Identifying N2O formation and emissions from a full-scale partial nitritation reactor

Kris E. Mampaeya, Merle K. De Kreuk, Udo G.J.M. van Dongen, Mark C.M. van Loosdrecht, Eveline I.P. Volcke

Department of Biosystems Engineering, Ghent University, Coupure Links 653, 9000 Ghent, Belgium
Waterschap Hollandse Delta, Handelsweg 100, 2980 GC Ridderkerk, The Netherlands
Department of Biotechnology, Delft University of Technology, Julianalaan 67, 2628BC Delft, The Netherlands

A B S T R A C T

In this study, N2O formation and emissions from a full-scale partial nitritation (SHARON) reactor were identified through a three-weeks monitoring campaign during which the off-gas was analysed for N2O, O2, CO2 and NO. The overall N2O emission was 3.7% of the incoming ammonium load. By fitting the N2O emission to a theoretical gas stripping profile, the N2O emissions could be assigned to aerobically formed N2O and N2O formed under anoxic conditions. This was further substantiated by liquid N2O measurements. Under standard operation, 70% of the N2O emission was attributed to anoxic N2O formation. Dedicated experiments revealed that low dissolved oxygen concentrations (<1.0 g O2 L-1) and longer anoxic periods resulted in an increased N2O emission. Minimising or avoiding anoxic conditions has the highest effect in lowering the N2O emissions. As an additional result, the use of the off-gas N2O concentration measurements to monitor the gas-liquid mass transfer rate coefficient (kLa) during dynamic reactor operation was demonstrated.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Over the last decades, innovative methods for biological nitrogen removal from wastewater have been developed, increasing the sustainability compared to conventional processes, especially in terms of energy requirements. One of these innovative methods concerns the partial nitritation-anammox pathway, in which half of the ammonium is oxidized to nitrite, followed by the combination of ammonium and nitrite to form dinitrogen gas. The partial nitritation-anammox pathway involves up to 63% savings in aeration energy, avoids the need for external carbon source addition and leads to a lower sludge production and minimal CO2 emissions compared to nitrification-denitrification over nitrate (Strous et al., 1997). Among others, this pathway is very suitable to remove the ammonium from reject water originating from anaerobic digestion.

Nitrous oxide (N2O) is a potent greenhouse gas of which the effect is 298 times stronger than CO2 (IPCC, 2013). N2O can be formed during biological nitrogen removal from wastewater, such as by ammonia oxidising bacteria (AOB) responsible for nitrification (Ritchie and Nicholas, 1972). Two pathways for N2O formation by AOB are distinguished, namely the reduction of nitrite to N2O, termed nitrifier denitrification, and the oxidation of NH2OH, an intermediate during nitrification (Colliver and Stephenson, 2000). Besides, N2O is an obligate intermediate of heterotrophic denitrification (Hiatt and Grady, 2008).

N2O emissions show large variations between different wastewater treatment plants as well as diurnal and seasonal dynamics (Kampschreur et al., 2009; Ahn et al., 2010). The comparison between the innovative methods and conventional wastewater treatment in terms of N2O emissions is less straightforward than the energy savings. This contribution assesses the effect of dynamic reactor operation on N2O formation and emission from a full-scale partial nitritation SHARON reactor. In a SHARON reactor, ammonium is oxidised to nitrite, while further oxidation to nitrate is prevented, by keeping the temperature sufficiently high (35 °C) and the aerobic retention time sufficiently low (Hellinga et al., 1998). Identification of the conditions favouring or hindering N2O formation is a starting point for mitigation. Three operating modes were
distinguished during the monitoring campaign. “Standard operation cycles” are considered as reference for the N₂O emission factor, the assumptions made were validated by a prolonged aeration experiment. The second operating mode groups cycles with prolonged non-aerated periods due to an influent feed stop. Furthermore, additional dedicated experiments were performed, namely (i) lowering the DO set point, and (ii) halving the total cycle length. Based on the results of these dedicated experiments, N₂O mitigation options are proposed. As an additional result, it was demonstrated possible to monitor the $k_{La}$ of the reactor from the dynamic reactor operation.

2. Materials and methods

2.1. Process layout – SHARON reactor

A three-weeks monitoring campaign, from 15 June to 6 July 2010, was performed on the full-scale SHARON reactor in Rotterdam, the Netherlands. This reactor is part of the sludge handling facility and treats the anaerobic digestion reject water (Fig. 1). The effluent from the SHARON reactor contains ammonium and nitrite in about equimolar concentrations and is fed to an Anammox reactor. More details on the treatment plant are given by Kampschreur et al. (2008a), Mulder et al. (2001).

To keep a constant aerobic retention time despite the varying influent flow rates, the SHARON reactor (Fig. 2) is operated in 2-h cycles, consisting of an aerated period (DO set point = 2 g O₂ m⁻³) and a non-aerated period. The duration of the aerated period is calculated from the liquid inflow ($QR_L$) during the preceding cycle and the (constant) reactor volume ($VR$) such that a mean aerobic retention time of 1.35 days is established (van Loosdrecht and Salem, 2006). The liquid inflow; being the centrifuge outflow, varied between 0 (no flow) and 20–41 m³·h⁻¹, but is relatively constant during a cycle. The influent total ammonium (TNH) concentration varied between 1050 and 1500 g N m⁻³.

