Can modelling of GHGs be used to improve the process performance in WWTPs?

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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, careful cycle configuration design is essential to optimize the SBR operation and achieve a low overall carbon footprint through the avoidance of high N_2O emissions and energy requirements.

Keywords: greenhouse gases, biological nutrient removal, wastewater treatment plants, global warming potential, nitrous oxide, carbon footprint

Nomenclature	
AOB	Ammonia Oxidizing Bacteria
ASM1	Activated Sludge Model 1
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
SBR	Sequencing Batch Reactor
SE	Stripping Effectivity
WWTP	Wastewater Treatment Plant

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 [1]. During wastewater treatment, N_2O production and emission is mostly observed during the biological nutrient removal [2]. 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 [3-5].

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 Bacteria (AOB) [6]. It is common practice to apply the IWA Activated Sludge Models (ASM) [7] 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. [8].

2. Materials and Methods

The model presented in this paper was based on the ASM1 [7] and was modified to include phosphate consumption by nitrifiers and heterotrophs. Afterwards, N_2O production by AOB was considered based on the assumptions by Pocquet et al. [4]. Moreover, the heterotrophic denitrification contribution to the N_2O production was based on the conclusions by Hiatt and Grady [9]. Furthermore, recent studies have revealed that abiotic N_2O production pathways can have a non-negligible contribution to the emissions during wastewater treatment [10-11]. 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) [12] 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. [8] 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. [8] for the same influent are presented in the current work. 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 (13-40min) and two non-aerated phases (~25min). The reaction phase for Cycle C included the sequence of two shorter non-aerated phases (~25min) with a long aerated one (66min) between them. Feeding was continuous. 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 $N\text{-}N_2O$ 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 Fig. 1 and 2 for cycle B and cycle C, respectively.

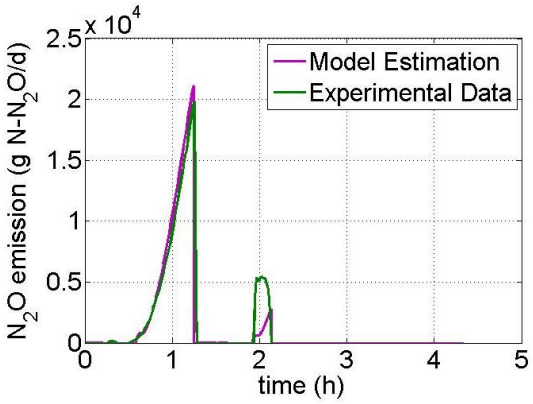

Figure 1. *Optimized Cycle B:* The N_2O instantaneous emission estimated by the model compared to the experimental data. Optimized DO setpoint during the aerated phases=1.6 mg L^{-1}.

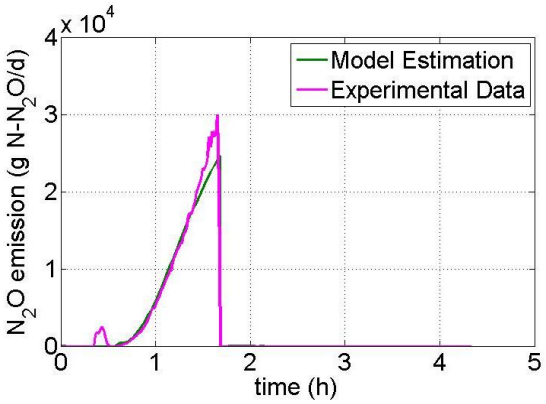

Figure 2. *Optimized Cycle C:* The N_2O instantaneous emission estimated by the model compared to the experimental data. Optimized DO setpoint during the aerated phases=1.66 mg L^{-1}.

N_2O emissions are expected to be negligible in the non-aerated phases due to the negligible stripping [13]. 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 [14]. During nitrification, insufficient aeration has an inhibitory effect [15], 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 Fig. 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 the emissions noted at the very beginning of the peak. It can be hypothesized that these emissions were rapidly recorded because 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 [16-18].

