



## Model-based identification of the dominant N<sub>2</sub>O emission pathway in a full-scale activated sludge system

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### ABSTRACT

Activated sludge models (ASMs), extended with an N<sub>2</sub>O emission module, are powerful tools to describe the operation of full-scale wastewater treatment plants (WWTPs). Specifically, such models can investigate the most contributive N<sub>2</sub>O production pathways and guide towards N<sub>2</sub>O and carbon footprint (CF) mitigation measures. A common practice is to develop and validate models using data from a single WWTP. In this study, a successfully validated model in one plant (Slupsk/Poland) was extrapolated to another full-scale WWTP (Viikimäki/Finland). For this purpose, the previously developed ASM No. 2d with the N<sub>2</sub>O module was used. Moreover, the results of calibration and validation of that model were compared with those obtained on the basis of the ASM No. 3 with an N<sub>2</sub>O module. A novel, rigorous calibration protocol, based on the system engineering approach, was implemented to minimize the number of adjusted parameters without compromising the accuracy of model predictions. The validated model accurately predicted the behavior of the system in terms of the liquid N<sub>2</sub>O production in the bioreactor and gaseous N<sub>2</sub>O emissions. Model-based identification of N<sub>2</sub>O production pathways revealed the key role of heterotrophs due to their high abundance in the microbial community. The N<sub>2</sub>O emission factor (EF) at the studied plant was found between 0.9 and 0.94% of the influent TN-load for the validation and calibration period, respectively. Based on the model predictions, it was estimated that the aerobic zones contributed to over 93% of the N<sub>2</sub>O emitted to the atmosphere, while the remaining portion (7%) resulted from the N<sub>2</sub>O liquid-gas transfer in the non-aerated zones. The difference between the predicted N<sub>2</sub>O EF and the empirical EF calculation would lead to almost 1000 tonnes of CO<sub>2</sub> equivalent reduction of the annual CF of the plant, which highlights the importance of model applications in CF studies.

### 1. Introduction

Traditionally, the operation of wastewater treatment plants (WWTPs) has solely been focused on efficient removing pollutants and nutrients from wastewater to protect public health and aquatic environment. More recently, new considerations have been postulated with respect to the energy efficiency and mitigation of greenhouse gas (GHG) emissions, which became important measures of the sustainability of WWTPs (Chen et al., 2020a).

Accumulated GHG emissions can be expressed as carbon footprint (CF) (Delre et al., 2019). Among the GHG emitted from WWTPs, nitrous oxide (N<sub>2</sub>O) has received growing attention. It is estimated that the wastewater treatment sector is responsible for 3–5% of the global anthropogenic N<sub>2</sub>O emission (Mannina et al., 2019). Furthermore, N<sub>2</sub>O

generated in wastewater treatment processes can dramatically affect the total CF of WWTPs. High shares, exceeding 50%, of N<sub>2</sub>O emissions in CF of the biological nutrient removal (BNR) WWTPs have been reported in the literature (Koutsou et al., 2018).

It is challenging to determine precisely an N<sub>2</sub>O emission factor (EF) (Sun et al., 2017). The empirical EFs are frequently reported based on the influent total nitrogen (TN) load, and the removed loads of TN or ammonium (NH<sub>4</sub><sup>+</sup>-N). The choice of the EF may significantly affect the total calculated CF of WWTPs. High uncertainties in terms of CF have been shown when using the national GHG inventories approach (Nayeb et al., 2019).

Mechanistic activated sludge models (ASMs) are powerful tools to investigate the dominant N<sub>2</sub>O production pathways and guide towards mitigation measures. Although modelling studies are a favorable

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approach to determine N<sub>2</sub>O emissions (Sun et al., 2017), there are still several challenges in practical applications of mechanistic N<sub>2</sub>O models due to their complexity and over-parametrization (Vasilaki et al., 2019). Moreover, full-scale monitoring campaigns of N<sub>2</sub>O emissions are necessary for reliable evaluation of N<sub>2</sub>O emission models (Gruber et al., 2020; Ribera-Guardia et al., 2019). It should be noted that the number of full-scale practical modelling studies is still limited in the literature (see Table 1).