The SHARON reactor is completely covered and permanently kept in underpressure (~200 Pa) to prevent odour emissions. However, due to the underpressure, ambient air infiltrates in the SHARON reactor with an (unknown) flow rate $Q_{G, inf}$. This infiltrated air does not only affect the outgoing gas flow rate of the SHARON reactor, thus being $Q_{G, inf} + Q_R^G$, but also affects the elemental mass balances (in kg) for O, C and N (denoted by superscript ‘X’) over the reactor:

\[
\begin{align*}
\sum Q_R^L(t) \cdot C_{L, in}^X &+ \sum Q_{G, inf} \cdot C_{G, inf}^X = \sum (Q_R^G + Q_{G, inf}) \cdot C_{G, 2}^X \\
&+ \sum Q_R^L(t) \cdot C_{L, in}^{RX} - \sum Q_R^L(t) \cdot C_L^X(t) + M_X^{Reaction} - \Delta M_X^{Acc}
\end{align*}
\]

Eq. (1) equals the sum of the net gaseous and liquid inflow of an element X and its net production during biological reactions $M_X^{Reaction}$, reduced with its accumulation $\Delta M_X^{Acc}$, to a gap $M_X^{Gap}$, which is ideally zero. The average infiltrated air flow rate ($Q_{G, inf}$) was calculated by closing the elemental oxygen balance, i.e. by fulfilling $M_O^{Gap} = 0$.

2.2. Monitoring campaign

2.2.1. Monitoring campaign

The liquid feed flow rate ($Q_R^L$), gas flow rates ($Q_{G, 1}, Q_{G, 2}$), reactor

Fig. 1. Layout of the Rotterdam sludge handling facility with indication of sampling points. $Q_L$: liquid flow rate, $Q_G$: gas flow rate.
temperature, pH and DO were logged every minute by a SCADA system. Liquid grab samples of the influent and effluent of the SHARON reactor were taken during daily and standard photometric cuvette tests (Hach-Lange). The influent was analysed for TNH (single measurement), the effluent was analysed for TNH (single measurement), total nitrite (TN02, single measurement) and nitrate concentrations (single measurement). The influent was assumed to contain a constant biodegradable COD value of 100 g BOD m⁻³, as confirmed by weekly BOD₃ measurements. The total Kjeldahl nitrogen concentration was not measured but was estimated as 105.3% of the influent TNH concentration, based on the findings of Hellinga et al. (1998). The inorganic carbon concentration was assumed to be present in an equimolar ratio to influent total ammonium concentration (TNH), which was verified by grab sampling and standard photometric cuvette test.

2.2.2. Dedicated gas phase analyses

The air emission from the sludge handling building (C_G1) and the SHARON off-gas (C_G2) were analysed on-line for CO₂, O₂, NO and N₂O through an Emerson MLT4 Rosemount FTIR analyser, preceded by a condenser (4 °C). The off-gas temperature was verified to be constant, at 30 °C, by daily measurements. The gas stripping method described by Mampaey et al. (2015) was applied during selected periods to monitor the dissolved N₂O concentration through a gas phase measurement. The three gas streams were sampled at a constant flow rate of 1 standard litre per minute (slm). The transport delay between the sampling point and gas analyser amounted to 45 s and was taken into account during data analysis.

2.2.3. N₂O emission and formation rate

The total N₂O emission (kg N) was calculated directly from the off-gas measurements (Eq. (2)) as

\[
N_2O = \sum \left( Q_{G}^R(t) + Q_{G,inf}^G \right) C_{G}^{N_2O}(t) \tag{2}
\]

The N₂O profile in the off-gas of the SHARON reactor (ppm) can be described by Eq. (3) (Mampaey et al., 2015):

\[
C_{G2}(t) = a_1^F + a_2^F \exp \left( - \left( a_3^F + D_G^F \right) t \right) - a_4^F \exp \left( - a_5^F t \right) \tag{3}
\]

This expression is valid during aerated as well as non-aerated periods, assuming a constant N₂O formation rate \( R^G \) (g N min⁻¹) during each period. The constant \( a_4^F \) is proportional to the N₂O formation rate \( R^G \), the second term is related to the interphase transfer rate in the reactor, the third term is related to headspace dilution (Mampaey et al., 2015). The parameter values \( a_i^F \) are determined by fitting Eq. (3) to the measured data by minimising the sum of squared residuals (\( \sum (y - y) \)) with the simplex algorithm (Nelder and Mead, 1965).

The aerobic N₂O formation rate \( R_G^G \) (g N min⁻¹) is calculated from the value of \( a_4^F \) through Eq. (4). The parameter \( f_c \) represents a conversion factor from ppm N₂O to g N m⁻³ and corrects for the removed water vapour resulting from the temperature decrease between the reactor off-gas and the condenser aeration gas and the from, which amounts to 1.3%, assuming saturation (42.46·10⁻³ bar at 30 °C and 8.13·10⁻³ bar at 4 °C, (Moran and Shapiro, 2002)).

\[
R_G^G = a_4^F Q_G^F f_c \tag{4}
\]

\[
f_c = \left( \frac{28 \text{ g N mol}^{-1} \cdot 101.325 \text{ Pa}}{10^6 \text{ ppm} \cdot 8.3145 \text{ m}^3 \cdot \text{Pa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \cdot 303 \text{ K} \cdot 0.987} \right) = 1.112 \cdot 10^{-3} \text{ g N m}^{-3} \text{ ppm}^{-1}
\]

The total aerobic N₂O formation is calculated by multiplying the formation rate \( R_G^G \) with the duration of the aeration period.