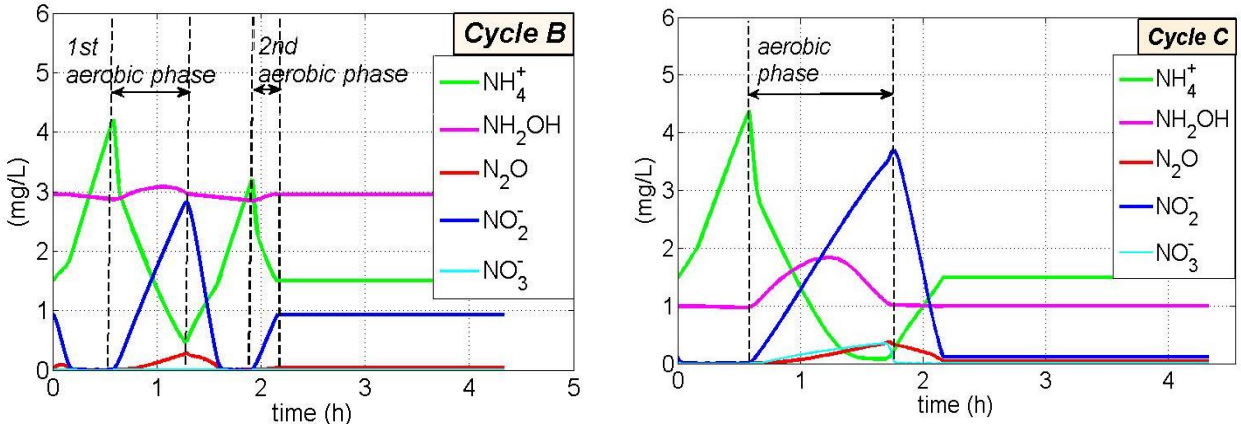

Figure 3. *Optimized Cycles type B & C:* The evolution of the NH_4^+, NH_2OH, N_2O, NO_2^- and NO_3^- concentrations.

The difference in the emission factors between cycle B and C indicated that the cycle configuration for a specific wastewater can lead to different emission factors. Thus, it is important to carefully select the percentage of aerobic phases in a cycle, the number of and anoxic phases, as well as the DO setpoint for aerobic phases.

For instance, with the DO setpoint ranging between 0 and 3 mg L^{-1} during the aerobic phases of Cycle B, long-term simulations of 1500 consecutive cycles were executed to ensure steady-state and evaluate the effect on N-removal and N_2O emissions. DO higher than 1.1 mg L^{-1} was required to achieve N-removal higher than 95%, but DO higher than 2 mg L^{-1} needed to be ensured so that the N2O emission factor can be satisfactorily low (i.e. around 1%) (Fig. 4).

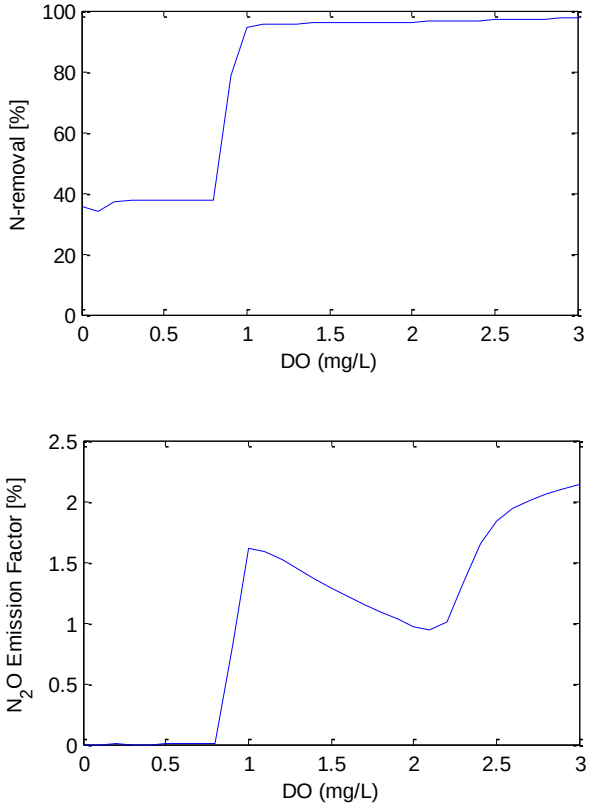

Figure 4. N-removal efficiency (above) and N_2O emission factor (below) as function of the DO setpoint during the aerobic phases of the SBR of the current study when operating under the cycle B configuration.

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_2O emission because of stripping. In this frame, process optimization is important. Under optimized SBR operation, satisfying nitrification along with moderate N_2O emissions and reasonable energy requirements are more likely to be achieved.

This work will hopefully constitute a flexible model for the prediction and mitigation of N_2O emissions in full-scale SBR WWTPs with the added value of easily adapting to different cycle types.

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