for PI feedback controller for denitrification (biological reduction of nitrate to nitrogen gas), would cause overfeeding the external carbon source. In-situ Clark-type N$_2$O sensors, recently introduced for industrial scale use (Unisense Environment) could potentially open a new horizon in the automation of biological processes and particularly denitrification. To demonstrate the applicability of such probes for automation, two in-situ N$_2$O probes were used in two treatment plants in parallel with NOx-N probes. The effects of operational conditions such as COD/N ratios and the correlation between NOx and N$_2$O were investigated at those plants. N$_2$O production at non-detect dissolved oxygen concentrations and pH of 7–7.2 were found to be a function of influent nitrogen load or the ratio of COD/N$_{INFLUENT}$. Finally, using an N$_2$O probe as a proxy sensor for nitrates is proposed as a measured variable in the PI feedback in the automation of the denitrification process with a NOx set point of <1.2 mg N/L.

Key words | automation, denitrification, microC®, nitrous oxide (N$_2$O), real time control (RTC)

INTRODUCTION

In order to protect our environment, legislation at the Federal and State levels is being promulgated to reduce nutrient discharge limits from municipalities as well as industries. As more States and Provinces face stricter discharge limits, plant operators will need to develop plans to meet these lower limits. Adding external carbon sources to promote denitrification and biological phosphorus removal has been a reliable and proven approach to meet lower limits in the past decade. However, a thorough assessment of all the options, in addition to the efficient implementation of an external carbon source and automation strategies, are key to developing a long-term sustainable denitrification program with the lowest operational cost. Despite advances in the control and automation of wastewater treatment plants (WWTPs) over the last few decades, the search for appropriate instrumentation for real time control (RTC) at WWTPs still remains a very actual issue (Kaelin et al. 2008). Different in-situ and ex-situ probes and analyzers for real time measurement of nitrate and nitrite have been under attention to be employed as a control parameter in the automation of the denitrification process. The greenhouse gas effect of nitrous oxide (N$_2$O), known to be 300 time more potent than CO$_2$, as an obligate intermediate in the four-stage denitrification cycle and as a byproduct of nitrification, has been studied and recognized extensively (Ni & Yuan 2015; Du et al. 2016; Mannina et al. 2016). Nitrous oxide production during denitrification is found to be governed by different enzymatically catalyzed pathways influenced by a range of environmental factors including nitrate concentration, temperature and the availability of an electron donor (Jafari et al. 2015; Pang et al. 2015; Wang et al. 2015). Zhang et al. (2016) investigated the mechanism...
of N2O accumulation from a molecular level in denitrifying bio-filter water treatment systems at low carbon to nitrogen (C/N) ratios of 0.65–3.0 and suggested that the key drivers of the N2O accumulation were indeed enzymatic, facilitated by qnorB/nirK, nosZ/(narG + napA), amx/(nirS + nirK), narG/bacteria and qnorB/bacteria.

The Intergovernmental Panel on Climate Change (IPCC) guidelines in 2006 stated that direct N2O emission from WWTPs is a minor source of N2O emission and the largest N2O emission from nitrogen in wastewater occurs by nitrification and denitrification in estuaries and rivers (Kampschreur et al. 2009). However, the IPCC implicitly assumes that, in general, no nitrogen is removed during wastewater treatment (Eggleston et al. 2006). In contrast, several measurements at laboratory scale and full scale WWTPs have shown that N2O can be produced in substantial amounts during different biological processes of the nitrogen removal cycle in WWTPs (Osada et al. 1995; Wicht & Beier 1995; Tallec et al. 2006; Kampschreur et al. 2008). Foley et al. (2010) provided an overview of N2O emission from seven full scale biological nitrogen removal (BNR) WWTPs showing that N2O emission ranged from 0.006-0.253 kg N2O-N per kg N denitrified, corresponding to 6% to 25% of overall denitrified nitrogen load.

The use of N2O wastewater sensors has been extensive in literature; however, the N2O parameter has only recently been introduced in full scale wastewater process monitoring and the potential of N2O as a control parameter in the automation of biological processes, such as denitrification, has never been investigated.

The N2O parameter yields important new insights into the nitrogen transformation from ammonium to free nitrogen. Through this nitrogen transformation, N2O is a natural intermediate and, in particular, a key analyte in the understanding and control of denitrification.