The value of \( a_5^F \) is the reactor headspace dilution rate, i.e.

\[
a_5^F = \frac{Q_G^R(t) + Q_G,inf}{V_G^F} \tag{5}
\]

The SHARON operating cycles start with aeration followed by a non-aerated period. However, the N₂O which accumulated during the non-aerated period is stripped in the subsequent aerobic period. Therefore, the cycles considered during data analysis start with the non-aerated period (of preceding operating cycle) followed by an aeration period. The average N₂O formation rate of the non-aerated periods, i.e., the average anoxic N₂O formation rate, was calculated from the difference between total N₂O emission (Eq. (2)) and the aerobic N₂O formation (Eq. (4)), assuming that the final liquid phase N₂O concentrations do not vary between cycles.

2.3. Estimating the interphase transfer rate in dynamic systems

Cyclic reactor operation, e.g. characterized by aerated and non-aerated periods, results in accumulation and subsequent stripping of gaseous components such as N₂O. As a result, the concentration dynamics of such gaseous components can be described by a double exponential profile (Eq. (3)). Given that the value \( a_5^F \) is proportional to the \( k_{La} \) (Eq. (6), Mampaey et al. (2015)), the reactor volumetric gas–liquid mass transfer rate coefficient of the corresponding component, e.g., \( k_{La} \) (in min⁻¹), can be estimated through Eq. (6) (Mampaey et al., 2015):

\[
k_{La} = \frac{a_4^F Q_G^G \cdot H^{N_2O}}{Q_G^G \cdot H^{N_2O} - a_5^F V_L} \tag{6}
\]

The volumetric gas–liquid mass transfer rate coefficient of another component X than the one for which the gaseous profile is measured, can be related to the one calculated by Eq. (6) through Eq. (7), which takes into account the diffusion coefficients of both components and is valid for low soluble components and a liquid interphase in turbulent motion (De heyder et al., 1997).

\[
k_{La} X = k_{La}^{N_2O} \sqrt{\frac{D_X}{D_{N_2O}}} \tag{7}
\]

3. Results

3.1. Elemental mass balances

A mass balance for oxygen was set up over the entire monitoring campaign considering the oxygen concentration in the aeration gas inflow and outflow, as well as the oxygen requirement for the biological conversion reactions, the accumulation of oxygen in the system and the outflow of dissolved oxygen (Supporting Information - Table S.1).

By closing the elemental O₂ balance, the (average and not measurable) infiltrated airflow rate (Q_G,inf, Fig. 1) was calculated as Q_G,inf = 910 m³ h⁻¹, which represents 24% of the off-gas flow rate on average. The value Q_G,inf = 910 m³ h⁻¹ was used in the mass balances for C and N.

From the oxygen present in the aeration air (Q_G,inf·C_O2), 14.6% was consumed by biological reactions. Given that the oxygen in- and outflow from the liquid phase as well as oxygen accumulation were negligible, the oxygen consumption equals the oxygen transferred to the liquid phase. In the elemental carbon mass balance (Supporting Information - Table S.2), the incoming C-species were CO₂.
in the aeration air, COD and inorganic carbon (CO$_2$, HCO$_3^-$, CO$_3^{2-}$) in the liquid feed flow. It was reasonably assumed that all inorganic carbon was stripped as CO$_2$, therefore, the liquid outflow of inorganic carbon was neglected (effluent pH was 6.5–6.7) and so was accumulation of inorganic carbon in the reactor. The CO$_2$ uptake by the AOB biomass was calculated stoichiometrically from the ammonium conversion (Henze et al., 2000). The gap in the C-balance was small (+1.5%). The overall nitrogen mass balance (Supporting Information - Table S.3) was set up based on the influent total Kjeldahl nitrogen concentration. Since the influent originates from an anaerobic digester (HRT 40 days) it was assumed that the influent did not contain nitrite or nitrate. Heterotrophic denitrification ($N_2$ formation) was neglected. The gap in the N-balance was small (−2.9%).

3.2. Standard operation cycles

First, the reactor dynamics and associated $N_2O$ formation were assessed during standard operation. A standard operation cycle is a cycle for which there is continuous liquid feeding during the preceding and current cycle and an DO set point of 2.0 g O$_2$ m$^{-3}$ is maintained during aeration. In total, 114 cycles are considered as standard operation, accounting for 228 h. The measurement data of a typical cycle are shown in Fig. 3.

On average, 52 (±7)% of the incoming TNH load was converted to nitrite, while the nitrate concentration remained below 10 g N m$^{-3}$ (data not shown), underlining the stable partial nitritation process in the reactor. The aeration flow rate of the SHARON reactor is controlled at a DO set point of 2.0 g O$_2$ m$^{-3}$, which was obtained 20 min after the aeration was turned on, with an overshoot up to 3.0 g O$_2$ m$^{-3}$ (Fig. 3E). During non-aeration, it took 6 min to utilise the residual DO. The pH (Fig. 3E) exhibited a cyclic profile, decreasing from 6.73 to 6.56 during aeration because of ammonium oxidation and increasing by the same amount during the non-aerated period through influent addition without ammonium conversion. Given that virtually all buffer (inorganic carbon) is stripped, small variations in ammonia conversion indeed provoke a measurable pH variation.

At the start of aeration, the measured $N_2O$ off-gas concentration increased, reaching a peak value after 8 min, after which the off-gas concentration decreased exponentially and levelled off to a constant value. The small (hardly noticeable) dip in the off-gas $N_2O$ profile at time 51 min was caused by opening one of the reactor lids for taking a liquid sample. Note that similar (more pronounced) effects were observed in the other gas phase profiles (NO, CO$_2$ and O$_2$).

