

Full-scale comparison of N₂O emissions from SBR N/DN operation versus one-stage deammonification MBBR treating reject water – and optimization with pH set-point

L. Kanders, J-J. Yang, C. Baresel and J. Zambrano

ABSTRACT

To be able to fulfill the Paris agreement regarding anthropogenic greenhouse gases, all potential emissions must be mitigated. Wastewater treatment plants should aim to eliminate emissions of the most potent greenhouse gas, nitrous oxide (N₂O). In this study, these emissions were measured at a full-scale reject water treatment tank during two different operation modes: nitrification/denitrification (N/DN) operating as a sequencing batch reactor (SBR), and deammonification (nitrification/anammox) as a moving bed biofilm reactor (MBBR). The treatment process emitted significantly less nitrous oxide in deammonification mode 0.14–0.7%, compared to 10% of total nitrogen in N/DN mode. The decrease can be linked to the changed feeding strategy, the lower concentrations of nitrite, a lower load of ammonia oxidized, a shorter aeration time, the absence of non-optimized ethanol dosage or periodic lack of oxygen as well as the introduction of biofilm. Further, evaluation was done how the operational pH set point influenced the emissions in deammonification mode. Lower concentrations of nitrous oxide were measured in water phase at higher pH (7.5–7.6) than at lower pH (6.6–7.1). This is believed to be mainly because of the lower aeration ratio and increased complete denitrification at the higher pH set point.

Key words | biological nitrogen removal, deammonification, nitrous oxide (N₂O) emissions, pH, greenhouse gases

L. Kanders (corresponding author)
Purac AB,
Box 1146, SE-221 05 Lund,
Sweden
E-mail: linda.kanders@purac.se

L. Kanders
J. Zambrano
School of Business, Society and Engineering,
Mälardalen University,
Box 883, SE-721 23 Västerås,
Sweden

J-J. Yang
C. Baresel
IVL Swedish Environmental Research Institute,
Box 210 60, SE-100 31 Stockholm,
Sweden

INTRODUCTION

One of the most urgent challenges for our planet currently is to limit emissions of greenhouse gases. We will still be able to fulfill the Paris agreement (UNFCCC 2015) if anthropogenic gases peak by 2020 and halve by 2030, according to Rockström *et al.* (2017). To do this, a ‘carbon roadmap’ should be applied to all sectors of society. Political, economic and technological development must align, and engagement is needed from stakeholders including decision makers and operational staff. Biological nitrogen removal (BNR) during wastewater treatment is a potential source of nitrous oxide (N₂O), a potent greenhouse gas that also promotes depletion of the stratospheric ozone layer (Ravishankara *et al.* 2009). Control and mitigation of this gas are needed to contribute to the fulfillment of the agreement.

When treating highly concentrated nitrogen-rich water with low organic carbon content, such as reject water from sludge dewatering after anaerobic digestion, the risk

of nitrous oxide emissions is evident. Thus, the choice of deammonification (nitrification + anammox) over the nitrification/denitrification (N/DN) process should be considered, not only because of the lower aeration demand and lack of need for an external carbon source, but also owing to the potential for lower nitrous oxide emissions (Fux & Siegrist 2004). This would suggest that an N/DN process with intermittent feed, such as in a sequencing batch reactor (SBR), would emit more nitrous oxide than a deammonification plant of the same size, operating on the same wastewater and the same daily load.

In the last decade, the scientific community have proposed causal explanations for the relations in nitrous oxide formation in wastewater treatment. The three most widely accepted explanations for biological formation of nitrous oxide are (i) the oxidation of hydroxylamine, (ii) nitrifier denitrification, and (iii) heterotrophic denitrification. The first two of these are performed by ammonium oxidizing

bacteria (AOB) during aerobic conditions, and the last is performed by heterotrophic bacteria during anoxic conditions. To navigate a BNR system aiming for low N₂O production, the following boundary conditions are taken into account, based on the literature on these processes: ammonium oxidation rate (AOR) (Law *et al.* 2012), nitrite concentration in water (Kampschreur *et al.* 2008), and oxygen conditions (Tallec *et al.* 2006). Continuous feeding is further recommended by Law *et al.* (2011) to avoid shock loading of the system.

In contrast to boundary conditions, which are usually decided at the design stage, the operational conditions, and more specifically, the influence of process pH on the emissions, are of interest in this study. Changing the pH set point could be a simple tool for an operator to control the process and potentially the N₂O emissions. pH has profound direct effects on the AOB and nitrite oxidizing bacteria (NOB) kinetics; by influencing the enzymatic reactions and the stability of the bacterial cell wall and membrane (Vangsgaard *et al.* 2013) as well as indirect effects; by influencing the substrate speciation (i.e. NH₄⁺/NH₃ and NO₂⁻/HNO₂). The influence of pH on nitrous oxide production in aerobic conditions has been studied (Hynes & Knowles 1984; Law *et al.* 2011; Li *et al.* 2015; Rathnayake *et al.* 2015), but the reducing aspects of N₂O must also be taken into consideration. The nitrous oxide reductase (N₂OR) enzyme, which controls reduction of N₂O to N₂, is highly pH-dependent (Pauleta *et al.* 2013a). Therefore, the anoxic phases are of interest. In addition to the biological pathways, abiotic production (Soler-Jofra *et al.* 2016) and stripping effects are also pH-dependent.

Since so many reactions are pH-dependent, simulations of nitrous oxide emission that have pH as a parameter have been shown to require complicated models and this is still a challenging task. Simulation models must consider proton production (nitrification), proton consumption (denitrification) and equilibrium with bicarbonate buffer, as well as carbon dioxide stripping (Y Ma *et al.* 2017). When working with biofilm structures, this adds complexity (see examples in Vangsgaard *et al.* 2013; Y Ma *et al.* 2017). Moreover, intermittent aeration contributes to both aerobic and anoxic environments in the water and in the stratified biofilm. Together, this complexity, which encompasses several biological reaction pathways, and chemo-physical influence, all affected by pH, means that hypothesis testing is best carried out with a full-scale set-up in order to evaluate and compare actual emissions between the different operation modes.

