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Development of an Extended ASM3 Model for Predicting the Nitrous Oxide Emissions in a Full-Scale Wastewater Treatment Plant

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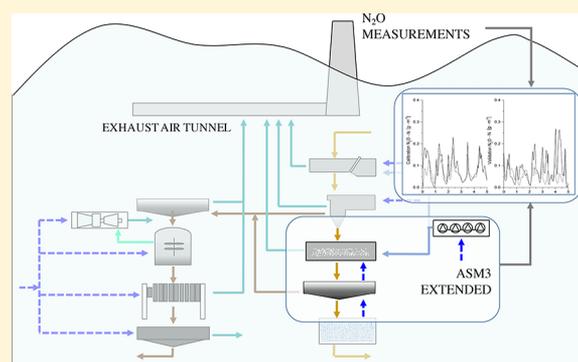
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Supporting Information

ABSTRACT: An Activated Sludge Model #3 (ASM3) based, pseudomechanistic model describing nitrous oxide (N₂O) production was created in this study to provide more insight into the dynamics of N₂O production, consumption, and emissions at a full-scale wastewater treatment plant (WWTP). N₂O emissions at the studied WWTP are monitored throughout the plant with a Fourier transform infrared analyzer, while the developed model encountered N₂O production in the biological reactors via both ammonia oxidizing bacteria (AOB) nitrification and heterotrophic denitrifiers. Additionally, the stripping of N₂O was included by applying a *K*₁*a*-based approach that has not been widely used before. The objective was to extend the existing ASM3-based model of the plant and assess how well the full-scale emissions could be predicted with the selected model. The validity and applicability of the model were tested by comparing the simulation results with the comprehensive online data. The results show that the ASM3-based model can be successfully extended and applied to modeling N₂O production and emissions at a full-scale WWTP. These results demonstrate that the biological reactor can explain most of the N₂O emissions at the plant, but a significant proportion of the liquid-phase N₂O is further transferred during the process.



INTRODUCTION

Municipal wastewater treatment plants (WWTPs) have been recognized as potential sources of greenhouse gas (GHG) emissions.¹ In particular, the research focus has been on nitrous oxide (N₂O), which is a significant GHG with approximately 300 times greater global warming potential than that of CO₂. N₂O is the most significant GHG emitted during wastewater treatment processes.² Additionally, it constitutes the most important ozone-depleting emission of the 21st century.³ Given the significant environmental hazards posed by N₂O, mitigating N₂O emissions is of utmost importance and will greatly impact the sustainability of WWTPs.

In WWTPs, N₂O can be emitted the biological nitrogen removal processes, including during autotrophic nitrification, autotrophic denitrification, and heterotrophic denitrification, which have been identified as the major emission sources in wastewater treatment. Due to the challenges of directly monitoring N₂O emissions at WWTPs, N₂O emissions are often estimated by applying a fixed standard emission factor. This approach has several limitations: the fixed emission factor is not only inconsistent with respect to recent studies, which show great variation in the reported N₂O emissions from

individual WWTPs,^{2,4,5} but it might also lead to underestimating the real level of emissions.^{2,6} Furthermore, the fixed emission factor does not take into account the impact of the different process conditions and configurations on N₂O emissions, which, we assume, affect the ultimate N₂O production rates significantly.

With improved instrumentation and long-term monitoring, there is a growing interest in the mathematical modeling of N₂O production in WWTPs. This would enable plant-specific estimations of N₂O production, since such modeling would take into account each individual plant's layout, process configuration, and operational characteristics. Furthermore, a comprehensive mathematical N₂O model can become a powerful tool for developing new N₂O-emission mitigation strategies at WWTPs.⁷

Currently, there are several different models available for estimating N₂O production. While all the models are based on

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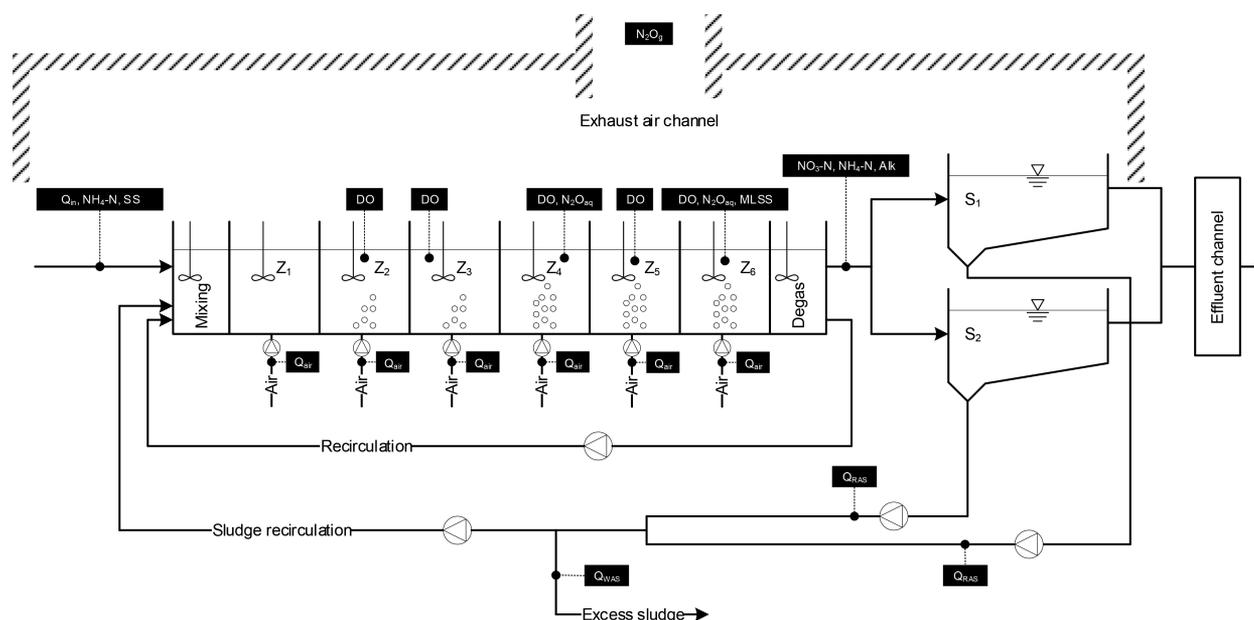