The double exponential profile of Eq. (3) was fitted to the measured $N_2O$ off-gas profile during aeration, yielding Eq. (8) (in ppm$_e$).

\[
C_{G,2}(t) = 63.8 + 1.098.7\cdot \exp(-0.0415\cdot t) - 1.096\cdot \exp(-0.3203\cdot t)
\]  

(8)

During the non-aerated period, the SHARON off-gas NO$_2$ concentration decreased further due to dilution of the SHARON reactor headspace by infiltrated air.

The infiltrated air flow rate ($Q_{infl}$) was estimated from the value of $Q_R^G = 0.3203\text{min}^{-1}$ and Eq. (5) as 970 ± 115 m$^3$ h$^{-1}$, which is close to the value $Q_{infl} = 910$ m$^3$ h$^{-1}$ calculated from the oxygen mass balance.

The total gaseous $N_2O$ emission of the typical cycle (anoxic period and subsequent aeration) displayed in Fig. 3 amounted to 2201 g N, of which 2142 g N was emitted during aeration. The $N_2O$ emission during aeration resulted from two contributions. The first part concerns stripping of aerobically formed $N_2O$, the second part concerns stripping of $N_2O$ which had accumulated during the anoxic period, as depicted in Fig. 3A. The aerobic $N_2O$ formation rate was calculated through Eq. (4) and amounted to 4.89 g N min$^{-1}$ (Eq. (9)).

\[
R^G = a^G R:C_fe = 63.8 - 69.03\cdot 1.112\cdot 10^{-3} \text{ g N min}^{-1} = 4.89 \text{ g N min}^{-1}
\]

(9)

The total aerobic $N_2O$ formation over this cycle accounts for 376 g N of the emission. The difference, 2201–376 = 1825 g N, is attributed to anoxic $N_2O$ formation, stripped in the aerated phase, which yields an average anoxic $N_2O$ formation rate of 41.49 g N min$^{-1}$.

The same procedure was performed on all standard operation cycles to calculate the average aerobic and anoxic $N_2O$ formation (Table 1); 3.8% of the TNH load is emitted as $N_2O$ (Table 2).

The interphase transfer rate was estimated from the $N_2O$ profiles of the individual standard operation cycle through Eq. (6). An average $k_{H_{N2O}}$ value of 108 d$^{-1}$ for $N_2O$ was obtained, yielding a value of 127 d$^{-1}$ for O$_2$ through Eq. (7), given $D_{O_2} = 2.5\cdot 10^{-3}$ m$^2$ s$^{-1}$ and $D_{N_{2O}} = 1.8\cdot 10^{-3}$ m$^2$ s$^{-1}$ (Perry and Green, 1984).

The $N_2O$ profile in the SHARON off-gas (Fig. 3B) increased when aeration was turned on and levelled off at a constant value. When aeration was turned off, the CO$_2$ concentration decreased due to introduction of ambient air in the headspace.

The NO profile (Fig. 3C) showed a similar profile as the off-gas CO$_2$ profile, the NO increased to a constant value of 40 ppm during aeration and decreased during non-aerated periods. The off-gas NO profile (Fig. 3D) showed an inverse trend compared to the CO$_2$ and NO profile since it was transferred from the gas phase to the liquid phase; the off-gas concentration decreased during aeration and increased during non-aerated periods.

3.3. Experiments

3.3.1. Prolonged aeration experiment

The results of the prolonged aeration experiment are shown in Fig. 4. The experiment comprised 22.8 h of continuous aerobic conditions (DO set point = 2.0 g O$_2$ m$^{-3}$), which is equivalent with the duration of 11 cycles. Prior to the experiment, there was an anoxic period of 129 min due to a lack of influent flow. During this non-aerated period, one of the DO probes was cleaned and recalibrated, which is reflected in the DO profile prior to the experiment (Fig. 4). Over the experiment, the effluent nitrate concentration increased from 8 to 21 g N m$^{-3}$ (data not shown).

During aeration, the off-gas $N_2O$ concentration followed the double exponential profile of Eq. (3), which was fitted as Eq. (10). A constant value was attained after 120 min. The aerobic $N_2O$ formation rate was calculated as 6.2 g N min$^{-1}$, (Eq. (4)), from the constant term in Eq. (10).

\[
C_{G,2}(t) = 107.4 + 2.365\cdot \exp(-0.0254\cdot t) - 2.472\cdot \exp(-0.3868\cdot t)
\]

(10)

The $N_2O$ emission over the experiment amounted up to 13,825 g N (1.5% of the TNH load, Table 2), the part of the emission caused by aerobic $N_2O$ formation was 8514 g N. From the difference, the average anoxic $N_2O$ formation rate was calculated as 41.22 g N min$^{-1}$.