In this study, N₂O was measured in the off-gas and water phase from full-scale reject water treatment at a Swedish

municipal wastewater treatment plant (WWTP), first with the plant operating in N/DN mode and after reconstruction, operating in deammonification mode at several pH set points. The change in pH was obtained by intermittent aeration. The objectives were, first, to show that a reject water treatment plant operating in deammonification mode emits less nitrous oxide than one operating in N/DN mode, and second, to show that the operating conditions, and pH set point in particular, have a significant influence on the nitrous oxide emissions from the plant. The goal is to find simple operational conditions that can be applied for many reject water treatment plants to minimize nitrous oxide emissions and hence the total carbon footprint of the wastewater treatment process.

MATERIAL AND METHODS

Full-scale reactor

The reject water treatment process at Slottshagen WWTP in Norrköping, Sweden, treats 250 kg total nitrogen (TN) d⁻¹ and has a volume of 1,000 m³. The reject water originates from sludge dewatering after mesophilic digestion of primary and wasted active sludge from Slottshagen WWTP, with total nitrogen load of 1,650 kg d⁻¹ (135,000 pe). The reject water treatment process was originally built and operated as an SBR with nitrification and denitrification with ethanol dosage and was reconstructed to deammonification with a moving bed biofilm reactor (MBBR) in 2017.

Experimental design

Operation in N/DN mode with SBR in 2012

Data for this study were collected between 9th April and 20th May 2012. The SBR was operated with a cycle length of 8 h. The cycle started with 2 h filling, followed by 1 h of ethanol dosing during the 3.5 h denitrification phase (no aeration, only mixing), thereafter 3.5 h nitrification (aeration) and 1 h sedimentation including 0.45 h decantation. During nitrification, the set-point of oxygen was 2.0 mg DO L⁻¹. During decantation, a short period (seconds) for the withdrawal of excess sludge is included. Some of these N₂O measurements are reported in Stenström *et al.* (2014), which also contains further details about the SBR operation.

Operation in deammonification mode with MBBR in 2018

The filling degree was 40% with suspended carriers (K1H, Kaldnes) and the process was aerated intermittently at 2.0 mg DOL⁻¹. The intermittent aeration had a cycle of 60 minutes and was regulated with a PI regulator with output of 5–50% aeration time to maintain the pH set point. This aeration creates periodic aerobic and anoxic environments in the water. During the anoxic period, the process is mixed with three top-mounted mixers. The blower has a capacity of 1,400–2,600 Nm³ h⁻¹ (Sulzer, HST 2500-1-H) and distributes air with a coarse bubble system (Purac AB). The air flow from the reactor was calculated from the energy used by the blower, which has a linear correlation.

The deammonification process had been in stable operation for 6 months at pH setpoint 7.4 before the measuring campaign was performed in July and August 2018. The pH settings were changed approximately every 2 weeks (after 2.5–3 HRT) in order to exchange the majority of suspended biomass during the new set point, and in random order; pH 7.6, 6.6 and 7.1. The change of pH set point was linked to aeration strategies to avoid adding any chemicals in the process that could cause additional stress to the microbiological fauna. The flow set point was 8 m³ h⁻¹, although on a few days the flow was occasionally lower.

To verify the above N₂O measurements, a short-term measurement campaign was carried out in October 2018, measuring only in the water phase. The pH settings were changed every third day, in order to retain the suspended biomass. Since the first test resulted in a drifting process with accumulating nitrate concentration, the pH set point was changed to less extreme values; pH 6.7, 7.1 and 7.5. These were changed in random order with one repetition, resulting in the series 7.5, 7.1, 6.7, 7.5, 7.1, 6.7.

Chemical analysis and on-line instrumentation

Nitrogen compounds (NH₄-N, NO₂-N and NO₃-N) were analysed with Hach cuvette tests (LCK 305, 342, 339; Hach Lange, Germany) using a spectrophotometer (Dr Lange Xion 500). TN was analysed according to SS-EN ISO 11905 using a FIAstar 5000 analyzer. Organic compounds (TOC) were determined according to Swedish standard method SS-EN 1484 using Shimadzu TOC-L CPN. Total suspended solids and alkalinity were determined according to Swedish standard methods SS-EN 872:2005 and SS 028139-1, respectively. All samples were grab samples.

Flow (Siemens MAG), temperature (Endress and Hauser, RTD) and ammonia (WTW, Ammolylt 700IQ) of the reject water influent together with dissolved oxygen (Hach Lange, LDO), pH, temperature (Endress and Hauser, Orbipac) and ammonium (WTW, Ammolylt 700IQ) in the reactor were monitored and the data were collected.

On-line N₂O monitoring

To be able to distinguish the net formation and degradation of N₂O in the water phase from the stripping of gas to the atmosphere, measurements were done in both the water phase and the off-gas from the process.

Gas phase

In 2012, the N₂O concentration in off-gas was measured online by Teledyne analytical instrument (ModelGFC-7002E) and the process airflow data were used to calculate nitrous oxide emissions. In 2018, a Fresenius spectrophotometer (GA2020) was used to measure the N₂O in the off-gas. The off-gas was collected via three tubes located in each corner of a theoretical triangle placed on top of the circular basin. The meter took samples every minute from one point for two to three days and then changed sampling point in a rotating scheme. Monitoring of the off-gas was only done during the long-term test.

Liquid phase

For both measurement campaigns, N₂O measurements in the water phase were taken with a microsensor (Unisense, Aarhus, Denmark). Data were collected every minute in the programmable logic controller (PLC) system. The sensor was calibrated before the long-term test at 33 °C and before the short-term test at 29 °C.

Calculations and statistical analysis

Before the data were synthesized, it was manually cleaned of outliers based on process operation. Data from operational stops were ignored.