The biological production and turnover of N2O is tightly linked to the level of ammonia, nitrite and nitrate in wastewater and also closely related to the amount of available chemical oxygen demand (COD) (Wunderlin et al. 2012). In this work, the concept of using an in-situ Clark-type N2O probe as a control parameter in automation of the external carbon source for the process of denitrification was investigated in two full scale BNR plants in Europe and the USA. The reliability and accuracy of ion selective electrode (ISE) and ultraviolet (UV) NOx probes were studied in four treatment plants. This work introduces a novel concept for automating the external carbon source (in this study a proprietary glycerol-based MicroC® 2000, containing 70% glycerol as a readily biodegradable COD, 28% water and 2% proprietary additives, containing an rbCOD of 1,100,000 mg/L) in a denitrification process with very stringent nitrogen limits, using an in-situ N2O probe.

**Theory of N2O production in WWTPs**

Figure 1 depicts the biological pathways of the nitrogen cycle occurring in a BNR facility. In general, N2O emission can occur in four biological processes of (1) nitrification, (2) denitrification, (3) nitriifer denitrification and (4) nitrate ammonification. Nitrification or conversion of ammonia to nitrate is mediated by two groups of bacteria: ammonia oxidizing bacteria (AOBs) that convert ammonia to nitrite (pathway 1 in Figure 1), and nitrite oxidizing bacteria (NOBs) that convert nitrite to nitrogen gas (pathway 2 in Figure 1). Under O2 stress condition in the aerobic zone, AOB denitrification is reported to be the predominant pathway in N2O production, which has been identified as the major factor leading to nitrous oxide emission (Kampschreur et al. 2009; Adouani et al. 2015; Colliver & Stephenson 2000).

![Figure 1](https://iwaponline.com/wst/article-pdf/77/2/426/242833/wst077020426.pdf)
In a comprehensive study on the quantification of N₂O emissions at 12 WWTPs across the United States, Ahn et al. (2010) showed that aerobic zones generally contribute more to N₂O emission than anoxic zones from BNR plants. It was also concluded that high nitrite, ammonium, and dissolved oxygen (DO) concentrations were positively correlated with N₂O emissions from aerobic zones and minimizing transient or permanent buildup of ammonium or nitrite, especially in the presence of DO, are expected to have low N₂O emissions.

As shown in Figure 1, N₂O is an obligate intermediate of the denitrification process in the nitrogen reduction chain, and incomplete denitrification can lead to N₂O emission. Thus, potentially N₂O can be used as an effective measured variable in the automation of denitrification if a reliable in-situ probe is commercially available. Although denitrification can also occur by some facultative denitrifiers under both aerobic and anoxic conditions, in WWTPs it was generally agreed that anoxic heterotrophic is the dominant N₂O production. However, it was shown later in the literature that N₂O is emitted predominantly in the aerated zones, but it remains unclear whether nitrifying or denitrifying microorganisms are the main source of N₂O emissions (Kampschreur et al. 2009; Ahn et al. 2010). High nitrite and DO concentrations were shown in the literature to positively correlate with N₂O emissions in anoxic zones (Ahn et al. 2010).

**Principles of UV absorption and ion selective technologies**

Wastewater sensors for nitrate and nitrite are based on either offline analyzers using spectrophotometers and colorimetry methods, ion selective membranes/electrodes, or UV detection.

UV absorption technology relies on the principle that molecular bonds absorb UV light. Nitrate and nitrite both have a very strong absorption at 214 nm in the UV range, while most dissolved organics have a strong absorption at 254 nm. This property has been used to develop UV spectrum based in-situ nitrate/nitrite monitors. As the concentration of nitrate or nitrite increases, UV absorption also increases. Normally with one xenon flash lamp beam in a probe, this technology is unable to differentiate between nitrate and nitrite, and the overall absorbance of UV is calculated proportional to NOx absorbance (de Silva & Fu 2006). In addition, the technology is limited due to potential interferences including a high and changing concentration of nitrite or organic compounds absorbing UV light in the vicinity of the measuring wavelength, a high concentration of suspended solids, age of sludge, color and temperature (de Silva & Fu 2006). The presence of suspended solids in the water will create a scattering of the light. This has to be compensated for, which is normally done with a reference UV source (ER) whose spectrum is outside the nitrate adsorption range to account for the interferences. A built-in photometer measures the primary beam, while a second beam of UV light provides a reference standard and corrects for interference caused by turbidity and organic matter.

