Modeling of N_2O Emissions in a Full-Scale Activated Sludge Sequencing Batch Reactor

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Abstract. Nitrous oxide (N_2O) is a greenhouse gas with a significant global warming potential. A dynamic model was developed to estimate the N_2O production and emission in a full-scale sequencing batch reactor (SBR) municipal wastewater treatment plant (WWTP). Based on the Activated Sludge Model 1 (ASM1), the model considered all known biological and abiotic N_2O production pathways along with the application of a 'stripping effectivity' (SE) coefficient for reflecting the non-ideality of the stripping model. N_2O data of two different cycles (types B and C) were used for the model calibration. Cycle B involved the alternation amongst aerated and non-aerated phases, whereas cycle C included a unique long aerobic phase. Optimizing the dissolved oxygen (DO) and SE parameters for both cycles provided a good fit of the model (DO = 1.6 mg L^{-1} and SE = 0.11 for cycle B, and DO = 1.66 mg L^{-1} and SE = 0.11 for cycle C). In both cases, N_2O emission peaks were related to high nitrite concentration in the liquid phase. Nitrifier denitrification was identified as the predominant biological pathway for N_2O generation. Although SBR operation occurred at similar DO and SE values for both cycles, the emission factor was significantly different; 0.8% for cycle B and 1.5% for cycle C, indicating the impact of cycle configuration on the N_2O emission. Thus, optimized SBR operation is essential in order to achieve a low overall carbon footprint through the avoidance of high N_2O emissions and energy requirements.

Keywords: N_2O emissions · Sequencing batch reactor · Full-scale modeling

1 Introduction

Nitrous oxide (N_2O) is a greenhouse gas (GHG) with a global warming potential 265 times higher than carbon dioxide in a 100-year period (IPCC 2013). During wastewater treatment, N_2O production and emission is mostly observed during the biological nutrient removal (Pan et al. 2016). With such a significant greenhouse effect, the development of mathematical models estimating N_2O dynamics emerges as an effective way to study the effect of operational conditions to decrease the carbon footprint in WWTPs. The implementation of these models will enable the establishment of mitigation strategies and, subsequently, optimal plant design and process control (Mannina et al. 2016; Pocquet et al. 2016; Massara et al. in press).

Three different biological pathways have been suggested for N_2O production during the biological nitrogen (N) removal in wastewater treatment plants (WWTPs): nitrifier denitrification, incomplete hydroxylamine (NH_2OH) oxidation and heterotrophic denitrification. The first two occur through the activity of Ammonia Oxidizing

Table 1 List of the 20 processes considered in our ASM-type model for 4-step nitrification-denitrification combined with a 2-pathway model for N_2O production by AOB and two abiotic processes.

Process Number	Process	
1	Hydrolysis	Aerobic Hydrolysis
2		Anoxic Hydrolysis ($NO_3^- \rightarrow NO_2^-$)
3		Anoxic Hydrolysis ($NO_2^- \rightarrow N_2$)
4		Anaerobic Hydrolysis
5	Heterotrophic organisms	Aerobic Growth on Ss
6		Anoxic Growth of Heterotrophs on Ss ($NO_3^- \rightarrow NO_2^-$)
7		Anoxic Growth of Heterotrophs on Ss ($NO_2^- \rightarrow NO$)
8		Anoxic Growth of Heterotrophs on Ss ($NO \rightarrow N_2O$)
9		Anoxic Growth of Heterotrophs on Ss ($N_2O \rightarrow N_2$)
10		Lysis
11	Nitrifying organisms	NH_3 oxidation to NH_2OH with oxygen consumption
12		NH_2OH oxidation to NO coupled with oxygen reduction (AOB growth here)
13		NO oxidation to NO_2^- coupled with oxygen reduction
14		NO reduction to N_2O coupled with the NH_2OH oxidation to NO_2^- (N_2O from NH_2OH oxidation pathway)
15		HNO_2 reduction to N_2O coupled with NH_2OH oxidation to NO_2^- (N_2O from nitrifier denitrification pathway)
16		Aerobic Growth of NOB
17		Lysis of AOB
18		Lysis of NOB
19	Abiotic N_2O production	NH_2OH decomposition to N_2O
20		N-nitrosation of NH_2OH (HNO_2 as nitrosating agent)

Bacteria (AOB) (Wunderlin et al. 2012). It is common practice to apply the IWA Activated Sludge Models (ASM) (Henze et al. 2000) for the description of biological chemical oxygen demand (COD) and nutrient removal in WWTPs. However, the original ASM models take no account of the N_2O production and quantification. Hence, the aims of this work were: (i) to create an ASM-type model integrating the N_2O dynamics for a full-scale municipal sequencing batch reactor (SBR) plant, and (ii) calibrate the developed model with real N_2O emission data from the previous relevant study of Rodriguez-Caballero et al. (2015) (Table 1).