The N₂O emissions, (E_{N₂O-N}) were calculated using the following expression:

$$E_{N_{2}O-N} = \sum_{i=1}^{1440} (c_{N_{2}O-N(g)} Q_{air} * \Delta t_i * 60 * 24) \quad (1)$$

where E_{N_2O} (kg d⁻¹) is the emission rate per day, $c_{N_2O-N(g)}$ is the N₂O-N concentration in the off-gas (recalculated from ppmv N₂O to kg N₂O-N m⁻³ using molar volume at the current temperature), Q_{air} is the airflow from the blower (m³ min⁻¹) and time interval Δt (min).

It is assumed that stripping of N₂O from the water phase to gas phase is negligible during non-aerated (anoxic) conditions (Baresel *et al.* 2016). By relating the emissions (E_{N_2O}) to the total nitrogen load (TN) or the ammonium load (NH₄-N), the formation factor (F) is calculated as follows:

$$F_{TN} = \frac{E_{N_2O-N}}{TN} \quad (2a)$$

$$F_{NH_4-N} = \frac{E_{N_2O-N}}{NH_4-N} \quad (2b)$$

Statistical analysis of variance (1-factor ANOVA) was performed on N₂O data from the long-term test. In the short-term test, 2-factor ANOVA was used with pH and flow as variables and N₂O(aq) as a response, using the

Excel Analysis Toolpak (Microsoft Office) to evaluate whether there was a significant difference between the datasets.

RESULTS AND DISCUSSION

N₂O emissions in N/DN in SBR mode versus deammonification in MBBR mode

An overview of the process data and results from 2012 and 2018 is presented in Table 1. Similar loads and influent ammonium concentrations between the different operation modes provide a stable basis for comparison. pH was not regulated during the N/DN operation mode, whereas the process in deammonification mode had different pH set points. The N/DN operation mode had significantly higher N₂O concentrations in the water phase (13.2 versus 0.10–0.41 ppm) as well as in the gas phase (973 versus 8–43 ppm) resulting in higher total emissions of nitrous oxide (10.4% versus 0.14–0.71%). The calculated emissions

Table 1 | Overview of process data and results for the two different techniques, N/DN and deammonification, and three different pH set points with deammonification

Nitrogen process		N/DN	Deammonification (nitrification/anammox)		
		SBR	MBBR with continuous inflow and intermittent aeration		
Technique					
Year		2012	2018 - long-term study		
pH set-point		Not controlled	6.6	7.1	7.6
Load	kg NH ₄ -N _{in} d ⁻¹	210	195	210	155
NH ₄ -N _{in}	mg L ⁻¹	1000	941 (±81)	894 (±81)	1,022 (±128)
pH-measured		6.2–7.5	6.74 (±0.18)	7.05 (±0.06)	7.68 (±0.16)
DO (during aeration phase)	mg DO L ⁻¹	0.3–2.0	1.9 (±0.1)	2.3 (±0.3)	1.8 (±0.2)
Average aeration time	%	44% ^a	34 (±5)	38 (±4)	22 (±11)
Temperature	°C	~30	35.1 (±1.2)	32.5 (±0.3)	36.0 (±0.1)
NH ₄ -N _{out}	mg L ⁻¹	30–90	154 (±38)	247 (±15)	124 (±27)
NO ₂ -N _{out}	mg L ⁻¹	10–25	3.9 (±1.0)	3.8 (±1.6)	1.8 (±1.0)
NO ₃ -N _{out}	mg L ⁻¹	90–150	257 (±128)	330 (±36)	73 (±38)
TOC/TN ratio		1.0–1.2 ^b	0.2	0.2	0.3
N reduction TN		80%	67%	50%	86%
NH ₄ -N		95%	88%	79%	91%
Daily N ₂ O average in water	mg N ₂ O(aq) L ⁻¹	13.2	0.41 (±0.09)	0.21 (±0.03)	0.10 (±0.05)
Daily average in off-gas N ₂ O(g)	ppm	973	39 (±42)	43 (±38)	8.1 (±12.5)
F _{TN}		10.4%	0.71%	0.71%	0.14%
F _{NH₄-N}		12.5%	0.81%	0.81%	0.16%

Data are presented with mean and standard deviation in brackets where available.

^aDifferent blower used in 2012.

^bIncluding external ethanol dosage. A ratio COD/TOC = 4.0 is used for ethanol.

for the SBR mode is one of the highest emissions documented in a WWTP (Stenström *et al.* 2014). By comparison, in a review by Massara *et al.* (2017) in which the formation factor (F_{TN}) of seven full-scale plants is summarized, these emissions are in the top range. On the other hand, the emissions measured in deammonification mode are among the lowest, compared to those of the other seven plants in the review.

The major reasons for the difference in emissions may be explained by several factors: the difference in feeding strategy (intermittent versus continuous) (Law *et al.* 2011), the lower concentration of nitrite in the water (Schneider *et al.* 2013), the decreased load of ammonium oxidized by AOB (C Ma *et al.* 2017), the shorter aeration time (Domingo-Félez *et al.* 2014) and the introduction of biofilm (Park *et al.* 2000), all in favour of the later operation mode. In addition, a functional control for ethanol dosing was not in place when performing measurements in SBR mode, neither did the blower reach the oxygen set-point of 2.0 mg DO L⁻¹ at all times.

Potential explanations for significant higher N₂O-emissions during N/DN in SBR mode compared to deammonification mode include that in the SBR mode feeding was intermittent, occurring for only 2 h of an 8 h cycle, in contrast to the continuous feeding that was used in the MBBR mode. The average concentration of nitrite (10–25 versus 1.8–3.9 mg L⁻¹) was much higher in the SBR mode than in the MBBR mode (see Table 1); this difference is also linked to the way of operation. In SBR mode the aeration was fixed at 3.5 h versus the range of 3–30 minutes in

deammonification mode. Further, the deammonification process only allows half of the ammonia to be converted by AOBs; this has been listed as one of the largest contributors of nitrous oxide production when treating reject water (Blum *et al.* 2018). Additionally, a shorter daily average aeration time (44% versus 22–38%) could potentially contribute to lower emissions, with less time for stripping gas, although in this case, the two scenarios cannot be compared in this respect because both blower and aeration system were changed between the measurements.