ISE is based on a potentiometric principle, i.e. the measurement of an electric potential (voltage) difference between a reference electrode, showing a constant potential, and a measurement electrode. The difference between reference and measurement electrodes depends on the natural logarithm of the ion activity (Kaelin et al. 2008). The ISE nitrate electrode responds to numerous interfering anions such as cyanide, bisulfide, bicarbonate, carbonate, and phosphate, which sometimes necessitate pH adjustment (usually to lower values, i.e. 4, to remove those anions). Chloride can also be present in a wastewater stream in abundance and can affect the accuracy of nitrate ISE probes at a threshold of 500 mg Cl/L. If the samples are measured ex-situ, using silver sulfate reagent will eliminate the interference of ions such as chloride, bromide and iodide. Nitrite also has an interference effect on the nitrate ISE readings with cross sensitivity of 1:100 (NO₂⁻/NO₃⁻). Since ISE probes measure ion activity instead of concentration, an ionic strength adjuster (ISA) can be used to fix the ionic strength (in case of nitrate ion, ammonium sulfate (NH₄)₂SO₄ can be used).

**METHODS**

**Analytical methods**

Data from four full scale WWTPs in Massachusetts (municipal), Virginia (a municipal and a poultry plant) and Pennsylvania (beef) were used to highlight the reliability and accuracy of NOx in-situ ISE and UV probes. Samples from influent, effluent and different basins and reactors of the full scale treatment plants investigated in this study were collected for analysis. Total suspended solids (TSS), volatile suspended solids, (VSS) were analyzed in accordance with Standard Methods 2540D, 2540E respectively (APHA/AWWA/WEF 1998). HACH methods and testing kits were used to analyze total and soluble chemical
oxygen demand (TCOD and SCOD), total nitrogen (TN), NH₄-N, NO₂-N, NO₃-N, and PO₄. In different treatment plants, different HACH Benchtop Spectrophotometers were used (HACH Odyssey DR/2800, DR/3900 and DR/6000). Nitrate and nitrite, as the main focus of this study, were measured in the laboratory using different ranges of HACH TNT vials (NO₃ TNT Plus 835 Vial LR 0.1–13.5 mg N/L, NO₂ TNT Plus 836 Vial HR 5–35 mg N/L, NO₂ TNT Plus 839 Vial LR 0.015–0.6 mg N/L and NO₂ TNT Plus 840 Vial HR 0.6–6.0 mg N/L). Occasionally, at some of those treatment plants, alkalinity was measured by titration with 0.01 N H₂SO₄ in accordance with Standard Method No. 2320 (APHA/AWWA/WEF 1998). DO, and occasionally pH and ORP profiling, were conducted onsite using HACH HQ40d Portable pH, conductivity, DO, and ORP meters.

**In-situ NOₓ probes**

In this study, an industrial scale in-situ Clark type N₂O sensor (Unisense Environment A/S, Denmark) was used in the anoxic basin of an A2O process to investigate the correlation between the N₂O concentration in the basin with the operational conditions of the anoxic reactor as well as the concentrations of other intermediates in the nitrogen cycle. The probe is based on a miniaturized Clark-type sensor with an internal reference and a guard cathode. In addition, the sensor is equipped with an oxygen front guard, which prevents oxygen from interfering with the N₂O measurements (Andersen et al. 2001). Driven by the external partial pressure, N₂O from the environment will penetrate through the sensor tip membrane and be reduced at the metal cathode surface. The sensor amplifier converts the resulting current to a signal. The sensor measures N₂O specifically and without any interference from other analytes in their normal ranges within wastewater (Jenni et al. 2012). Working range of the sensor is between 0–1.5 mg/L N₂O-N with a detection limit of 0.005 mg/L N₂O-N.