Figure 1. Schematic representation of the ASP and the locations of the online analyzers: mixing zone = 500 m³, Z_1 = 1500 m³, Z_2 – Z_6 = 1900 m³, degassing zone = 385 m³, S_1 and S_2 = 6700 m³, Q_{in} = influent flow, SS = suspended solids, NH_4-N = ammonia nitrogen, Q_{air} = air flow, DO = dissolved oxygen, N_2O_{aq} = dissolved nitrous oxide, N_2O_g = gaseous nitrous oxide, Q_{RAS} = return activated sludge, Q_{WAS} = waste activated sludge, NO_3^-N = nitrate nitrogen, $MLSS$ = mixed liquid suspended solids, Alk = alkalinity.

the known metabolic pathways of N_2O production, there is still much variety in their structure depending on the number of pathways included, stoichiometry, and kinetics.⁸ The single-pathway models describe N_2O production through one of the ammonia oxidizing bacteria (AOB) reactions (i.e., either AOB denitrification or NH_2OH oxidation), whereas the two-pathway model employs both of the production routes. Since the two-pathway models increase the number of parameters included, leading to laborious calibrations, the single-pathway models are potentially more convenient in certain environments, such as environments with high dissolved oxygen (DO) concentrations ($>1.5 \text{ g}\cdot\text{m}^{-3}$).⁹ Several comprehensive reviews of the current N_2O models^{7,8} and general GHG models that include N_2O production⁶ have been published. While modeling has proved to be a potentially applicable tool for estimating N_2O production and emissions at WWTPs, there is still a need for further research because only a limited number of studies have been conducted on full-scale WWTPs^{7,10,11} using comprehensive online data. Previously, a few Activated Sludge Model (ASM) type, single-pathway models have been applied to modeling full-scale WWTPs,^{10,11} but in none of the previous publications has an Activated Sludge Model #3 (ASM3) based model been used. The ASM3 provides more accurate reaction kinetics¹² and allows for easier calibration. It is also commonly used for modeling not only within the field of wastewater engineering and related disciplines but also by stakeholders as an inherent part in WWTP design and operation.

The modeling of N_2O emissions and related monitoring data campaigns have traditionally focused solely on biological reactors. Thus, there is no clear understanding of how well the models can explain the total N_2O emissions on a plantwide scale. Moreover, there is a clear lack of knowledge regarding the contribution of post-aeration processes to N_2O dynamics. On a practical level, it is challenging to determine the total N_2O emissions at open-ditch plants, whereas underground plants are more convenient for monitoring N_2O emissions on a plantwide

scale. Furthermore, in order to provide more insights into N_2O dynamics, the stripping of N_2O should be considered for both the gaseous and liquid phase. Generally, the stripping of N_2O has neither been widely discussed nor mentioned in the literature with regard to the modeling of N_2O production and emissions, even though it has a crucial impact on the modeled N_2O emissions as well as the N_2O production model. Moreover, from an environmental perspective the liquid-phase N_2O has not traditionally been seen as being as significant as the gaseous emissions,¹³ even though the contribution of the liquid-phase N_2O , if emitted later on, can be significant in terms of the overall carbon footprint of the plant.¹⁴

The objective of this study was to create an ASM3-based, pseudomechanistic N_2O model describing N_2O production via AOB and heterotrophic denitrifiers at a full-scale WWTP. Moreover, the stripping of N_2O was included and an attempt was made to identify the main sources and sinks of N_2O in the treatment process. The goal was to create a tool for aiding a plant's process control, and thus, the model was created to be ASM3 compatible and kept as simple as possible. The validity and applicability of the model were tested by comparing the simulation results with the comprehensive monitoring online data collected from the underground plant of Viikinmäki WWTP. Furthermore, the capability of the model to explain the plantwide emissions, and thus, the sufficiency of the selected modeling approach, was assessed.

■ MATERIAL AND METHODS

Field Site Description. Viikinmäki WWTP is the largest wastewater treatment facility in the Nordic countries, with a population equivalent to 1 100 000 p.e. The WWTP treats wastewater from the metropolitan area of Helsinki, accounting for a total of up to 800 000 inhabitants. The plant also receives industrial wastewater, which accounts for approximately 7% of the total inflow. The average influent concentrations and

operation are presented in Table 1 as [Supporting Information \(SI\)](#). In this underground plant, the air from the process tunnels is conducted outside via an exhaust air channel.