In Figure 1, a mapping of dissolved oxygen (DO) and nitrous oxide in water and nitrous oxide in gas is shown for two selective days. This figure may explain additional reasons for the higher emissions in SBR mode. These patterns unveil the highest concentration of N₂O in the gas at the start of the aeration. During this time, produced nitrous oxide is simultaneously stripped off to the environment and the concentrations of the gas in the water phase is therefore low. The oxygen set-point of 2.0 mg/L was not reached and only 0.3–0.7 mg DO/L, was measured in the bulk phase. At these low oxygen concentrations, possibly nitrifier denitrification production pathways could be contributing to the nitrous oxygen production (Kampschreur *et al.* 2009). As the aeration later stops and switches to sedimentation, the oxygen sensor is indicating higher oxygen concentrations. This most probably is false and instead linked to the high nitrite concentrations in the water as this time, which has been experienced before at the plant (Stenström *et al.* 2014). During mixing, both reject water

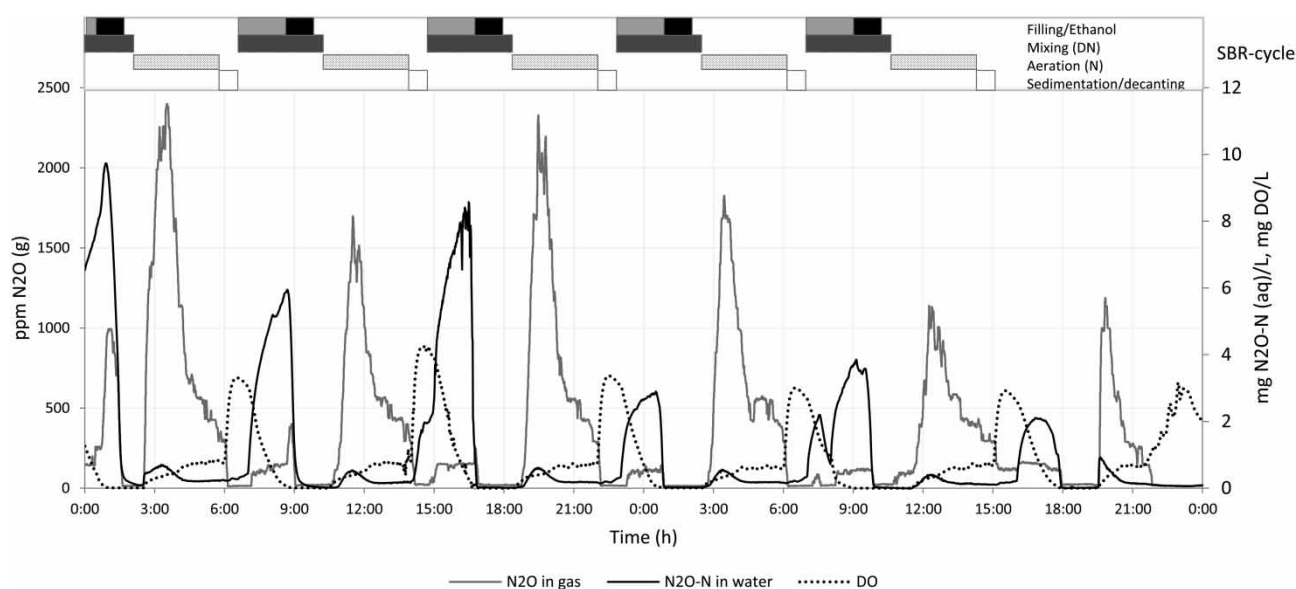


Figure 1 | Mapping of minute data of concentrations of nitrous oxide in gas and water and dissolved oxygen in water for the SBR operating in N/DN mode. Data are shown for two days during the measurement period of 2012 (48 hours, 22 and 23 of March 2012).

and thereafter ethanol is dosed. First, a net production of nitrous oxide in water can be seen and thereafter a net reduction, possibly due to first incomplete and thereafter complete denitrification. The change of reject water treatment also introduced biofilm into the process and could be a last contributing factor for lowering the emissions. A biofilm system has proved to be more effective for reducing N₂O than a suspended system (Park *et al.* 2000). The impact of the biofilm mode cannot be distinguished here but will be discussed further. All these operational changes in sum lead to tenfold lower emissions in the deammonification mode with MBBR than in N/DN in SBR mode.

The effect of pH set point and N₂O concentrations (aq) N₂O emissions (g) during long-term measurements

Daily averages of nitrous oxide in the water phase (mg N₂O L⁻¹) and nitrous oxide emissions (kg N₂O d⁻¹) during the 48-day long-term study in 2018 are shown in Figure 2 and Table 1. Significantly lower emissions were observed at a higher pH set point in deammonification mode. The differences in N₂O(aq) and actual N₂O emissions were analyzed statistically using 1-factor ANOVA and concluded to be significant between all pH set points with a confidence interval of 95%.

At first, the nitrogen conversion at pH 7.6 is high and normal, but in the later phases, at pH 6.6 and 7.1, the total nitrogen conversion fell from >80% to 50% due to nitrate accumulation. This was most probably due to

accumulation of NOBs when more intensive aeration was used to decrease and maintain pH at 6.6. When the nitrate production had ceased after a few weeks with normal aeration times, a short-term measurement campaign with various pH set points was repeated. The reasons for lower emissions at higher pH set point will be discussed further by looking at the data in detail.