Off-gas O$_2$, CO$_2$ and NO profiles follow similar trends as during the standard operation cycles. Note that the pre-programmed control algorithms caused a peak in the airflow every 2 h, which also caused noticeable peaks in the DO and in the gas phase NO concentration. Overall, the NO increased over the prolonged...
Fig. 3. Measurement results from a typical cycle under standard operation conditions. A. Off-gas N2O profile, data fit (Eq. 3) during aeration is shown by solid red line, data fit during non-aeration is shown by cyan dash-dotted line. Estimated aerobic N2O formation shown by green dotted line. B. Off-gas CO2 profile, data fit during aeration is shown by solid red line, data fit during non-aeration is shown by cyan dash-dotted line. C. Off-gas NO profile. D. Off-gas O2 profile. E. SHARON reactor DO and pH. F. SHARON reactor aeration flow rate and liquid feeding rate. The aeration on and off switch are shown by a dashed magenta and solid black line respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

<table>
<thead>
<tr>
<th>Condition</th>
<th>Emission Total</th>
<th>Total formation</th>
<th>Formation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic conditions</td>
<td>2698 ± 1051 g N (97.1 ± 0.5%)</td>
<td>865 ± 287 g N (34 ± 15%)</td>
<td>11.1 ± 3.8 g N.min⁻¹</td>
</tr>
<tr>
<td>Anoxic conditions</td>
<td>82 ± 39 g N (2.9 ± 0.5%)</td>
<td>1915 ± 1009 g N (66 ± 15%)</td>
<td>44.1 ± 17.3 g N.min⁻¹</td>
</tr>
</tbody>
</table>
### Table 2

<table>
<thead>
<tr>
<th>Reference</th>
<th>N-load [kg TNH d⁻¹]</th>
<th>N₂O emission factor [–]</th>
<th>Aerobic N₂O formation rate [g N.min⁻¹]</th>
<th>Anoxic N₂O formation rate [g N.min⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study partial nitritation reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average over monitoring campaign</td>
<td>755 kg TNH d⁻¹</td>
<td>3.7%</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>Standard operation cycles (DO = 2 g O₂ m⁻³)</td>
<td>894 kg TNH d⁻¹</td>
<td>3.8%</td>
<td>11.1 ± 3.8</td>
<td>44.1 ± 17.3</td>
</tr>
<tr>
<td>Short cycles</td>
<td>1193 kg TNH d⁻¹</td>
<td>1.8%</td>
<td>14.0 ± 0.8</td>
<td>22.1 ± 4.7</td>
</tr>
<tr>
<td>Prolonged aeration</td>
<td>965 kg TNH d⁻¹</td>
<td>1.5%</td>
<td>6.2</td>
<td>41.2</td>
</tr>
<tr>
<td>Lowered DO set point (DO = 1 g O₂ m⁻³)</td>
<td>914 kg TNH d⁻¹</td>
<td>3.9%</td>
<td>14.7</td>
<td>31.5</td>
</tr>
<tr>
<td>DO = 0.6 g O₂ m⁻³</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stand-alone (partial) nitritation reactor</td>
<td>323 kg TNH d⁻¹</td>
<td>18.5%</td>
<td>27.4</td>
<td>84.0</td>
</tr>
<tr>
<td>Kampeschreur et al. (2008a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DO = 2.5 g O₂ m⁻³</td>
<td>980 kg TNH d⁻¹</td>
<td>1.7%</td>
<td>6.4</td>
<td>27.9</td>
</tr>
<tr>
<td>Desloover et al. (2011)</td>
<td>DO = 1 g O₂ m⁻³</td>
<td>427–521 kg TKN d⁻¹</td>
<td>5.1–6.6%</td>
<td>N.A.</td>
</tr>
<tr>
<td>Gustavsson and Jansen (2011)</td>
<td></td>
<td></td>
<td>3.8%</td>
<td>N.A.</td>
</tr>
<tr>
<td>Pijuan et al. (2014) (pilot nitritation reactor)</td>
<td>128 g TNH d⁻¹</td>
<td>2.2–19.3%</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>1 Stage partial nitritation – anammox reactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Joss et al. (2009)</td>
<td>625 kg TNH d⁻¹</td>
<td>0.4–0.6%</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>Weissenbacher et al. (2010)</td>
<td>DO = 0.3 g O₂ m⁻³</td>
<td>290 kg TKN d⁻¹</td>
<td>1.3%</td>
<td>N.A.</td>
</tr>
<tr>
<td>Castro-Barros et al. (2015)</td>
<td>1053 kg TNH d⁻¹</td>
<td>2%</td>
<td>11.7–21.7</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

**Fig. 4.** Measurement results from a prolonged aeration experiment. A. Off-gas N₂O profile, data fit during aeration is shown by solid red line, data fit during non-aeration is shown by cyan dash-dotted line. Estimated aeration N₂O formation shown by green dotted line. B. Off-gas CO₂, NO and O₂ profile. C. SHARON reactor DO and pH. D. SHARON reactor aeration flow rate and liquid feeding rate. The aeration on and off switch are shown by a dashed magenta and solid black line respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
The aerobic formation rate was calculated as 27.4 g N m^{-3} attributed to aerobic N2O formation, based on Eq. (12). The dissolved N2O concentration decreased from 2.85 g N m^{-3} during the prolonged aeration, the dissolved N2O concentration decreased by 1.4 g N m^{-3} due to stripping of dissolved N2O.

3.3.3. Lowered DO experiments

During the short cycles experiment, the NO off-gas concentration during the aerobic phases gradually increased over the experiment, similar as during the prolonged aeration experiment (Fig. 5). The DO set point was reached 17 min after start of aeration, after an initial overshoot up to 3 g O2·m^{-3}, which is similar as under standard operation conditions.

4. Discussion

4.1. Estimating $k_La$ in dynamic systems

Aeration energy makes up a large fraction of the energy consumption of wastewater treatment plants. Significant energy savings can be obtained when the interphase transfer efficiency, $k_La$, is monitored (Leu et al., 2009). In this contribution, it will be demonstrated how the measured off-gas profile of a component, in this case N2O, from a dynamically aerated reactor can be used to estimate its volumetric gas–liquid mass transfer coefficient ($k_La^{N_2O}$). The $k_La$ for other gases can be related to the one for the measured gas phase component through their diffusion coefficients (Eq. (7)).