The treatment process consists of influent pumping, screening, grit removal, primary sedimentation, and biological treatment. Biological treatment at the Viikinmäki WWTP is based on an activated sludge process (ASP) and denitrifying postfiltration. The plant has altogether nine identically configured ASP lines, one of which was studied in this work. Each biological reactor in the ASP is divided into six zones, including one anoxic predenitrifying zone, two alternating switch zones, and three aerated nitrifying zones. Additionally, each biological reactor is equipped with a mixing zone and a degassing zone ([Figure 1](#)).

Adjustments to the aeration process and control of the switch zones in each ASP lines are performed based on online ammonium measurements at the end of the biological reactor. Under normal process conditions, three or four of the six zones are aerated. The ASP is normally run at a DO set point of $3.5 \text{ g O}_2 \cdot \text{m}^{-3}$ using proportional–integral (PI) control for each of the aerated zones.

Process Monitoring. The WWTP is fully automated and monitored via online analyzers. The most important analyzers used in this study are listed in Table 2 as [SI](#). The locations of the online analyzers at the studied ASP line are presented in [Figure 1](#).

In addition to online process monitoring, the plant is monitored via laboratory analysis. The most important analyses used in this study are presented in Table 3 as [SI](#). The samples were collected from influent, mechanically treated water, secondary clarified water, and effluent water.

N₂O Analyzer Equipment. The plant's total N₂O emissions have been continuously measured and monitored since 2012 via a Gaset CEMS II system situated in the exhaust air channel.² Since the WWTP was built underground, the measurements cover the gaseous N₂O emissions of the whole biological process, including denitrifying postfiltration. The Gaset CEMS II system—which consists of an online Fourier transform infrared (FTIR) analyzing unit, an industrial computer unit, and a sampling system—is connected to the plant's automation system, which stores the data in the WWTP's internal database.

The fourth and the sixth zones of the aeration tank were equipped with online, Clark-type, microsensors (Unisense A/S, Denmark) placed directly in the tank. The sensors continuously measured the dissolved N₂O concentrations during the liquid phase with a measurement range of 0.1–500 μM . The liquid-phase N₂O in zones 4 and 6 was monitored during two measurement campaigns consisting of 12 days and 5 days, respectively, in April 2017. Zone 4 was the first continuously aerated zone in the ASP, and it was selected in order to measure N₂O production during aeration without significant accumulation from the previous zones. Zone 6 was the last aerated zone under study, and it was selected in order to validate the dynamics of liquid-phase N₂O in the aeration reactor by capturing the variation in liquid-phase N₂O in two zones simultaneously. The sensors were two-point calibrated prior to the measurement campaigns. Additionally, switching zone 3 was monitored using the online microsensor during another measurement campaign for 14 days (22.3–3.4.2017) in order to capture N₂O production during the anoxic and aerated phases prior to zone 4.

In order to estimate the liquid-phase N₂O concentrations after the aeration basin, hourly grab samples were taken from the plant's effluent and from the secondary clarifier (average retention time: 8.5 h) influent and effluent during a 6 h period (9 a.m. to 3 p.m.) in a two-day measurement campaign in 2016 and another measurement campaign in 2017. The samples were collected in a lidded container (0.01 m^3) and measured immediately using a Unisense N₂O sensor.

Model Description. The proposed extended ASM3 model considers, in addition to the original ASM3 processes, N₂O production through both the NH₂OH oxidation pathway via AOB and heterotrophic denitrification. The NH₂OH modeling approach for N₂O production was assumed to be suitable due to the dynamic and relatively high DO concentrations ($1.5\text{--}3.8 \text{ g O}_2 \cdot \text{m}^{-3}$) in the aerated zones of the ASP and the low concentrations of NO₂[−] (0.1 and $0.7 \text{ g N} \cdot \text{m}^{-3}$).^{8,9} The [SI](#) in Table 4 summarizes the full list of state variables included in the extended ASM3 model.

The model was created stepwise by first extending the original nitrogen conversion processes in the ASM3 into two-step nitrification and two-step denitrification reactions. Following this, denitrification was extended into a four-step denitrification reaction and the NH₂OH pathway was implemented. The stepwise approach was used in order to better identify the mistakes during each step. The extension of the ASM3 to describe the two-step nitrification and two-step denitrification reactions was done according to specifications in [ref 15](#).

The assumptions for the four-step denitrification reaction and N₂O production via heterotrophic denitrification are based on the Activated Sludge Model for Nitrogen (ASMN).¹⁶ This approach was chosen because it can be assumed that the denitrification reaction at the WWTP is not carbon limited. Additionally, there is limited knowledge on carbon oxidation and nitrogen reduction kinetics; such knowledge is required for the other denitrification modeling approaches, such as the indirect coupling approach.^{8,17,18} The ASMN is based on ASM1, and therefore it did not originally include the storage reactions, anoxic endogenous respiration, and anoxic respiration of the storage substances that were additionally extended in this work for the ASM3 (processes p3a–c, p5a–c, p7a–c, and p9a–c in the [SI](#) for Table 5). Here, the two-step denitrification reaction¹⁵ was further extended into a four-step denitrification reaction according to the reaction kinetics and stoichiometry described in the ASMN. Additionally, the description of terms in the ASMN was done according to specifications in [ref 19](#).