Multiple Double Wavelength Spectrophotometer (DWS) (NITRATAX plus sc, Hach Lange GmbH, Germany) with different measuring slits of 1 mm and 2 mm were also used in both anoxic and aerobic basins of four full scale treatment plants with different range of NOₓ concentrations [0–30 mg NOₓ-N/L]. DWSs measure UV absorbance at a wavelength of 218 nm at a measuring receiver (EM – element for measuring) and at 228 nm at a reference receiver (ER – element for reference) (Huebsch et al. 2015). The recorded measurements at two different wavelengths at EM and ER are designed to compensate for interference of organic and/or suspended matter (Thomas et al. 1990) by interpreting the difference between the absorbance values at EM and ER, which is expressed by ΔE. In comparison, a UV sensor using only one single wavelength is not able to compensate for additional interferences (van den Broeke et al. 2006). There is another UV measuring method using the Multiple Wavelength Spectrophotometer (MWS), which measures absorbance at 256 different wavelengths between 200 and 750 nm within 15 s (Rieger et al. 2004). Both sensors feature the possibility to export the monitored absorbance values and the calculated concentrations. As a result of the different measuring methods, the DWS makes no difference between NO₃-N and NO₂-N, and therefore reports the NO₂-N concentration (or total oxidized nitrogen, TON) instead of NO₃-N (Huebsch et al. 2015). In general, the maintenance MWS is more expensive than DWS with a much shorter warranty on their light source (3 years versus 5 years). In addition, an ammonia and nitrate ISE probe was used in this investigation (AN-ISE sc Combination, Hach Lange GmbH, Germany) in a post anoxic reactor to study the performance of the probe at low nitrate concentrations.

**Automation strategies**

Conventional industrial process automation systems employ control strategies to maintain a desired process output. In general, the elements that compose these systems are: measured variables, manipulated variables, and process set points. The control logic of these automated systems is to record measured sensor readings, compare them to the process output set point (called ‘controller error’ – the difference between the measured value and set point), and to adjust the manipulated variable (in our case MicroC® injection to supply the electron donor for heterotrophic bacteria) to drive the measured variable (NOₓ-N effluent) closer towards the set point, thereby minimizing the controller error.

Two widely employed control algorithms in wastewater treatment are feedforward control and feedback control. A feedforward control algorithm is a mathematically constructed control scheme in which a correlation between process inputs (using the kinetics of denitrification) and the desired controller output can be constructed. This control strategy is ideally suited for processes in which changes to inlet conditions, called disturbances, can be measured. However, feedforward control is not objective based, meaning the controller is only responding to the mathematical model, presented in a study by Andalib et al. (2015), and not on how well the mathematical model performed. Conversely, feedback control is error based, meaning the controller is responding to differences in...
outlet conditions and is a measure of how well the system is performing. The most common feedback controller used in wastewater treatment is known as proportional-integral or PI control. The controller strategy in this work was adopted from a velocity form of digital PI shown in Equation (1). The proportional component of the algorithm corresponds to the present state of the error, while the integral component corresponds to the history of previous errors over a specified time period.

Feedback PI Control Algorithm (Equation (1))

\[ CV_n = CV_{n-1} + K_c \left( \frac{1}{T_I} E \Delta t \right) \]

where: \( CV_n \) = current output; \( CV_{n-1} \) = previous output; \( K_c \) = controller gain; \( E \) = current error; \( T_I \) = integral time constant; \( \Delta t \) = change in time; \( \Delta E \) = change in error.

The inherent variability of wastewater at municipal treatment facilities favors the utilization of a combination of feedforward and feedback control to effectively deliver supplemental carbon to a denitrification process to reach a desired NOx effluent concentration. Such a combination was employed in the Nitrack® controller automated MicroC® dosage system by EOSi, with the following control strategy: the feedforward component of the algorithm ‘predicts’ how much MicroC® is required and the feedback component ‘adjusts’ the MicroC® dosing to drive the effluent NOx concentration toward the controller set point. This control strategy is especially useful in pre-anoxic operations where the influent BOD concentration is present but cannot be measured online.

**RESULTS AND DISCUSSION**

**Reliability of NOx in-situ probes**

UV absorption technology and ISE inline probes are employed in many applications but also have limitations due to sensor drift, high calibration needs and interference from other ions, biomass or colored compounds. Another problem encountered in the routine operation of in-situ probes is the accumulation of dirt around electrodes, therefore the cleaning mechanism on a probe should also be considered as an important parameter in probe selection. As a result, in many automation denitrification applications where lower NOx set points (~0.5 ± 0.5 mg NOx-N/L) are required to meet the stringent nitrogen discharge limits of 3 mg TN/L, the reliability of UV and ISE sensors is subject to error.