The discussion on the preferable N<sub>2</sub>O model is still ongoing with several extensions and modifications of the original approaches developed recently (Vasilaki et al., 2019). In terms of N<sub>2</sub>O production by ammonia oxidizing bacteria (AOB), two categories of N<sub>2</sub>O models have been proposed, including single-pathway models and two-pathway models. The single pathway models consider either AOB denitrification or hydroxylamine (NH<sub>2</sub>OH) oxidation pathways, while the two-pathway approach has been employed to integrate both N<sub>2</sub>O production pathways (Ni and Yuan, 2015). To predict N<sub>2</sub>O production by heterotrophic denitrification, the process needs to be modeled as a multiple-step process. Two distinct concepts have been proposed, which are the direct coupling approach represented by the Activated Sludge Model for Nitrogen (ASM-N) (Hiatt and Grady, 2008) and the Activated Sludge Model with Indirect Coupling of Electrons (ASM-ICE) (Pan et al., 2013). Inclusion of all major N<sub>2</sub>O production pathways results in complex and over parameterized models impairing reliable calibration and validation. Short-term calibration and validation of the models under specific operational conditions limits their accuracy when the system varies significantly. For N<sub>2</sub>O production by AOB, the single-pathway models have simplified structures and a fewer number of parameters, which brings convenience to model calibration. The multiple-pathway models have the potential to describe all the N<sub>2</sub>O data with different operational conditions, but may require more efforts on model calibration due to a higher number of parameters (Vasilaki et al., 2019). For the single pathway models of AOB reported in the literature, most variable kinetic parameter was, the reduction factor for N<sub>2</sub>O production. Regarding the ASM-ICE of heterotrophic denitrifiers, information on the nitrogen reduction kinetics was required for its calibration (Ni and Yuan, 2015).

Models are being calibrated and validated uniquely for a specific WWTP. The conclusions of the modelling study in terms of N<sub>2</sub>O pathways and emissions are plant specific. Therefore, continuous improvement and application based on the existing mathematical models are highly recommended (Chen et al., 2020b). Until now, there has been no reported study, addressing confirmation of the existing N<sub>2</sub>O models.

In response to this demand, the present study aimed at confirmation of the applicability and universality of an existing N<sub>2</sub>O model on another full-scale WWTP. Blomberg et al. (2018) developed Activated Sludge Model No. 3 (ASM3) with an N<sub>2</sub>O extension and implemented at the full-scale Viikinmäki WWTP (Finland). In the present study, the same data set was used to evaluate the extended Activated Sludge Model No. 2d (ASM2d-N<sub>2</sub>O) validated elsewhere (Zaborowska et al., 2019). Furthermore, both model predictions were compared in terms of a few goodness-of-fits criteria and identification of the major pathways for N<sub>2</sub>O production. A rigorous calibration protocol, based on the system engineering approach, was proposed to minimize the number of adjusted parameters without compromising the accuracy of model predictions, specifically in terms of liquid N<sub>2</sub>O production and N<sub>2</sub>O emission. Ultimately, the model predictions for N<sub>2</sub>O emissions resulted in estimation of new EFs and comparison with the empirical EF calculations.