The assumptions for N₂O production through the NH₂OH pathway are based on a previous single-pathway model¹⁰ corresponding to four new biological reactions (presented in Table 5 as [SI](#): p10a1–p10a4, [SI](#)). A few modifications were made to the original model: (i) the bacteria yield was added in p10a1 and p10a2 (Table 5 as [SI](#)), (ii) the N₂O production (p10a4) kinetics employ a reaction-specific growth rate instead of a reduction factor, and (iii) the AOB growth was attributed to the p10a2 process. The p10a4 process describes N₂O production via the NH₂OH pathway. In the model, it is assumed that N₂O is produced during the reduction of NO, which is in turn produced during the oxidation of NH₂OH. During the production of N₂O, NH₂OH is also consumed as an electron donor.

Since NO is an intermediate in both of the described N₂O production pathways, the component was divided into NO_{AOB}

and NO_{DEN} by adding two separate state variables attributing the AOB-related production of NO and heterotrophic denitrification-producing NO, respectively. This made it possible to prevent the NH_2OH pathway reaction during heterotrophic denitrification and vice versa. In the model, the NH_2OH oxidation pathway for N_2O production does not require DO, thus theoretically part of the NO produced during denitrification could have been utilized by the AOB via the NH_2OH pathway under anoxic conditions.

A comprehensive modeling study that includes data quality proofing, influent fractionation, and model construction was already done at the plant.²⁰ The influent fractions were created based on the previous findings according to the online analyzers' data and laboratory results collected from the ASP influent channel (Table 3 as SI). The variation in the soluble components was assumed to follow the pattern of the influent $\text{NH}_4\text{-N}$, while the variation in the particulate matter was assumed to follow the pattern of the SS measurement. Phosphorus was implemented in the influent model as a constant value since it does not have an impact on the N_2O dynamics in wastewater treatment.

N_2O Stripping. Prior studies have shown that aerated zones in the ASP are the primary emission sources of N_2O ,²¹ since the liquid-phase N_2O is mainly stripped during the aeration phase. The stripping of N_2O in each of the zones was estimated using a mathematical approach^{22,23} based on the modeled N_2O concentrations ($S_{\text{N}_2\text{O}}$) and air flow (Q_A) in the aerated zones. Equation 1.1 is as follows:

$$R_{\text{N}_2\text{O}} = H_{\text{N}_2\text{O}}^{\text{pc}} S_{\text{N}_2\text{O}} (1 - e^{-K_L a_{\text{N}_2\text{O}} V_R / H_{\text{N}_2\text{O}} Q_A}) \frac{Q_A}{V_R} \quad (1.1)$$

where, $R_{\text{N}_2\text{O}}$ is the stripped N_2O , that is to say, the emission rate of N_2O ($\text{g}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$); $H_{\text{N}_2\text{O}}^{\text{pc}}$ is the Henry's constant ($\text{mol}\cdot\text{L}^{-1}\cdot\text{bar}^{-1}$) at the process temperature, which was calculated according to ref 24; $K_L a_{\text{N}_2\text{O}}$ is the mass transfer coefficient for N_2O at the process temperature, which was calculated according to ref 4 for each zone separately, V_R is the volume of the aerated zone (m^3), and Q_A is the air flow in the zone ($\text{m}^3\cdot\text{d}^{-1}$).

The stripping from the anoxic zones was first calculated based on an approach proposed in ref 22, but it proved to be negligible compared to the aerated zones as it was only less than 1.5% of the total emissions from the aerated zones. This was due to the low stripping effect of the nonaerated zones compared to the aerated zones. Additionally, the measured liquid-phase concentrations of N_2O in the anoxic zones were smaller compared to those in the aerated zones. For the sake of simplicity, the stripping of N_2O from the anoxic zones was not included in the model.

The measured N_2O emissions that cover the emissions of the whole plant were scaled in order to compare the measured and modeled N_2O of the studied ASP line. The nine identically configured ASP lines were assumed to contribute evenly in relation to the inflow ($\text{m}^3\cdot\text{d}^{-1}$) to the measured N_2O emissions in the exhaust air channel. The contribution of the studied ASP line to the total N_2O emissions was estimated based on the percentage of the total wastewater treated in the ASP line, which is on average 10–12%. The total air flow ($\text{m}^3\cdot\text{d}^{-1}$) through the exhaust air channel was estimated based on the plant's ventilation ($100 \pm 10 \text{ m}^3\cdot\text{d}^{-1}$) and used for estimating the hourly emissions ($\text{kg N}_2\text{O}\cdot\text{N}\cdot\text{h}^{-1}$).

Model Calibration and Validation. The model simulation was performed using GPS-X (version 6.5). The ASP was modeled using a tanks-in-series model with eight zones (a mixing zone, anoxic predenitrifying zones, and aerated nitrifying zones, accounting altogether for six reactors and a degassing zone) and two parallel secondary clarifiers (Figure 1). The denitrifying postfiltration was excluded from the model because its N_2O emissions have been observed as insignificant.²⁵ According to good modeling practice, a steady state simulation was conducted prior to every further simulation of the desired period of time.

The model was calibrated using the comprehensive online data collected from the plant (Table 2 as SI). The model was validated and tested for a period of 5 days, which was done together with another monitoring data campaign at the plant (Table 2 as SI). The process conditions during the calibration and validation phases were stable. Since the aerated zones are automatically controlled and the influent load to the plant varies constantly, the aeration periods differed slightly. During the calibration (8–19.4.2017) phase, zones 4–6 were continuously aerated, the switching zone 3 was aerated 12 times for two to 3 h, and zone 1 was anoxic. During the validation (25–30.4.2017) phase, zones 4–6 were continuously aerated, the switching zone 3 was aerated four times for periods of 2–4 h, and zone 1 was anoxic.