The cyclic operation of the SHARON reactor in this study results in accumulation of N2O during anoxic periods and stripping of N2O during aeration. During aeration, the dynamic off-gas N2O concentration profile can be described by a double exponential profile (Eq. (3)). The $k_La^{N_2O}$ is calculated from the estimated value of $a_T^0$ via Eq. (6) (Mampaey et al., 2015), which can then be related to the oxygen transfer rate $k_La^{O_2}$. In case the $k_La$ value is not required as such but the profile in time is, e.g. to detect fouling, the profile of $a_T^0$ can be monitored instead. The accuracy of the $k_La$ estimation increases with increasing aeration duration as more data are available to fit Eq. (3).

The most commonly applied method for oxygen transfer testing is the off-gas method (ASCE, 1997; Redmon et al., 1983). In case the dissolved oxygen profile is measured as well, the oxygen transfer rate $k_La^{O_2}$ can be estimated from a data fit to the DO profile, while the oxygen saturation concentration $C_T^{sat}$ is either taken from literature or estimated simultaneously. Both parameters $C_T^{sat}$ and $k_La$ are correlated (Boyle et al., 1974), so the value of $C_T^{sat}$ influences the $k_La$ estimation. As for the required measurement duration for the off-gas method, Boyle et al. (1974) applied durations until the DO reached a value of 70 or 90% of $C_T^{sat}$ to adequately capture the DO profile, which is 1 or 2 times the time constant (τ) related to the interphase transfer. They also assessed the impact of the uncertainty in estimating $C_T^{sat}$ on the $k_La$ estimation and concluded that tests longer than twice τ do not improve the precision of the $k_La$ estimation. Stenstrom et al. (2006) advocated for durations up to 6 times the time constant to yield an accurate estimation of the DO saturation concentration ($C_T^{sat}$).

In the dynamic reactor $k_La$ estimation method presented in this study, the $k_La$ (for N2O) is measured online, during standard dynamic operation. The requirement of a sufficient aeration period, be it 2 or 6 times the time constant, does not constitute a disadvantage since it is part of normal reactor operation. The time constant of the SHARON reactor amounts to $\tau = \frac{1}{\alpha \cdot \beta \cdot \delta} = 23$ min (Mampaey et al., 2015). During standard operation, the aeration length was about 4 times the time constant; under the shortened cycles experiments it was still twice as long.

Another advantage of the dynamic reactor $k_La$ estimation method is, that it does not require any dissolved concentration profile. This feature is particularly useful for the $k_La$ measurement of gases for which no dissolved probe is available, e.g. methane. For instance, the CH4 measurement data presented by Pijuan et al. (2014) adequately capture the double exponential profile.
expressing accumulation and stripping associated with periodic aeration and would be suitable for estimating the $k_1\text{eff}^{\text{aer}}$.

4.2. $N_2O$ emission from a full-scale partial nitritation reactor

The $N_2O$ emission factors (EF) over the entire measurement campaign and for the different experiments are summarized in Table 2. The validity of the data measured in this study is supported by the closed (<5%) elemental balances of O, as well as C and N, which are interconnected.

The average EF was 3.7% of the TNH-load, of which 34% is attributed to aerobic $N_2O$ formation while 66% is attributed to anoxic $N_2O$ formation (Table 1), even though the anoxic period makes up a smaller fraction of the time (64% versus 36%, respectively). This corresponds to an aerobic and anoxic $N_2O$ formation of 1.2% and 2.5%, respectively, expressed in g $N_2O-N$ formed per g TNH-N influent load. The EF of 3.7% measured in this study is higher than the 1.7% measured by Kampschreur et al. (2008a) on the same reactor. We analysed the data of Kampschreur et al. (2008a) for the contribution of aerobic and anoxic $N_2O$ formation according to the method applied in this study (Supporting Information Figure S.4).

Of the total $N_2O$ emission reported by Kampschreur et al. (2008a), 41% was attributed to aerobic $N_2O$ formation while 59% was attributed to anoxic $N_2O$ formation, the aerobic period making up 71% of the cycle duration while this was 64% in this study. The resulting aerobic and anoxic $N_2O$ formation were quantified as 0.7% and 1%, respectively, expressing in g $N_2O-N$ formed per g TNH-N influent load, respectively. It is clear that the aerobic formation expressed per influent load is almost the same for both studies on the same reactor, while the anoxic formation differs.

---

**Fig. 5.** Measurement results from a prolonged non-aerated period. A. Off-gas $N_2O$ profile, data fit during aeration is shown by solid red line, data fit during non-aeration is shown by cyan dash-dotted line. Estimated aerobic $N_2O$ formation shown by green dotted line. B. Off-gas CO$_2$, NO and O$_2$ profile. C. Gas stripping device gas phase $N_2O$ concentration and corresponding liquid phase $N_2O$ concentration. D. SHARON reactor DO and pH. E. SHARON reactor aerator flow rate and liquid feeding rate. The aeration on and off switch are shown by a dashed magenta and solid black line respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
The overall EF of 3.7% measured in this study lies in the range of reported values of other full-scale partial-nitrification reactors. The EF of systems for which the partial nitration and anammox reactions take place in two separate reactors (two-stage partial nitritation - anammox systems) is typically higher than their one-stage alternatives (Table 2), even though more long-term measurement data are required to fully validate this. The higher N2O EF for stand-alone partial nitritation reactors (in two-stage systems) compared to single-stage partial nitritation-anammox systems is related to the prevailing concentrations of ammonia and nitrite, being higher than in single-stage partial nitritation-anammox reactors. The anammox bacteria as such does not produce N2O (Kartal et al., 2011). But independent of the configuration, be it one-stage or two-stage, it is clear that the operation mode accounts for variations in the EF.