## 2. Materials and methods

### 2.1. Characteristics of the WWTP

Viikinmäki WWTP, located in the metropolitan area of Helsinki, is the largest facility in Finland with the population equivalent (PE) over 1 million. Except for the biogas units, the entire plant is built underground. Fig. 1a shows a scheme of one out of nine parallel, identically configured activated sludge lines. The basic annual influent characteristics are given in the Supplementary Information (SI) (Table S1). In 2017, the average influent flow rate was 289,000 m<sup>3</sup>/d in which industrial wastewater accounted for approximately 7% of the total influent flow. The average nitrogen load of Viikinmäki WWTP was 16 g N/PE/d and 15.4 g N/PE/d during the calibration and validation period, respectively. The average solids retention time (SRT) of the plant was approximately 9 days during both calibration and validation periods. The air from the process tunnels is conducted outside through an exhaust channel which helps measure gas emissions, including N<sub>2</sub>O. In terms of hydrodynamic conditions, the biological reactors are non-ideal flow reactors and are divided into six zones (Z1 to Z6), including two anoxic pre-denitrifying zones (Z1 and Z2), one intermediate (aeration on/off) zone (Z3), and three aerated nitrifying zones (Z4 to Z6). In addition, a mixing zone is located prior to Z1 and a degassing zone follows the last aerobic reactor. Under typical operating, aeration at compartments Z4 to Z6 is run at a DO set point of  $3 \pm 0.33$  g O<sub>2</sub>/m<sup>3</sup> using a proportional-integral (PI) control algorithm. Adjustments to the aeration process and control of the intermediate compartments are performed based on ammonium based aeration control (ABAC). Under normal process conditions, three or four of the six compartments are aerated.

### 2.2. Model development

A computer model of Viikinmäki WWTP (Fig. 1b) was built in GPS-X 8.0 simulation platform (Hydromantis, Canada). This section is dedicated to description of the subsequent steps in model development from experimental data collection through the hydrodynamic and biokinetic sub-models selection.

#### 2.2.1. Experimental data collection

The process monitoring in Viikinmäki WWTP was fully automated and monitored via online analyzers. The collected data included temperature, alkalinity (via ADI, 2045TI analyzer), dissolved oxygen (DO), chemical oxygen demand (COD), mixed liquor suspended solids (MLSS) (via BTG RD-20/10 analyzer), NH<sub>4</sub><sup>+</sup>-N (via A-ISE sc analyzer), nitrate (NO<sub>3</sub><sup>-</sup>-N) (via Nitratax plus analyzer), liquid N<sub>2</sub>O concentrations in the first and the last aerobic compartments (via Unisense analyzer) and total N<sub>2</sub>O emissions (via Gasmet FTIR analyzer) in the exhaust channel. For model calibration and validation, the same sets of data (two measurement campaigns consisting of 12 days and 5 days) were used as previously described by Blomberg et al. (2018).

#### 2.2.2. Influent characterization model

The influent organic and nitrogen fractions were adopted from the study of Blomberg et al. (2018). The state variables included in the influent characterization model can be found in the SI (Table S2). The influent fractions were determined based on the previous findings according to the online analyzers data and laboratory results collected from the bioreactor inlet. The variation in the soluble organic components was assumed to follow the pattern of the influent NH<sub>4</sub>-N, while the variation in the particulate organic matter was assumed to follow the

**Table 1**Theoretical (without actual N<sub>2</sub>O measurements) and practical (with N<sub>2</sub>O measurements) full-scale modelling studies on N<sub>2</sub>O production and emission in WWTPs.