Detailed study of nitrous oxide at the different pH set points

Figure 3 shows a detailed study of N₂O in the water and gas phase during aeration cycles in the different operation modes. During aeration (DO = 2 mg L⁻¹), nitrous oxide is emitted to the air and the concentration in the water phase decreases. Focusing on the anoxic phase (DO = 0 mg L⁻¹) the N₂O-N(aq) curve shows an increasing trend at pH 6.6, whereas at pH 7.6 the concentration first increases and later decreases. The net production at the beginning of the anoxic phase (non-aeration) between the different pH set points appears to be broadly similar. Random measurements of the slope taken during the first 5 minutes support this theory (data not shown here). However, at the higher pH set points, denitrification with net consumption of N₂O can also be seen, giving the line an A-shaped form. At lower pH set points, this results in a net production of N₂O during the anoxic phase in the water phase, which is stripped off during aeration. In comparison, at the higher pH, the net production during the anoxic phase is very

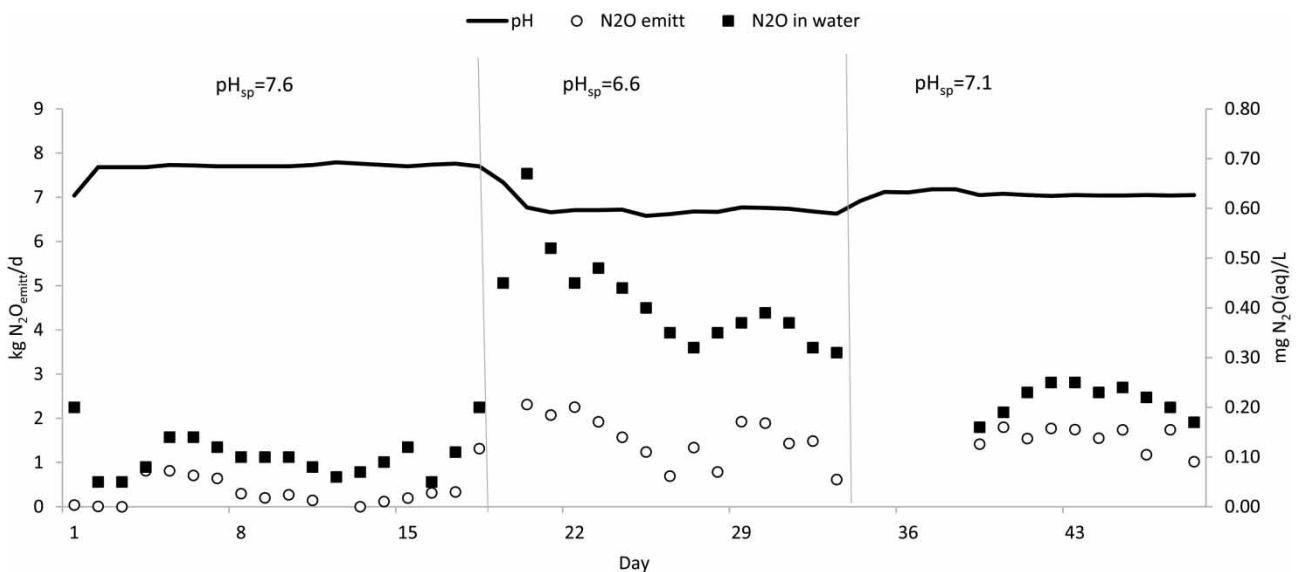


Figure 2 | Overview of long-term pH study in deammonification mode in 2018. Nitrous oxide in water (N₂O in water) and emitted nitrous oxide (N₂O emitted) during three operation modes with the pH set point of 7.6, 6.7 and 7.1 for a total time of 48 days. Data between day 34 and 38 are missing due to a logging failure in the database.

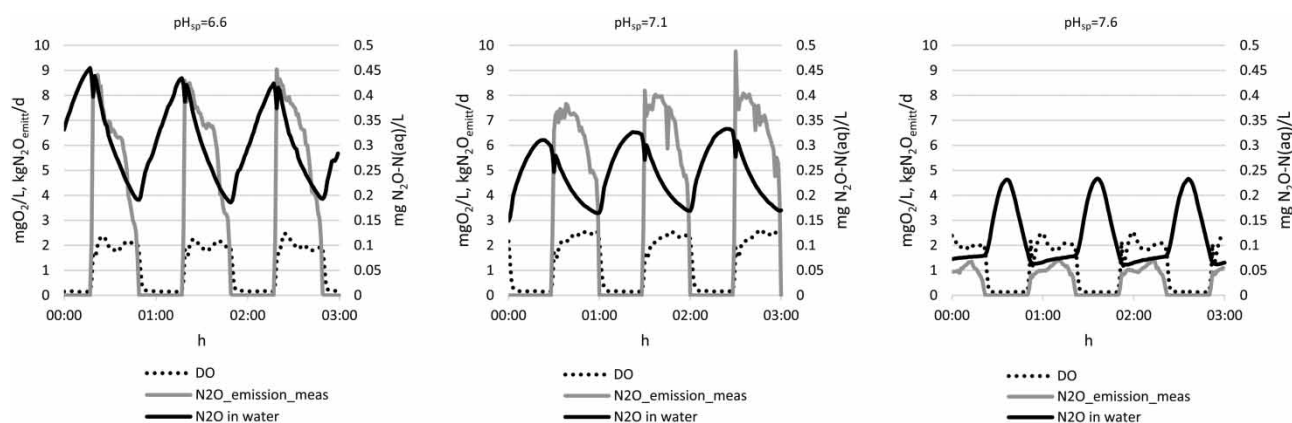


Figure 3 | Detailed study of dissolved oxygen (DO), nitrous oxide in water (N₂O in water) and emitted nitrous oxide (N₂O emitt) during three aeration cycles (each cycle is 1 h) in deammonification mode. Three representative hours are shown for one representative day (day 17, 30 and 46) from each phase.

low, which results in lower N₂O concentrations in the off-gas during aeration and hence lower emissions (kgN₂O d⁻¹) at the higher pH.