Parameter Estimation and Goodness-of-Fit Evaluation. Given the rising number of kinetic parameters that derived from the performed extension steps, calibration of the final extended ASM3 model was challenging. Therefore, parameter estimation was performed following the specifications in ref 26 while a detailed description for a specific modeling case can also be found in ref 27. The proposed approach examines the model's kinetic parameter correlation and is based on constructing a confidence region that encompasses the likelihood confidence region. The estimation of the single kinetic parameters (θ) was done using the residual sum of squares (RSS) objective function $J(\theta)$:

$$J(\theta) = \text{RSS} = \sum_{i=1}^N (y_i - \hat{y}_i)^2 \quad (1.2)$$

where, N is the number of measurements, y_i are the measured data, and \hat{y}_i are the outputs predicted by the model.

Calculation of the confidence regions for the optimized parameters was performed using the following eq 1.3:

$$\text{SSR}(\theta) \leq \text{SSR}(\theta_0) \left(1 + \frac{p}{n-p} F_{p;n-p}^{\alpha} \right) \quad (1.3)$$

Here, $\text{SSR}(\theta_0)$ refers to the minimum sum of the squared residuals, p refers to the number of parameters, n refers to the number of measured values, and $F_{p;n-p}^{\alpha}$ refers to the F value taken from the F -distribution for a confidence interval $\alpha = 0.05$ with p and $p - n$ degrees of freedom. For the present study, we used $F_{2,\infty}^{0.05} = 2.996$, which is also in accordance with that used in ref 28.

The increasing complexity of the model demands not only appropriate parameter estimation but also goodness-of-fit measures to evaluate the quality of the model. Therefore, the modified Nash–Sutcliffe coefficient (E_i) was determined using eq 1.4,²⁹ where M_i refers to the measured data, E_i to the modeled data, and M to the mean of the measured data.

$$E_j = 1 - \frac{\sum_{i=1}^N |M_i - E_i|}{\sum_{i=1}^N |M_i - \bar{M}|} \quad (1.4)$$

As E_j can be sensitive to extreme values, the modified version applies absolute values to reduce the effect of the squared terms. A Nash–Sutcliffe coefficient of 1 corresponds to a perfect match of the modeled and measured data, whereas a coefficient of 0 indicates that the model's prediction is as accurate as the mean of the measured data.³⁰ A coefficient below 0 refers to a simulation worse than the average of the measured data.

Additionally, the root mean square error (RMSE) was calculated for selected parameters using eq 1.5, where n represents the number of measured values, y_i are the modeled values, and \hat{y}_i are the measured values. The smaller the RMSE value, the closer the modeled and measured values.

$$\text{RMSE} = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2} \quad (1.5)$$

RESULTS

Liquid N₂O Monitoring Results. The average liquid-phase N₂O concentrations in aerated zone 4 were 0.04 and 0.03 g N·m⁻³, whereas they were 0.09 and 0.11 g N·m⁻³ in aerated zone 6 during the calibration and validation phases (Figure 3). An online measurement campaign in switching zone 3 showed that, during the anoxic periods, the average N₂O concentration in zone 3 was 0.027 g N·m⁻³, whereas we observed peak concentrations of up to 0.16 g N·m⁻³ during or directly following the aerated periods. The online and grab-sample measurements at the WWTP show that liquid-phase N₂O accumulated in the ASP and that the measured N₂O concentrations were notably higher in the aerobic environments compared to the anoxic environments.

We collected the hourly grab sample measurements from the influent and effluent of the secondary clarifiers and the plant effluent. The measured values prior to the secondary clarification varied between 0.38–0.43, 0.50–0.59, and 0.29–0.31 g N·m⁻³ during the first, second, and third measurement campaigns. The measured values in the effluent of the secondary clarification varied between 0.31–0.36, 0.35–0.49, and 0.32–0.34 g N·m⁻³ during the first, second, and third measurement campaigns. We simulated similar concentrations of liquid-phase N₂O in the secondary clarification effluent in the model, with concentrations of 0.32 and 0.30 g N·m⁻³ during the calibration and validation phases, respectively.

This indicates that a notable proportion of the N₂O produced in the aeration reactor is further conveyed from the ASP. Additionally, part of the N₂O can be conveyed from the secondary clarifier back to the mixing zone of the biological reactor along with return activated sludge (RAS) and internal sludge recycling.

During the first measurement campaign, we did not detect N₂O in the effluent of the plant except for in one sample measurement of 0.01 g N·m⁻³. Consistently, during the second and the third measurement campaigns the detected effluent concentrations were low, varying between 0.00–0.05 g N·m⁻³.

Parameter Estimation. The kinetics and stoichiometric parameter set (Table 6 as SI) consisted of 63 parameters with 23 stoichiometric and 40 kinetic parameters. We carried out the calibration procedure based on the knowledge acquired about

the process. We chose a match between the simulated and online data in the SI for Table 2 as the main criteria for defining the quality of the model prediction in terms of the nitrogen conversion reactions and kinetics—that is to say, nitrification, N₂O production, and denitrification—using the monitoring data (Figure 1, Table 2, SI).