Concerning stand-alone partial nitritation reactors, Desloover et al. (2011) reported an N2O EF of 5.1–6.6% under standard operation of a partial nitritation sequencing batch reactor (SBR), operated at a low DO setpoint (0.75 g O2 m−3) and a short SRT of 1.7 d. The EF increased to up to 9% after a period of non-feeding, combined with non-aeration, indicating an increased N2O formation under anoxic conditions, similar to our observations. Note that the nitrite concentration in both systems was relatively high: about 115 ± 25 g N m−3 (Desloover et al., 2011) and 66 ± 98 g N m−3 (this study). Pijuan et al. (2014) monitored a pilot-scale airlift nitritation reactor with pH control (at 7.5 ± 0.2), enabling 92% ammonium conversion to nitrite (reactor nitrite concentration: 580 g N m−3); they observed an increased N2O EF at decreasing DO concentrations: from an EF of 2.2% at high DO concentrations (4.5–7.5 g O2 m−3) to 6.1% at a DO of 1.1 g O2 m−3. Changing to SBR operation, a peak in off-gas N2O concentration was observed after the settling period resulting in a high EF of 19.3%. It is clear that in these stand-alone (partial) nitritation reactors, in which high nitrite concentrations prevail, anoxic periods or a low DO promote N2O formation, contributing to the high EF.

As for single-stage partial nitritation-anammox systems, Joss et al. (2009) measured an EF of 0.4 and 0.6% in a suspended growth SBR, for a continuous and intermittent aeration period, respectively. Weissenbacher et al. (2010) measured a relative low EF of 1.3%, considering the low DO concentration of 0.3 g O2 m−3. Castro-Barros et al. (2015) found a higher N2O emission and formation for a single-stage partial nitritation-anammox reactor when increasing the aeration intensity (mean N2O EF = 2%; EF during high aeration intensity = 2.5%; EF during low aeration intensity = 1%). This observation contrasts with the higher N2O emission for lower DO concentration reported on a single-stage nitritation reactor by Pijuan et al. (2014).

4.3. N2O formation mechanisms

The cyclic aerobic-anoxic reactor operation resulted in a typical off-gas N2O profile observed during aerated periods, consisting of a peak emission at the start of aeration and a subsequent decrease, related to dissolved N2O accumulation and stripping (Fig. 3). By fitting a dynamic double exponential profile (Eq. (3), Mampaey et al. (2015)) to the experimental data, a distinction could be made between aerobically and anoxicly formed N2O. In this analysis, the aerobic N2O formation rate was assumed constant a priori, as calculated by Eq. (4). This assumption was validated by the prolonged aeration experiment, during which the N2O off-gas concentration, clearly reached the constant value (Fig. 4; Eq. (11), \( \Delta \alpha = 107.4 \) ppm) - the length of the aeration period during standard operation cycles being insufficient for this purpose. Dissolved N2O measurements with a gas stripping device (Mampaey et al., 2015) confirmed the N2O formation under anoxic conditions. The peak in N2O formation upon turning on aeration being due to anoxic N2O formation contrasts with the attribution of increased N2O emissions upon transition from anoxic to aerobic conditions to an instantaneous increase in the N2O formation rate by a pure culture AOB in a lab-scale setup (Yu et al., 2010).

Anoxic conditions increasing the N2O EF was also observed by Kampschreur et al. (2008a), Desloover et al. (2011), Gustavsson and Jansen (2011), Joss et al. (2009), Weissenbacher et al. (2010). The most striking measurement was an increase in EF of Pijuan et al. (2014) from 2.2% to 19.3% by switching from continuous to SBR operation. The off-gas profile in the latter study suggests stripping of accumulated N2O after the settling period, which seems to imply that the increased N2O emission can be traced back to the settling period. Even though the, the bulk DO concentration was still higher than 2 g O2 m−3 during the settling period, anoxic conditions are expected to occur inside the granule. Furthermore, Gustavsson and Jansen (2011) measured an EF of 3.8% from a partial nitritation SBR; the N2O emission was positively correlated to anoxic period, indicating an increased N2O formation rate under anoxic conditions compared to aerobic conditions.

The N2O formation during the non-aerated periods observed in this study could be explained by several mechanisms. Heterotrophic denitrification on the NOx amount of organics can be present in the influent and resulting from biomass decay constitutes a first possibility, given that the reactor is characterized by high nitrite concentrations (about 661 g N m−3). The presence of nitrite indeed promotes N2O emission for heterotrophic denitrification (Vonschulthess et al., 1994). During the non-aerated period, both the pH and the dissolved N2O concentration increased. The pH increase can be attributed to the alkalinity present in the influent and (biological) reactions, as a pH increase was measured during a non-aerated period without influent feeding (Fig. 5D). Complete utilization of the influent BOD concentration (100 g COD m−3) for heterotrophic denitrification of nitrite to N2O would lead to an EF of 3.1% at most, given that 2.48 g COD is required per N (Hiatt and Grady, 2008). However, reasonably assuming that 36% of the BOD is used for denitrification, since the anoxic conditions only account for 36% of the time, yields an upper limit on the EF of 1.1%. To obtain the measured EF of 2.6% would require an additional amount of 50 g COD m−3 available for denitrification, which is highly unlikely to originate from decay during anoxic conditions only. Furthermore, the possible amount of N2 formation is small, since the N mass balance is closed. As a result heterotrophic denitrification is most likely not the only contributor to the N2O anammox formation. One could think of accumulated NH2OH remaining in the anoxic phase as a trigger for subsequent N2O formation by nitrifier denitrification (Zheng et al., 1994; Goreau et al., 1980; Kampschreur et al., 2008b) or oxidation of NH2OH with nitrite (Law et al., 2013).