The concentrations in the water mirror the net production of nitrous oxide, although the current production may be higher at the time, since there may be a simultaneous consumption of N₂O occurring in the biofilm. In a study by Eldyasti *et al.* (2014), a thicker biofilm was shown to contribute to lower N₂O emissions than a thinner biofilm. N₂O can accumulate in the water when there is an imbalance between the production and consumption of N₂O, whether it is produced in the biofilm or in the water phase. Denitrification (NO₃⁻ → NO₂⁻ → NO → N₂O → N₂), which starts to occur during anoxic phases, is controlled by the enzymes NaR, NiR, NoR and N₂OR, where N₂OR is the most pH sensitive (Schneider 2013). The pH optimum for N₂OR is in the range of 8.0–9.5 (Pauleta *et al.* 2013b), which indicates that higher pH would enhance the transformation of N₂O to N₂. Results from this study indicate that more nitrous oxide is reduced via complete denitrification at higher pH. This is consistent with an early publication on denitrification in soil, which showed that the denitrification of N₂O was strongly inhibited below neutral pH (Wijler & Delwiche 1954).

These results are in line with the conclusions from a modeling study performed by Wang *et al.* (2016); the main contributor of nitrous oxide at low oxygen concentration (DO = 0.5 mg L⁻¹) in these types of systems are the heterotrophic bacteria, whereas the AOBs are the main contributor at higher oxygen concentrations. Figure 3 shows the production and reduction of nitrous oxide during the anoxic phase and the concurrent emissions during the aerated phase. The assumption is made that no stripping of gas occurs during mixing. Hence, the emissions during aeration

are the sum of the two sources: (i) nitrous oxide produced during aeration and (ii) nitrous oxide formed (but not stripped) during the anoxic phase.

Many publications report that a large part of the emissions are emitted during the first few minutes of the aeration phase. This may be a result of not only a high reaction rate of the oxidizing process, but also due to a large contribution of nitrous oxide produced during the anoxic phase, which owing to modest solubility in water stays in the water phase. Once the aeration starts, nitrous oxide is emitted by stripping. This pattern is also seen in Figure 3, especially at the lower set point. When analyzing Figure 3 it should be emphasized that the aeration time (50% of 60 minutes) and the air flow are comparable between the compared hours.

Regarding nitrous oxide formation during the aerobic phase, no conclusions can be drawn from this study. Previously, Law *et al.* (2011) have shown that in a partial nitrification system under aerobic conditions, the highest formation rates at higher pH are due to higher substrate availability as NH₄⁺ goes towards NH₃, which is an indirect effect of pH. Li *et al.* (2015) showed the highest production rates at higher pH but lower accumulation rates. They suggest that a combination with high DO and high pH can reduce N₂O accumulation.

The effect of pH set point of N₂O concentrations (aq) during short-term measurements

During the 48-day long-term pH study, the changes in aeration strategy for changing the water pH contributed to a drift in the process towards NO₃ accumulation. The increase of nitrate concentration in the water could potentially influence the conclusions of the study. Therefore, the changes

in pH set points were further verified using a short-term test. After the process had re-stabilized and the nitrate production was back to normal ($\text{NO}_3\text{-N}/\text{N}_{\text{red}} < 10\%$), a second round with pH adjustment was done. Experience from the first test showed that the response of emissions to changing pH set point was relatively quick. Therefore, each set point was maintained for three days; but since it took one day for the pH to stabilize at the new set point, only data from the last two days were used for analysis. Only data from the anoxic phase are presented here; however, data including both anoxic and aerobic phases show the same trend. The inflow was automatically adjusted to either low flow ($6 \text{ m}^3 \text{ h}^{-1}$) or high flow ($12 \text{ m}^3 \text{ h}^{-1}$), depending on access of reject water. The dataset is shown in Figure 4(a) as box plots, and distinguishes the two different flows and the three different set points. In general, the data from the short-term study show lower nitrous oxide concentrations in the water phase ($< 0.35 \text{ mg N}_2\text{O L}^{-1}$) compared to the long-term measurements in 2018 ($< 0.70 \text{ mg N}_2\text{O L}^{-1}$) and much lower than measurements in 2012 ($\sim 13 \text{ mg N}_2\text{O L}^{-1}$).

From these results, it can be seen that operating with pH set point equal to 7.5 shows statistically significant lower N₂O concentrations in the water phase than the other set

points during anoxic conditions at both flow set points. The reason for this is believed to be two-fold. First, shorter average aeration times are used at higher pH set points (Figure 4(b)). The average aeration time is approximately 30% shorter for the highest set point than for the lowest. A shorter aeration time means that there is less time for stripping nitrous oxide into the atmosphere. However, comparing the means of nitrous oxide concentrations at the high flow between the highest and lowest pH, the difference is approximately 50%, thus the aeration time is unlikely to be the only reason for the difference. At the lower flow, the comparison is not very informative, since the absolute concentrations approach zero. The second factor for significant lower N₂O concentrations at pH set point 7.5 is the actual pH, which mainly is linked to the (in)complete denitrification, as discussed earlier.

The N₂O concentrations in the water phase are higher at the higher load (flow) than for the lower load. This is expected, since higher loads could generate more N₂O. Nevertheless, whereas the load was doubled, the nitrous oxide concentration in the water phase only increased by approximately 30%. This implies that the formation factor (which is related to load) is not equal in the two different load cases.