The task began with us calibrating the ammonia oxidation ($\mu_{\text{AOB,AMO}}$). In addition, as our particular interest was on N₂O production, we adjusted the $\mu_{\text{AOB,NOR}}$ until the modeling results were in accordance with the measured values, prioritizing the dynamics of the production of N₂O. We chose a value for the saturation coefficient of NH₂OH ($K_{\text{AOB,NH}_2\text{OH}}$) that was the same as the one for the saturation coefficient of nitrate and nitrite. We kept the remaining stoichiometric and kinetic parameters at the values given in the literature (Table 6, SI).

We found that the calibrated value of $\mu_{\text{AOB,AMO}} = 1.21 \text{ d}^{-1}$ was satisfactory with regard to the joint 95% confidence regions and also in line with the range given in literature, which varies between 0.768–5.184 d⁻¹.⁸ As exemplarily for the S_{N2O} (shown in Figure 2), the parameter estimation approach revealed a high

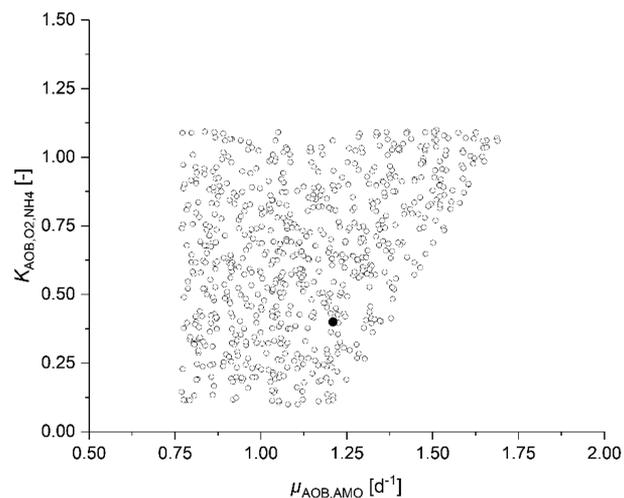


Figure 2. Joint 95% confidence region for the maximum AMO-mediated reaction rate for NH₄–NH₂OH ($\mu_{\text{AOB,AMO}}$) and the saturation/inhibition coefficient for O₂ in NH₄ oxidation ($K_{\text{AOB,O}_2,\text{NH}_4}$) in relation to the dissolved nitrous oxide concentration S_{N2O}.

number of possible parameter combinations. In this study, the model employs a maximum growth rate for the NOR-mediated reaction, that is to say, it employs the NH₂OH oxidation pathway instead of an anoxic reduction factor and the HAO-mediated reaction rate, as discussed in a study in ref 10. The calibrated value of 0.15 d⁻¹ found for the maximum NOR-mediated reaction rate is, however, equivalent to the range of the values presented in ref 10.

The original ASM1 is based on ASM1 processes, and in this study it was extended for ASM3, leading to seven new parameters in total. For the sake of simplicity, we applied the same yield coefficient values ($Y_{\text{H,NO}}$, $Y_{\text{H,N}_2\text{O}}$) for heterotrophic growth and for storage (X_{STO}) in anoxic growth ($Y_{\text{STO,NO}}$, $Y_{\text{STO,N}_2\text{O}}$) for all of the denitrifying reactions. Additionally, we used the reduction factor values presented in ref 15 for NO₂⁻ reduction under anoxic conditions ($\eta_{\text{H,end,NO}_2}$) (0.35–0.70) for calibrating the NO reduction and N₂O reduction values ($\eta_{\text{H,end,NO}}$, $\eta_{\text{H,end,N}_2\text{O}}$).

Modeling Results. The model was able to reproduce the variation in the measured liquid-phase N₂O concentrations

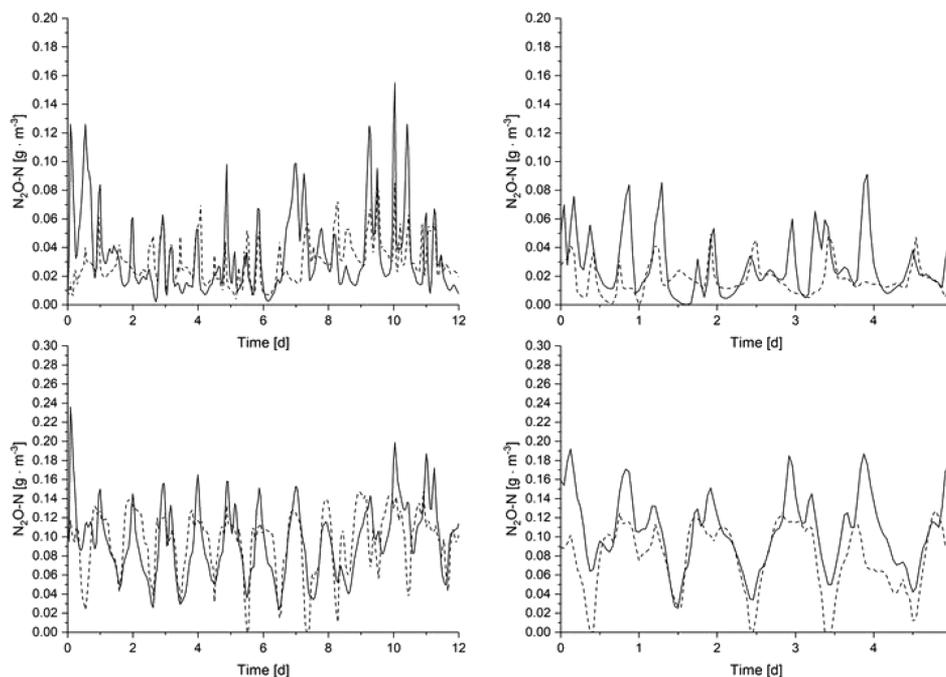


Figure 3. Modeled (dashed line) and measured (solid line) $\text{N}_2\text{O-N}$ concentrations in the liquid in the continuously aerated zones 4 (above) and 6 (below) during calibration (left) and validation (right).