In this work the viability and accuracy of different types of NOx-N UV probes (with 1 mm and 2 mm measuring gaps) and NOx ISE probes were investigated in four different biological nutrient removal treatment plants (BNRs) in the USA and the results are depicted in Figure 2(a)–2(f). Two of those plants were municipal (Figure 2(a)–2(d)) and two industrial (beef (Figure 2(e)) and poultry (Figure 2(f)) processing plants. In the first municipal plant, a NOx ISE probe was placed at the beginning of a post anoxic zone in the plug flow anoxic reactor and a NOx UV probe with a 2 mm measuring path length was placed at the end of the anoxic reactor. The ISE probe and the UV probe were calibrated on a weekly and monthly basis respectively. The plant operated with a mixed liquor suspended solids (MLSS) range of 1,400–2,500 mg/L during 4 months of assessment. As is apparent from Figure 2(a), the NOx laboratory analysis on daily composite samples was corresponding to the NOx trend recorded by ISE probe when NOx-N concentrations were greater than 1.5 mg N/L. The concentrations of NOx recorded by the ISE probe and laboratory analysis averaged 2.46 ± 0.9 mg N/L and 1.51 ± 0.64 mg N/L respectively, corresponding to a Relative Standard Error (RSE) of 53%. Since the concentration of NOx at the beginning of the anoxic zone averaged 1.5 mg N/L, the readings by ISE probe relatively agreed with the laboratory data. At the end of the anoxic reactor, where the concentration of NOx was lower, with the average concentration (measured in the laboratory on daily composite samples) of 1.3 ± 0.6 mg N/L and 0.52 ± 0.2 mg N/L from Jan-April and April to June respectively, the 2 mm UV probe was recording an average NOx of 1.6 ± 0.8 mg N/L and 1.0 ± 0.6 mg N/L, corresponding to an RSE of 20% from Jan to April and a much higher RSE of 88.6% from April to June. The daily moving average of the 2 mm NOx UV probe demonstrates that the probe was unable to reliably correlate with data by analytical chemistry (all analytical measurements were occasionally verified by standard solution and all the samples were spiked with acid to the pH of 2 at the time of sampling to prevent any denitrification in the samples before the filtration stage (10–20 minutes).

The second study was performed in a municipal plant with an A2O configuration. Two 2 mm UV probes were placed at the end of the anoxic zone and aerobic zone. The concentrations of NOx in the aerobic reactor recorded by the UV probe and laboratory analysis averaged 4.2 ± 1.1 mg N/L and 3.2 ± 1.0 mg N/L respectively, corresponding to an RSE of 28%. The concentrations of NOx in the anoxic reactor, however, were 1.4 ± 0.7 mg N/L and 0.4 ± 0.6 mg N/L according to the UV probe and laboratory
analysis, corresponding to an RSE of 247%. As shown in Figure 2(c) and 2(d), although the overall trends of daily average recorded by both probes correspond with the NOx measurements in the laboratory, it is apparent that when the concentrations of NOx are below 1.0 mg N/L, the probes were unable to give reliable readings. In the aerobic basin, where the concentrations of nitrate fluctuate between 2–4, there is a much better agreement between the laboratory and probe NOx values, as demonstrated by the value of 28% RSE. According to the above results, if a NOx set
point of below 1–1.5 mg N/L is targeted in a denitrification feedback automation system with the aid of an external carbon source, there might be great potential to deviate from the optimal dosage rate, simply due to the inaccuracy of probes below a NOx concentration of 1.2 mg N/L.

Despite the limitations, in-situ UV and ISE probes have brought great value to the control and automation of water and WWTPs. Figure 2(e) depicts the comparison of NOx values recorded by two UV probes with measuring path lengths of 1 mm and 2 mm respectively installed in parallel in a post anoxic zone of a beef processing treatment plant. The plant receives an influent TN of 250–300 mg N/L and treats it in a four-stage Bardenpho process to ensure a compliance TN limit of 5 mg N/L. As shown in Figure 2(e), the NOx concentrations in the post anoxic zone vary between 3 and 5 mg N/L and average at 3.65 ± 0.7 mg N/L based on laboratory analysis. All the laboratory analyses were conducted on samples that were filtered immediately after withdrawal and standard solutions were occasionally used for verification. During the trial, the 1 mm and 2 mm probes showed a comparable performance with average NOx concentration of 3.9 ± 1.2 mg N/L and 3.4 ± 0.7 mg N/L respectively, corresponding to an RSE of 6.8% in comparison with the laboratory analysis. Even though on 05/23/2016, the 1 mm UV probe recorded a value of 2 mg N/L higher than the values measured in the laboratory and the 2 mm UV probe, both probes and laboratory analysis were in a very good agreement. It is worth mentioning that the probes were submerged in an average MLSS of 5,700 mg/L without observing a detrimental effect on the performance of the probes.