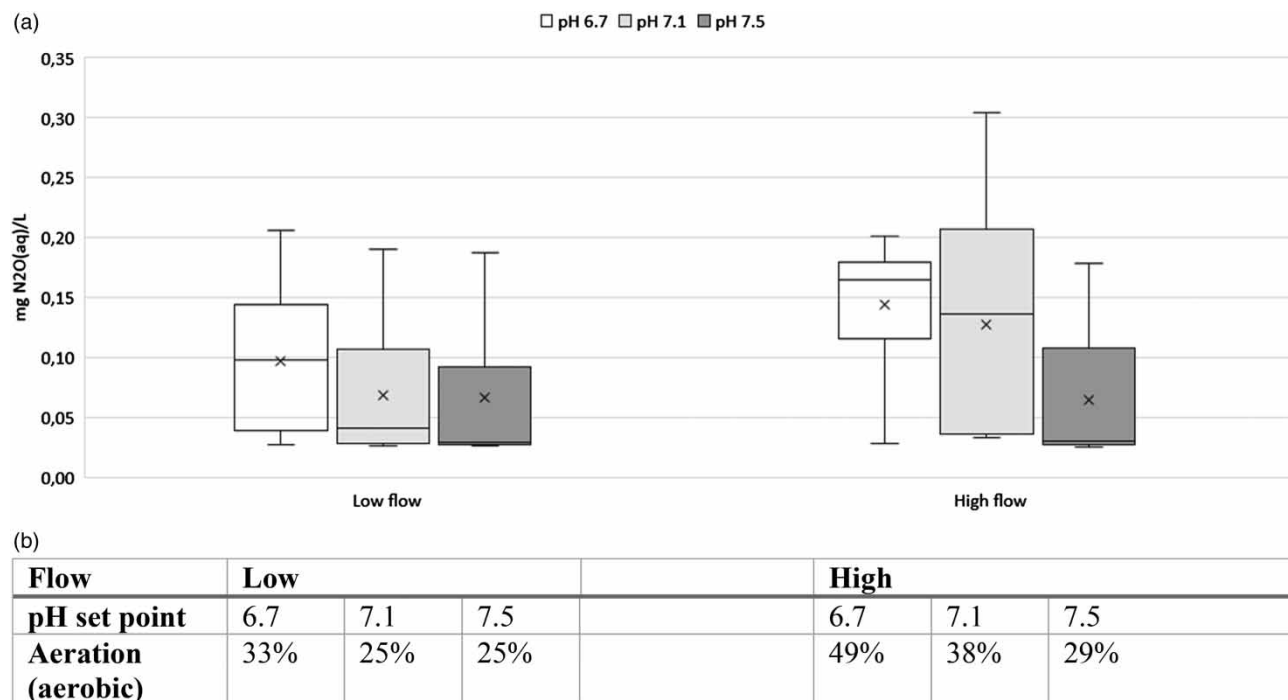


Figure 4 | Results from the short-term pH study from 2018 in deammonification mode. (a) Box plots show the dataset from N₂O in the liquid phase (mg/L) during the anoxic phase over two days with one repetition, for a total of four days for each set point. The upper and lower lines of the box mark the first and third quartile; the midline marks the median and the cross marks the mean of the dataset. $n_{\text{pH}=6.7} = 2162$, $n_{\text{pH}=7.1} = 2382$, $n_{\text{pH}=7.5} = 3070$ for the low flow and $n_{\text{pH}=6.7} = 1430$, $n_{\text{pH}=7.1} = 1626$, $n_{\text{pH}=7.5} = 718$ for the high flow. (b) Average time of aeration during one hour for the different pH set points and flows. The time of aeration is regulated by the PI-regulator with process pH as input and % of time aerated as output.

The effect of different pH on N₂O-emissions, as described earlier, may become more significant in biofilm systems. Vangsgaard *et al.* (2013) have shown how pH variation in water influences the variation of pH in the biofilm. A larger variation in the biofilm than in the water during intermittent aeration has been suggested by Y Ma *et al.* (2017). This indicates that the differences in pH in the biofilm environment between the set points are even larger than the set points measured and regulated in the water phase.

CONCLUSIONS

From this case study, it can be concluded that by changing the operation from nitrification/denitrification in SBR mode to deammonification in MBBR mode, this can provide a nitrous oxide emissions reduction of about 10 times.

Specifically, the study shows that monitoring nitrous oxide emissions during full-scale operation of a reject-water treatment process resulted in the following:

- Quantification of nitrous oxide emissions from the process resulting in planning of emission mitigation measures.
- Significantly lower nitrous oxide emissions (from 10 to <1% of TN_{in}) after conversion of the treatment process from N/D in SBR operation to deammonification in MBBR technique.
- Understanding of pH control in deammonification mode on further emissions reduction to as low as 0.14% of TN_{in}.

The conversion of the reject water treatment process from N/D in SBR operation to deammonification in MBBR technique has in the presented case saved 9.5 tonnes N₂O-N/year (26 kg N₂O-N/d) which corresponds to 2,800 tonnes CO_{2e}/year. These emission savings are linked to a reject water treatment for a municipal plant of 135,000 pe.

ACKNOWLEDGEMENTS

LK is financed by a Piiia scholarship from Vinnova (Swedish Governmental Agency for Innovation Systems), with co-funding from Purac AB and ABB AB. This research is also funded by IVL Swedish Environmental Research Institute Foundation (SIVL). The authors would like to thank Niclas Bornhold (IVL) for technical assistance with N₂O (g) measurements and Nodra (former Norrköping Vatten och Avfall) for their cooperation and contribution to the project.

We would also like to acknowledge Dr Maike Beier (ISAH, Hannover, Germany) for valuable input to the manuscript.