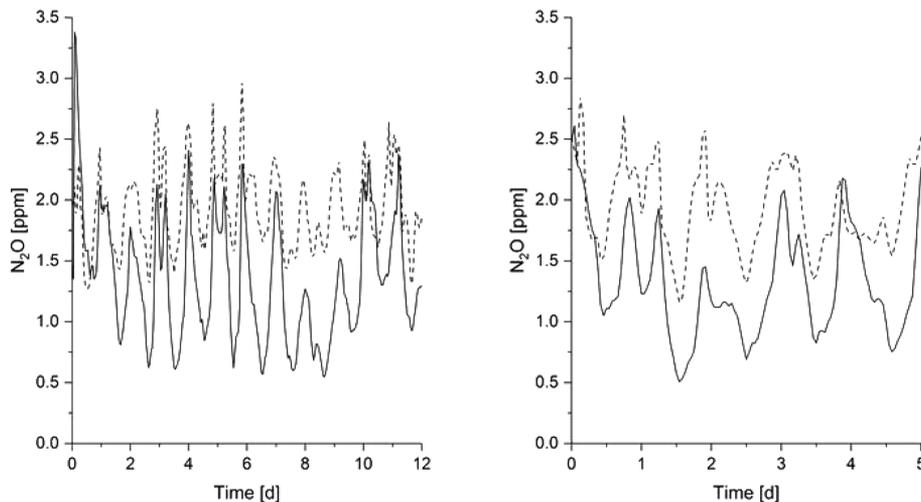


Figure 4. Modeled (dashed line) and measured (solid line) N_2O emissions during calibration (left) and validation (right).

during the calibration and validation phases in zones 4 and 6, the zones that were continuously aerated (Figure 3). Likewise, the model was able to reproduce the variation in N_2O in zone 6 more precisely than in zone 4. This could be due to the fact that the switching zone 3, while it is aerated, affects N_2O production in zone 4, which could not be fully captured by our model. Furthermore, the total concentrations of N_2O in zone 4 were lower than in zone 6, which means that the measured values and the modeling results for zone 4 were more sensitive to all kinds of variations in the full-scale WWTP. Altogether, the model was able to capture the dynamics of the liquid-phase N_2O in the aeration tank, which is demonstrated by the two simultaneous measurements in two different zones and additionally by the grab sample measurements in the secondary clarification influent and effluent.

The model was also able to capture the dynamics of the measured N_2O emissions in the exhaust air channel (Figure 4).

However, while the model was able to predict the variations in N_2O emissions, the basic level of the modeled values was notably higher compared to the measured emissions.

The ammonia oxidation is directly linked to all of the main nitrogen conversion reactions in the ASP. The model was able to reproduce the measured NH_4 peaks in the effluent of the ASP throughout the simulation (Figure 1, SI). During the calibration period, the modeled peaks were able to reach the measured values throughout the simulation. Consistently, the model was able to reproduce the measured peaks during the validation phase.

Additionally, the model was able to reproduce most of the measured NO_3^- variation in the effluent of the ASP (Figure 2, SI). During both the calibration and validation phases, the model was not able to simulate the variation during weekend periods (days 10–12 during calibration and days 3–5 during validation), which can be explained by the changes in the

characteristics of the influent since the proportion of industrial wastewater is smaller. The NO_3^- variation is directly linked to denitrification, and therefore, to variations in the organic load of the plant. Overall, estimating the diurnal variations in the organic load is difficult at full-scale plants, which is reflected in our modeling of the NO_3^- concentrations. Additional calibration results for the ASP, such as MLSS in the biological reactor and TSS in the ASP influent, are presented in the SI. The results of the Nash–Sutcliffe coefficients and RMSE are presented in the SI, Table 7.

DISCUSSION

The extended ASM3-based model included N_2O production through the NH_2OH oxidation pathway and heterotrophic denitrification pathway in addition to the original ASM3 processes. The model was able to capture the measured N_2O variation and dynamics during both liquid and gaseous phases at the plant. The model was able to reproduce most of the variation in the liquid-phase N_2O concentration in the continuously aerated zones 4 and 6 during the calibration and validation phases. These modeled results are also supported by previous NH_2OH oxidation pathway modeling approaches, as the model was able to capture the N_2O production dynamics in accordance with the DO dynamics.^{8,11}

These modeling results are in accordance with the measured N_2O concentrations and previous studies, suggesting that most N_2O production takes place in the aerated zones of the ASP.²¹ The previous N_2O emission study done at Viikinmäki WWTP demonstrated a correlation between the number of zones aerated and N_2O emissions,² which could be also related to increased AOB-related N_2O production due to increased aeration. However, the correlation can also be related to an increased ammonium load, which results in the need for an increased aeration volume. Altogether, given the low N_2O concentration in the anoxic zones of the ASP due to the N_2O mainly being consumed by denitrification and the notably smaller stripping effect compared to the aerated zones, we can assume that the contribution of the anoxic zones to the plant's gaseous-phase N_2O emission is negligible.