The last analysis occurred in a four-stage BNR treatment plant of a poultry plant. A 1-mm UV probe was placed in the post anoxic zone and the NOx reading was compared to the laboratory analysis over a year in 2015. As shown in Figure 2(f), a significant swing in the MLSS concentrations was observed during the evaluation ranging from 4,700 mg SS/L to 13,000 mg SS/L. Despite a very high solid concentration, a very good agreement between the laboratory analysis and UV probe was recorded with average values of 2.9 ± 2.5 mg N/L and 3.1 ± 2.0 mg N/L respectively, corresponding to a RSE of 5%. These results confirm the accuracy of the UV probes in different solids concentrations, when the NOx concentrations in the mixed liquor exceed the value of 1.2 mg N/L.

\textbf{N}_2\textit{O} \textit{profile in full scale denitrification}

Under anoxic conditions, in the absence or sparsity of oxygen as the terminal electron acceptor, there are a few operational conditions that are reported to cause production and emission of N\textsubscript{2}O. Otte et al. (1996) showed that the presence of oxygen in low amounts leads to N\textsubscript{2}O emission. It is well understood that oxygen inhibits both synthesis and activity of denitrification enzymes and N\textsubscript{2}O reductase is reported to be more sensitive that other enzymes. During the following study, the DO profile showed an undetected level of oxygen in the anoxic basins. Although pH has an important role in N\textsubscript{2}O emission in the denitrification process (it increases when the pH decreases, Hanaki et al. 1992), the pH effect is expected to be negligible since the pH of the two studies below were 7.0–7.2 throughout the investigation. There are other factors that increase N\textsubscript{2}O production in the nitrogen cycle, such as short SRT, low temperature, high salinity, and rapidly changing environmental conditions. However, during these studies, since the investigation was conducted at temperatures of 16–18 °C, adequate SRT, and normal salinity, the most effective parameter was postulated to be the COD/N ratio.

It is well understood that limited availability of biodegradable organic carbon during denitrification increases N\textsubscript{2}O production (Kampschreur et al. 2009). In a study by Schalk-Otte et al. (2000) on a pure culture of \textit{faecalis}, up to 32–64% of nitrogen was emitted as N\textsubscript{2}O when organic carbon became limiting and bacteria started utilizing internal stored poly-β-hydroxybutyrate (PHB). In an intermittently aerated activated sludge treating high-strength wastewater, Itokawa et al. (2001) showed that when the COD/N ratio was below 3.5, 20–30% of nitrogen was emitted as N\textsubscript{2}O. It was also suggested that a high N\textsubscript{2}O emission rate under low COD/N ratio operations was mainly due to endogenous denitrification in the presence of nitrite.

This study focuses on two treatment plants with manual and automated carbon addition to support denitrification and how the automation affected nitrous oxide emission and how it can be used in the control strategy.

The first study was conducted in a 200,000-PE sequencing batch reactor (SBR) WWTP (Plant A), with a sequential aeration strategy, with 20–35 minute on/off cycles which allowed both nitrification and denitrification. The municipal WWTP has an average daily flow rate of 26.3 ± 14 ML/d and average influent COD/N ratio of 7.83 ± 4.3 entering the process tanks. MLSS is controlled at 5,500–4,500 mg/L. The BNR process was monitored using online instrumentation, including online N\textsubscript{2}O measurements, NOx and real time GHG accounting. As shown in Figure 3, a clear correlation can be seen between the NOx (nitrate and nitrite) level and the amount of accumulated dissolved N\textsubscript{2}O. The on/off aeration sequence pattern was also depicted.
During the anoxic phase (aeration off), the DO was recorded as undetectable, suggesting that the concentration of dissolved N$_2$O was a strong function of nitrite (NO$_2^-$) and nitrate (NO$_3^-$) accumulation due to the lack of an electron donor (organic carbon substrate) in the anoxic phase. To demonstrate the correlation between the elevated N$_2$O and lack of electron donor in Plant A, two 30 liter doses of ethanol were added to the 4.000-m$^3$ SBR in two different sequential denitrification phases to enhance the denitrification. A clear decrease in the dissolved N$_2$O level was observed as a result of the manual external carbon source addition and decreased NOx level. Following the external carbon dosing with ethanol, the DO concentrations during aeration phases were increased to increase nitrification and build up more nitrate and nitrite, which resulted in increased levels of N$_2$O, as is apparent in Figure 3.