REFERENCES

- Baresel, C., Andersson, S., Yang, J. & Andersen, M. H. 2016 Comparison of nitrous oxide (N₂O) emissions calculations at a Swedish wastewater treatment plant based on water concentrations versus off-gas concentrations. *Adv. Clim. Chang. Res.* **7**, 185–191.
- Blum, J. M., Jensen, M. M. & Smets, B. F. 2018 Nitrous oxide production in intermittently aerated partial nitrification-anammox reactor: oxidic N₂O production dominates and relates with ammonia removal rate. *Chem. Eng. J.* **335**, 458–466.
- Domingo-Félez, C., Mutlu, A. G., Jensen, M. M. & Smets, B. F. 2014 Aeration strategies to mitigate nitrous oxide emissions from single-stage nitrification/anammox reactors. *Environ. Sci. Technol.* **48**, 8679–8687.
- Eldyasti, A., Nakhla, G. & Zhu, J. 2014 Influence of biofilm thickness on nitrous oxide (N₂O) emissions from denitrifying fluidized bed bioreactors (DFBBRs). *J. Biotechnol.* **194**, 281–290.
- Fux, C. & Siegrist, H. 2004 Nitrogen removal from sludge digester liquids by nitrification/denitrification or partial nitrification/anammox: environmental and economical considerations. *Water Sci. Technol.* **50**, 19–26.
- Hynes, R. K. & Knowles, R. 1984 Production of nitrous oxide by *Nitrosomonas europaea*: effects of acetylene, pH and oxygen. *Can. J. Microbiol.* **30**, 1397–1404.
- Kampschreur, M. J., Tan, N. C. G., Kleerebezem, R., Picoreanu, C., Jetten, M. S. M. & Van Loosdrecht, M. C. M. 2008 Effect of dynamic process conditions on nitrogen oxides emission from a nitrifying culture. *Environ. Sci. Technol.* **42**, 429–435.
- Kampschreur, M. J., Temmink, H., Kleerebezem, R., Jetten, M. S. M. & van Loosdrecht, M. C. M. 2009 Nitrous oxide emission during wastewater treatment. *Water Res.* **43**, 4093–4103.
- Law, Y., Lant, P. & Yuan, Z. 2011 The effect of pH on N₂O production under aerobic conditions in a partial nitrification system. *Water Res.* **45**, 5934–5944.
- Law, Y., Ni, B. J., Lant, P. & Yuan, Z. 2012 N₂O production rate of an enriched ammonia-oxidising bacteria culture exponentially correlates to its ammonia oxidation rate. *Water Res.* **46**, 3409–3419.
- Li, P., Wang, S., Peng, Y., Liu, Y. & He, J. 2015 The synergistic effects of dissolved oxygen and pH on N₂O production in biological domestic wastewater under nitrifying conditions. *Environ. Technol.* **36**, 1623–1631.
- Ma, C., Jensen, M. M., Smets, B. F. & Thamdrup, B. 2017 Pathways and controls of N₂O production in nitrification-anammox biomass. *Environ. Sci. Technol.* **51**, 8981–8991.
- Ma, Y., Domingo-Félez, C., Plósz, B. G. & Smets, B. F. 2017 Intermittent aeration suppresses nitrite-oxidizing bacteria in membrane-aerated biofilms: a model-based explanation. *Environ. Sci. Technol.* **51**, 6146–6155.

- Massara, T. M., Malamis, S., Guisasola, A., Baeza, J. A., Noutsopoulos, C. & Katsou, E. 2017 A review on nitrous oxide (N₂O) emissions during biological nutrient removal from municipal wastewater and sludge reject water. *Sci. Total Environ.* **596–597**, 106–123.
- Park, K. Y., Inamori, Y., Mizuochi, M. & Ahn, K. H. 2000 Emission and control of nitrous oxide from a biological wastewater treatment system with intermittent aeration. *J Biosci Bioeng* **90**, 247–252.
- Pauleta, S. R., Dell'Acqua, S. & Moura, I. 2013a Nitrous oxide reductase. *Coord. Chem. Rev.* **257**, 332–349.
- Pauleta, S. R., Dell'Acqua, S. & Moura, I. 2013b Nitrous oxide reductase. *Coord. Chem. Rev.* **257**, 332–349.
- Rathnayake, R. M. L. D., Oshiki, M., Ishii, S., Segawa, T., Satoh, H. & Okabe, S. 2015 Effects of dissolved oxygen and pH on nitrous oxide production rates in autotrophic partial nitrification granules. *Bioresour. Technol.* **197**, 15–22.
- Ravishankara, A. R., Daniel, J. S. & Portmann, R. W. 2009 Nitrous oxide (N₂O): the dominant ozone-depleting substance emitted in the 21st century. *Science* **326**, 123–125.
- Rockström, J., Gaffney, O., Rogelj, J., Meinshausen, M., Nakicenovic, N. & Schellnhuber, H. J. 2017 A roadmap for rapid decarbonization. *Science* **355**, 1269–1271.
- Schneider, Y. 2013 *Nitrous Oxide Foramtion During Biological Treatment of Ammonium-Rich Wastewater*. Leibniz Universität Hannover, Hannover, Germany.
- Schneider, Y., Beier, M. & Rosenwinkel, K. H. 2013 Nitrous oxide formation during nitrification and nitrification of high-strength wastewater. *Water Sci. Technol.* **67**, 2494–2502.
- Soler-Jofra, A., Stevens, B., Hoekstra, M., Picioreanu, C., Sorokin, D., van Loosdrecht, M. C. M. & Pérez, J. 2016 Importance of abiotic hydroxylamine conversion on nitrous oxide emissions during nitrification of reject water. *Chem. Eng. J.* **287**, 720–726.
- Stenström, F., Tjus, K. & La Cour Jansen, J. 2014 Oxygen-induced dynamics of nitrous oxide in water and off-gas during the treatment of digester supernatant. *Water Sci. Technol.* **69**, 84–91.
- Tallec, G., Garnier, J., Billen, G. & Gossiaux, M. 2006 Nitrous oxide emissions from secondary activated sludge in nitrifying conditions of urban wastewater treatment plants: effect of oxygenation level. *Water Res.* **40**, 2972–2980.
- UNFCCC 2015 Paris Agreement.
- Vangsgaard, A. K., Mauricio-Iglesias, M., Valverde-Pérez, B., Gernaey, K. V. & Sin, G. 2013 Ph variation and influence in an autotrophic nitrogen removing biofilm system using an efficient numerical solution strategy. *Water Sci. Technol.* **67**, 2608–2615.
- Wang, Q., Ni, B. J., Lemaire, R., Hao, X. & Yuan, Z. 2016 Modeling of nitrous oxide production from nitrification reactors treating real anaerobic digestion liquor. *Sci. Rep.* **6**, 1–8.
- Wijler, J. & Delwiche, C. C. 1954 Investigations on the denitrifying process in soil. *Plant Soil* **5**, 155–169.

First received 30 November 2018; accepted in revised form 29 April 2019. Available online 3 May 2019