To the best of the authors' knowledge, this study is the first of its kind to present the dynamics of liquid-phase N_2O using two simultaneous measurements in the aeration reactor. This demonstrates that the model can capture the dynamics of liquid-phase N_2O in the aeration process, and therefore, the model can be seen as a possible tool for studying the effects of different operational strategies on the mitigation of N_2O at the plant.

The modeled emissions during both the calibration and validation phases were relatively consistent with the dynamics of the measured N_2O emissions collected from the exhaust air channel. It is important to note here that the measured gaseous emissions represent the total N_2O emissions for the whole plant. Thus, in order to compare the modeled and measured N_2O emissions, we scaled the measurement for the studied treatment line. For instance, the model predicted slightly stronger fluctuations compared to the measured emissions, possibly because the fluctuations in measured emissions are more stable due to the contribution of all the ASP lines. Nevertheless, the modeling results suggest that the biological model is able to predict most of the variations in the emissions and that the most significant part of the emissions is produced in the aeration reactor.

While the model was able to capture the variation in the plant's N_2O emissions, the basic level of the modeled emissions was notably higher compared to the measured values during both the calibration and validation phases. The level of the modeled emissions could not be fixed via model calibration, that is, it could not be fixed by calibrating the N_2O production in the liquid phase. Therefore, an important concern demonstrated in this study is that the applied stripping model seems to overestimate the amount of stripped N_2O , at least during certain periods, which leads to an overestimation of the total emissions. Interestingly, another simulation from late summer 2016 showed a better fit for gaseous-phase emissions suggesting that the observed large variations in emissions³¹ are caused by changes in stripping, not necessarily in N_2O production. While the stripping model has a crucial impact on how the total emissions of N_2O are modeled, there has not been any discussion in the literature regarding the stripping models used in the previous N_2O modeling studies.

The grab sample measurements prior to the secondary clarification showed an average concentration of 0.40, 0.55, and 0.30 $\text{g N}\cdot\text{m}^{-3}$ during the first, second, and third measurement campaigns, respectively. Similarly, for instance, ref 4 reported liquid-phase N_2O concentrations of up to 0.3 $\text{g N}\cdot\text{m}^{-3}$ in the secondary clarification. Based on the measurements in the secondary clarification influent and effluent, we estimated that 10–50% of the N_2O entering the secondary clarification could potentially be emitted or consumed during the process, possibly due to the stripping of N_2O or else, to a smaller extent in this case, to heterotrophic denitrification leading to the generation of N_2 . While there is a lack of research regarding the N_2O emissions originating from the secondary clarification, these findings are supported by the results provided in ref 32, which demonstrate that more than 30% of the N_2O emissions can be emitted from the secondary clarifiers. In this case, significant stripping in the secondary clarifiers in relation to the anoxic zones is supported by the fact that the aeration tank is quite deep (12 m) compared to the clarifiers and very little sludge is stored in the secondary clarifiers. Overall, the contribution of secondary clarification to the dynamics of N_2O production and consumption should be further studied.

Nevertheless, the liquid-phase N_2O concentrations in the effluent of secondary clarification suggest that the major proportion of the liquid-phase N_2O is further conveyed to post-denitrifying filtration. Since the measured N_2O concentrations in the plant effluent were insignificant, we can assume that the N_2O is consumed during denitrifying postfiltration.

Moreover, the measured and modeled concentrations of liquid-phase N_2O in the secondary clarification demonstrate that an important proportion of the N_2O may not be stripped out during the aerated zones, unlike current assumptions suggest. The fate of this potential source of N_2O emissions later on in the process in the air or in the receiving water body should be further studied. Further research would be required in order to investigate the mitigation of emissions via denitrification. This modeling approach, including the stripping of N_2O , might also provide a useful tool to investigate whether the mitigation methods at the plant should be implemented during the process operation in order to restrict the production of N_2O or the stripping of N_2O during aeration.

While the results show that the NH_2OH oxidation pathway model was able to describe N_2O production at the studied Viikinmäki WWTP, it should be noted that the model may not be able to reproduce all N_2O production at other WWTPs. The

NH₂OH oxidation pathway models are reportedly applicable for environments with a relatively high DO concentration,^{9,10} whereas these models have not been able to predict N₂O production in environments with NO₂⁻ accumulation.¹¹ Furthermore, the results presented in this study do not necessarily rule out the possibility that the AOB denitrification could contribute to the ultimate N₂O emissions at the Viikinmäki WWTP. This N₂O production pathway, which is also known as nitrifier denitrification, implies the reduction of NO₂⁻ to NO and further to N₂O. According to current understanding, the pathway is favored during nitrification at low DO concentrations. A full investigation of the pathways that are dominantly contributing to the N₂O pool will require stable nitrogen and oxygen isotope analysis, which will be likely addressed in future research studies.

Nevertheless, in this study we extended the ASM3 for the first time by modeling N₂O production at a WWTP. The results show that an ASM3-based model can be successfully extended and applied to the modeling of N₂O production at a full-scale WWTP, as the model was able to produce not only the measured N₂O production but also the comprehensive online monitoring data collected at the plant. This study also introduced N₂O stripping into the process dynamics, which had been lacking from previous models. Overall, this is an important step toward applying N₂O models to a full-scale WWTP.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b00386.

Plant process characteristics, model process rate kinetics and parameters, goodness of fit values, and further modeling results (PDF)

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