The short cycles had a lower overall N2O EF than the standard operation cycles. This corresponds with the observation that N2O is mainly formed during anoxic periods, given that the, the overall anoxic period is slightly shorter due to DO presence after the aeration is turned off. The aerobic formation rate was higher for the short cycle operation than for standard cycles (14.0 vs. 11.1 g N min−1, respectively, see Table 2). This is attributed to more frequent changes from anoxic to aerobic conditions, stimulating N2O formation (Yu et al., 2010). The extent of this effect is however masked in the observations by the high contribution of stripping of N2O which has accumulated under anoxic conditions. Note also that care should be taken in the interpretation of the aerobic formation rate, as the aerobic N2O formation rate could be overestimated due to truncated data (Boyle et al., 1974). However, an accurate estimation of the aerobic N2O formation rate through Eq. (3) is assumed. A disadvantage of the increased aerobic period is the formation of nitrate, of which the concentration had increased
to 15 g N m\(^{-3}\). The pH during the short cycle operation was indeed observed lower than during standard operation, which could be the result of a slightly increased ammonium conversion combined with a lower N\(_2\)O EF, given that the buffer capacity of the system was depleted. During anoxic conditions, the liquid N\(_2\)O concentration increases in a more than linear way (Fig. 5C), indicating an increased anoxic N\(_2\)O formation rate with increasing length of the anoxic period. Pijuan et al. (2014) also reported an increased N\(_2\)O emission after the settling (anoxic) period.

The lowered DO experiments resulted in an increased aerobic N\(_2\)O formation rate and EF due to the nitritation emission after the settling (anoxic) period. Increased anoxic N\(_2\)O formation rate with increasing length of the anoxic period, which was also reported by Pijuan et al. (2014). The authors express their gratitude towards the staff of treatment plant ‘Sluisjesdijk’, Waterschap Hollandsche Delta.

### 5. Conclusions

- The N\(_2\)O off-gas profile of an intermittently aerated reactor could be used to monitor its interphase transfer dynamics and to estimate the corresponding rate \(k_4\) [\(\text{mol N\(_2\)O m}^{-3}\text{ DO day}^{-1}\)] (Ahn et al., 2010).
- The N\(_2\)O emissions during cyclic reactor operation can be traced back to aerobic and anoxic formation when fitted to a dynamic profile relying on a mass balance approach; online off-gas monitoring was applied to measure the dissolved N\(_2\)O reactor concentration.
- N\(_2\)O emissions from a full-scale suspended sludge partial nitritation reactor amount to 3.7% of the N-load. The anoxic N\(_2\)O formation was responsible for 66% of the N\(_2\)O emission, even though the anoxic period only accounts for 36% of the time.
- The N\(_2\)O formation rate was constant during aerobic periods and increased during anoxic periods, resulting in a higher mean anoxic N\(_2\)O formation rate for longer anoxic periods.

### Acknowledgements

The authors express their gratitude towards the staff of treatment plant ‘Sluisjesdijk’, Waterschap Hollandsche Delta.

### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2015.10.047.

### References


Leu, S.-Y., Rosso, D., Larson, L.E., Stenstrom, M.K., 2009. Real-time aeration efficiency monitoring in the activated sludge process and methods to reduce energy...
Novel method for online monitoring of dissolved N2O concentrations through a
application of the SHARON process for treatment of rejection water of digested
7 (4), 308–313.
New York.
of process parameters and operational mode on nitrous oxide emissions from a
nitritation reactor treating reject wastewater. Water Res. 49 (0), 23–33.
in mixed liquor using off-gas techniques. J. (Water Pollut. Control Fed. 55 (11),
1338–1347.
Ritchie, G.A.F., Nicholas, D.J., 1972. Identification of sources of nitrous-oxide pro-
duced by oxidative and reductive processes IN nitrosomonas-EUROPAEA. Bio-
chem. J. 126 (5), 1181.
Minimizing N2O emissions and carbon footprint on a full-scale activated sludge
sequencing batch reactor. Water Res. 71 (0), 1–10.
Stenstrom, M.K., Leu, S.-Y., Jiang, P., 2006. Theory to practice: oxygen transfer and
removal from concentrated waste streams with the anaerobic ammonium
oxidation (anammox) process in different reactor configurations. Water Res. 31
(8), 1953–1962.
van Dongen, U., Jetten, M.S.M., van Loosdrecht, M.C.M., 2001. The SHARON-
Technol. 44 (1), 153–160.
van Loosdrecht, M.C.M., Salem, S., 2006. Biological treatment of sludge digester
Vonschulthess, R., Wild, D., Gujer, W., 1994. Nitric and nitrous oxides from deni-
(6), 123–132.
nitrogen and carbon emissions from a full-scale deammonification plant. Water
Environ. Res. 82 (2), 169–175.
and specific directionality of autotrophic nitrous oxide and nitric oxide gener-