The second part of this study was conducted at a municipal treatment plant (Plant B) with an average daily flow rate of 23.4 ± 4.5 ML/d that used the glycerin-based MicroC® 2000 as a supplemental electron donor to augment biological nutrient removal (BNR) in an A$_2$O process depicted in Figure 4(a). The return activated sludge (RAS) and internal recirculation averaged 82% and 480% of the influent flow respectively during this study. MicroC® 2000 injection was automated by Nitrack® to the anoxic zone for denitrification using hybrid feedforward feedback control logic, described earlier. The BNR process was monitored using online instrumentation, including phosphate analyzers and 2 mm UV NOX-N and N$_2$O probes with the instrumentation layout depicted in Figure 4(a). The results of the study are shown in two separate graphs, Figures 4(b) and 5(a), to better illustrate the correlation between the key parameters in the N$_2$O emission. The NOx set points in the controller were adjusted at 1.0 mg N/L during the study depicted in Figure 4(b) and 1.2 mg N/L during the study depicted in Figure 5(a) respectively. As seen in the figures, the NOx-EFF concentration in the anoxic reactor during the first period (Figure 4(b)) averages 1.1 ± 0.17 mg N/L recorded by the UV probe, whereas the NOx-EFF increased to 1.30 ± 0.15 mg N/L in the second period (Figure 5(a)). In both cases, the laboratory analysis on the samples taken from the same location demonstrate a much lower NOx-N concentration, with an average value of 0.5 mg N/L, shown in the yellow rhombus in Figures 4(b) and 5(a). The blue line trends the influent nitrogen load to the anoxic reactor varying from 800 lb N/d to 1,500 lb N/d at nitrogen shock loads. Based on the influent load and the deviation of the effluent NOx-N from the set point of 1 mg N/L and 1.2 mg N/L, Nitrack® provides an appropriate amount of MicroC® 2000 in accordance with its kinetic to ensure a proper COD/N ratio in the process for complete denitrification. As shown by the green line in Figure 4(b), an increase in the influent nitrogen load corresponds to an increase in the provided COD/N ratio. During the first phase, when the NOx concentration trends at an average concentration of 1 mg N/L (where the NOx reading is subjected to error and consequently carbon may be overly injected), a very little or no dependency on the concentration of NOx and N$_2$O production is observed (Figure 4(b)). A similar conclusion can also be drawn from the first study in Plant A, where occasionally the NOx concentration did not match with the production of N$_2$O in Figure 4(b). When a higher NOx set point was targeted, a more meaningful correlation between the NOx concentration and N$_2$O were observed (Figures 4(b) and 5(a)). Nonetheless, the production of N$_2$O under anoxic
condition is shown to strongly correlate to the influent nitrogen load and correspondingly the COD/N ratio and is rather independent of NOx concentrations, shown in Figures 4(b) and 5(a) by vertical arrows. A proper control strategy by the controller has diminished the level of N2O emission in the plant, with an occasional maximum N2O production of 0.5 mg N2O-N/L in the first scenario with a set point of 1.0 mg NOx-N/L and 1.3 mg N2O-N/L in the second scenario with a set point of 1.2 mg NOx-N/L. Although the controller quickly addresses a proper COD/N, the initial effect of increased load results in N2O emission. To better understand the correlation between the COD/N influent ratio and N2O
production. Figure 5(b) was generated based on over 54,000 data points during the study. Although it is not possible to incorporate inline COD values in this evaluation, the nature of hybrid feed forward feedback control logic intrinsically accounts for the internal COD values. It is apparent from the figure that when the COD added to nitrogen influent is more than 3.5, N₂O over-production stops as there is enough readily biodegradable COD (rbCOD) to complete the denitrification process. The maximum amount of N₂O production (1.3 mg N₂O-N/L, or 3–5% of the influent nitrogen load) was observed to be at a COD/N of 2.5 where the first steps in the denitrification process likely took place with an average emitted N₂O concentrations of 1.3 mg N/L. Based on Figure 5(b), when the COD/N is below 1.0 the N₂O production decreases and halts, which is likely due to there being insufficient COD to complete the first steps in the denitrification pathway. Little conclusive evidence in the literature is available on whether N₂O accumulation
during denitrification depends on the COD/N ratio directly or indirectly through genetic variables. Zhang et al. (2016) found that the highest accumulation rate of N₂O (8.0 ± 0.4 g m⁻³ h⁻¹) was reached at the C/N ratio of 1.0, after which the rate declined sharply from 8.0 ± 0.4 g m⁻³ h⁻¹ to 0.2 ± 0.1 g m⁻³ h⁻¹ as the C/N ratio increased from 1.0 to 3.0, a similar bell-shaped dependency of N₂O emission to the COD/N ratio as that found in the current study. Yan et al. (2016) studied the effect of internal recirculation on N₂O production in an A₂O process and found that N₂O production increased in the anoxic zone on increasing the internal recycle ratio, which resulted in reduction of the nosZ gene (the enzyme responsible for conversion of N₂O to nitrogen gas). This may be caused by the detrimental effect of the increased oxygen level carried over to the anoxic zone. The ratio of the internal recirculation flow to the total flow entering the anoxic reactor (IR/Total) in this study is depicted in Figure 5(a) to show that at higher nitrogen load the ratio of IR/Total actually decreases, meaning we will not see any effect of N₂O or oxygen carryover from the nitrification reactor to the denitrification reactor. During the trial, the pH fluctuated between 7 and 7.2 consistently and the nitrite concentration was below 0.1 mg N/L, which nullified the effect of nitrite accumulation on N₂O production during the trial. In addition, when the external carbon was overdosed from 05/06/16 to 05/21/2016, shown in Figure 4(b), there was no N₂O emission in the anoxic zone, verifying that the N₂O carry over via IR due to nitrification was negligible.