2 Materials and Methods

The model presented in this paper was based on the ASM1 (Henze et al. 2000) and was modified to include phosphate consumption by nitrifiers and heterotrophs. Afterwards, it was coupled with the two-pathway model of Pocquet et al. (2016) for N_2O production by AOB. Moreover, the heterotrophic denitrification steps were imported from Hiatt and Grady (2008). Furthermore, recent studies have revealed that abiotic N_2O production pathways can have a non-negligible contribution to the emissions during wastewater treatment (Harper et al. 2015; Soler-Jofra et al. 2016). For that reason, abiotic N_2O production (i.e. NH_2OH decomposition to N_2O, and N-nitrosation of NH_2OH with nitrous acid as nitrosating agent) (Domingo-Félez and Smets 2016) was also considered. Thus, the final model incorporated all the currently known pathways for N_2O production.

The kinetic model was developed in MATLAB and implemented for an existing full-scale SBR performing COD and N removal in the municipal WWTP of La Roca del Valles (Barcelona, Spain) (48,000 population equivalents). Rodriguez-Caballero et al. (2015) examined different operational cycles to evaluate the effects on N_2O production. They continuously monitored both gaseous and dissolved N_2O using a gas analyzer and a microsensor, respectively, for 33 days between February and March 2014 corresponding to a total number of 143 cycles. Those measurements served for the calibration of the model presented in the current study.

Two different cycle types (type B and C) applied by Rodriguez-Caballero et al. (2015) for the same influent are presented in this abstract. They both began with a 10-min lag phase during which the mixed liquor was stirred before feeding started. Cycle B involved the alternation amongst two aerated (13–40 min) and two non-aerated phases ($\sim$25 min). The reaction phase for Cycle C included the sequence of two shorter non-aerated phases ($\sim$25 min) with a long aerated one (66 min) between them. Feeding was continuous. Details on the operational parameters and influent characteristics used in this work can be found in Rodriguez-Caballero et al. (2015).

N_2O stripping was modeled by using the dissolved N_2O concentration and the volumetric mass transfer coefficient (k_La) for N_2O. We also included a 'stripping effectivity' (SE) coefficient expressing the non-ideality of this typical simplified model.

3   Results and Discussion

The total N_2O emission (in g $N-N_2O$ d^{-1}) for a cycle was an additional simulated variable. The evolution of this variable in time was used for calculating the instantaneous N_2O emission. The results are given in Figs. 1 and 2 for cycle B and cycle C, respectively.
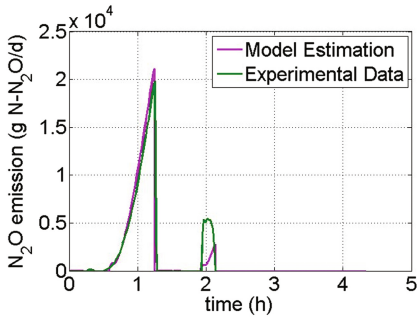

Fig. 1. *Optimized Cycle type B:* The N_2O instantaneous emission estimated by the model compared to the experimental data. Optimized DO setpoint during the aerated phases = 1.6 mg L^{-1}.
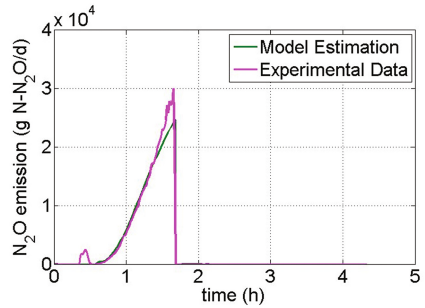
Fig. 2. *Optimized Cycle type C:* The N_2O instantaneous emission estimated by the model compared to the experimental data. Optimized DO setpoint during the aerated phases = 1.66 mg L^{-1}.

N_2O emissions are expected to be negligible in the non-aerated phases due to the negligible stripping (Ahn et al. 2010). In accordance with this idea, both the experimental data and our model linked the emissions with air flow or, equivalently, with the aerated phases. Within the attempt to calibrate the model, the SE parameter was firstly evaluated. For both cycle types, a rather satisfactory fitting to the experimental N_2O emission occurred under the same k_La modelling approach and SE value. It was noted that a SE equal to 0.11 contributed to a quite successful description of the experimental data in both cases, thus suggesting a clear influence of the stripping modeling on the final results.