Proposed control strategies using N₂O probe wastewater sensors

While real time anoxic effluent nitrate measurement is subject to error, at lower concentrations and other operational conditions such as higher ionic strength and solids concentrations, the nitrous oxide trend shows a fast response to changes in influent nitrogen load and COD/N ratio by the addition of a carbon source. Using the N₂O sensor as a proxy sensor for nitrites can open a new horizon in the automation of denitrification processes targeting lower total nitrogen (TN < 4 where the NOₓ set point is <1 mg N/L) at COD to nitrogen ratios much closer to theoretical values, without compromising the performance of the controller at different solids concentrations or interferences. This feature offers a viable resolution in the effluent measured variable, leading to greater proportional response from the feedback controller. The proposed chemical dosing controller strategy utilizes a combination of a feedforward control algorithm with nitrate as its measured variable and a feedback control algorithm with nitrous oxide as its measured variable, when a very low nitrogen set point is targeted.

CONCLUSION

In-situ UV and ISE nitrogen oxide (NOₓ) probes have brought great value to the monitoring and control and automation of nitrogen removal via denitrification. The performance of the UV and ISE NOₓ probes was investigated in four different treatment plants. The results show that the UV NOₓ probes operated efficiently at different solids concentrations and at NOx-N levels above 1.5 mg N/L. When the NOₓ concentrations trended below 1–1.5 mg N/L, the UV probes (despite their measuring slits) were not reliably measuring the NOₓ concentration. A very similar behavior was also observed with ISE type probes. In this work, the performance of ISE NOₓ probes was not investigated at high MLSS concentrations.

In-situ Clark type nitrous oxide probes were used in two BNR plants to monitor and study N₂O production and correlation with NOₓ and COD/N in anoxic reactor. At pH of 7–7.2 and non-detectable DO, the trend of nitrate and nitrous oxide were similar at low NOₓ concentrations (speculated at <0.5 mg N/L) when the COD/N in the influent was not sufficient for complete denitrification. In general, N₂O production under anoxic conditions had a better correlation to influent nitrogen load and COD/N ratio than NOₓ concentration. At complete denitrification, when the effluent NO3-N was below 0.3 mg N/L and nitrite was below 0.1 mg N/L, the production of nitrous oxide depended on the influent nitrogen load with insufficient COD/N ratio leading to an incomplete denitrification.

In treatment plants where a very stringent nitrogen limit is targeted with a very low nitrate set point (either in the pre or post anoxic zones), a combination of a feedforward control algorithm with nitrates as its measured variable and a feedback control algorithm with nitrous oxide as its measured variable was proposed for optimum automation of external carbon source dosage as well as mitigating N₂O as one of the most potent greenhouse gases (GHGs) when a very low nitrogen limit is targeted.

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