According to the Global Water Research Coalition, the nitrification-related microbial routes (i.e. the two AOB pathways) are considered as major hotspots for N_2O emissions in full-scale domestic WWTPs (GWRC et al. 2011). During nitrification, insufficient aeration has an inhibitory effect (Kampschreur et al. 2009), and can therefore lead to increased emissions through the AOB pathways. After the SE study, we explored the DO setpoint during the aerobic phases of each cycle as an important operational parameter. The results after the DO setpoint and SE optimization for cycles B and C are shown in Figs. 1 and 2, respectively. First, it can be seen that the simulation results are fitted well on the experimental ones. However, this version of the model with default kinetic parameters was unable to precisely capture the emission peak at the beginning of the 2nd aerated phase of Cycle B (Fig. 1); especially the part of
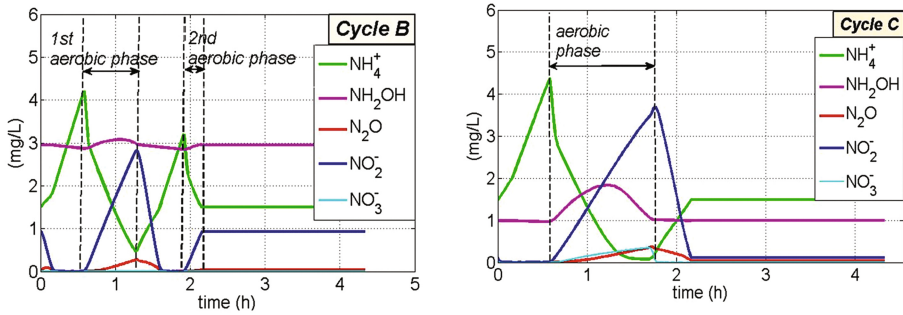
Fig. 3. *Optimized Cycles type B & C:* The evolution of the NH_4^+, NH_2OH, N_2O, NO_2^- and NO_3^- concentrations.

the emissions noted at the very beginning of the peak. It can be hypothesized that these emissions were rapidly recorded as a result of the stripping of the N_2O produced during the previous anoxic phase. This effect could be related to a N_2O denitrification rate during the anoxic phase lower than the value predicted by the model, which could lead to a higher final N_2O concentration at the end of the anoxic phase that would be stripped at the beginning of the aerobic phase. This divergence was not observed in cycle C because in this case only one aerobic phase existed. Specific experiments to evaluate N_2O denitrification rate would help to improve the model fitting. Secondly, we received the following output of the optimization process: optimal DO = 1.6 mg L^{-1} and SE = 0.11 (cycle B), optimal DO = 1.66 mg L^{-1} and SE = 0.11 (cycle C). Both cycle types were applied for the same influent. The optimal fit occurred at similar DO setpoint and SE. However, the emission factor differed significantly, being 0.8% for cycle B and 1.5% for cycle C. This is probably attributed to the long aerated phase of cycle C which can be connected with the higher N_2O emissions. As shown in Fig. 3 for both cycles, the N_2O concentration peaks coincided with the nitrite (NO_2^-) peaks in the liquid phase. This was observed for both the long aerobic phase of cycle C as well as for the 1st aerobic phase of cycle B; as mentioned above, the 2nd aerobic phase of cycle B was less successfully depicted in our simulations. Consequently, it can be deduced that nitrifier denitrification was the predominant AOB pathway for N_2O generation. The optimal fit was obtained for a rather low DO setpoint (1.6 mg L^{-1} for cycle B and 1.66 mg L^{-1} for cycle C). This observation is in agreement with past studies regarding the AOB pathways relative contribution; compared to incomplete NH_2OH oxidation, nitrifier denitrification has been suggested as increasingly contributing with the DO decrease (Anderson et al. 1993; Sutka et al. 2006; Kampschreur et al. 2008).

4   Conclusions

It can be concluded that the cycle configuration influences the emission magnitude. Long aerobic phases can increase the plant's carbon footprint due to the following: (i) higher energy requirements, (ii) higher N_2O production through the

nitrification-related pathways, and (iii) subsequent N$_2$O emission because of stripping. In this frame, process optimization is important. Optimal SBR operation includes the application of an optimal DO setpoint during aerobic phases of medium length. Under optimized SBR operation, satisfying nitrification along with moderate N$_2$O emissions and reasonable energy requirements are more likely to be achieved. In that sense, the implementation of cycles with multiple (shorter) aerated phases (e.g. cycle B in this work) instead of cycle configurations with few and relatively long aeration periods (e.g. cycle C in this work) seems more suitable.

This work will hopefully constitute a flexible model for the prediction and mitigation of N$_2$O emissions in full-scale SBR WWTPs with the added value of easily adapting to different cycle types.

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