Study	Studied WWTP	Size	Configuration	Model used	Software	N <sub>2</sub> O emission	Main pathway	Remarks
Theoretical study by Domingo-Félez and Smets (2020)	Lynetten, Copenhagen, Denmark	700,000 PE	phase-isolated AS	NDHA (nitrifier nitrification, nitrifier denitrification, heterotrophic denitrification, abiotic production)	MATLAB	EF <sub>N2O</sub> = 1.2% of the removed NH <sub>4</sub> <sup>+</sup> -N load (DO = 2.0 mg O <sub>2</sub> /L) EF <sub>N2O</sub> = 0.046 kg N <sub>2</sub> O/kg NH <sub>4</sub> <sup>+</sup> -N <sub>removed</sub> (DO = 0.5 mg O <sub>2</sub> /L)	In aerobic conditions, AOB denitrification and DHET denitrification pathway contributions increased at high NO <sub>2</sub> <sup>-</sup> and low DO concentrations; while the NH <sub>2</sub> OH oxidation pathway showed the largest contribution at high DO levels.	Low uncertainty in terms of N <sub>2</sub> O emissions achieved, the uncertainty of N <sub>2</sub> O emissions during model calibration is commonly overlooked in the literature.
Theoretical study by Massara et al. (2018)	Manresa (Catalonia, Spain)	27,000 m <sup>3</sup> /d	A <sup>2</sup> O configuration with enhanced biological phosphorus removal (EBPR)	ASM2d-N <sub>2</sub> O	MATLAB	EF <sub>N2O</sub> = 1–11% of the influent TN-load based on different DOs and stripping efficiencies	AOB denitrification was found significant contributor to N <sub>2</sub> O emissions.	Low aeration is recommended without disturbing the nitrification process.
Theoretical study by Pocquet et al. (2016)			SBR	2-P model, including both pathways for AOB	AQUASIM	EF <sub>N2O</sub> = 1% of the influent NH <sub>4</sub> <sup>+</sup> -N load	AOB denitrification pathway was dominant	The model confirmed that the decrease of the NO/N <sub>2</sub> O ratio can be explained by an increase of the AOB denitrification pathway to the detriment of the NH <sub>2</sub> OH oxidation pathway.
Practical study by Duan et al. (2020)	Adelaide, Australia	60,000 PE	SBR	ASMN	Python	2.08 tonnes of CO <sub>2e</sub> /year EF <sub>N2O</sub> = 0.58% of the influent TN-load	NH <sub>2</sub> OH oxidation pathway was found dominant	Intermittent aeration with a tight DO (2 mg O <sub>2</sub> /L) set point strategy could mitigate the EF levels by 0.2%
Practical study by Zaborowska et al. (2019)	Slupsk WWTP	220,000 PE	A2O configuration	ASM2d-N <sub>2</sub> O	GPS-X	EF <sub>N2O</sub> = 1.6% of the influent TN-load	DHET denitrification was found to be the main pathway of N <sub>2</sub> O production under both anoxic and aerobic conditions.	NH <sub>2</sub> OH oxidation, AOB denitrification and DHET denitrification pathways included. Strategies to minimize N <sub>2</sub> O production via decreasing dissolved oxygen concentration in the aerobic zone and increasing MLR rate.
Practical study by Blomberg et al. (2018)	Viikinmäki WWTP, Helsinki, Finland	1,100,000 PE	A2O configuration	ASM3-N <sub>2</sub> O	GPS-X	EF <sub>N2O</sub> = 1–3 ppm	NH <sub>2</sub> OH oxidation pathway was found dominant and the model could describe the N <sub>2</sub> O production	NH <sub>2</sub> OH oxidation and DHET denitrification pathways were included, AOB denitrification pathway was not included
Practical study by Arnell et al. (2017)	Käppala WWTP, Stockholm, Sweden	500,000 PE	A2O configuration	Benchmark Simulation Model No. 2 with GHG extension (BSM2G)	MATLAB	N <sub>2</sub> O emission rate = 30 kg N <sub>2</sub> O–N/d	Major N <sub>2</sub> O production and emissions occurred in the aerated zones	Plant-wide model plus LCA analysis, full N <sub>2</sub> O dynamics was not achieved, NH <sub>2</sub> OH oxidation pathway addition to the model is recommended
Practical study by Ni et al. (2015)		50 ML/day	Step-feed full-scale plug-flow activated sludge reactor	ASMN	AQUASIM	EF <sub>N2O</sub> = 0.69% of the influent TN-load (first step) and EF <sub>N2O</sub> = 3.5% of the influent TN-load (second step)	The AOB denitrification pathway decreased and the NH <sub>2</sub> OH oxidation pathway increased along the path of both steps.	The overall N <sub>2</sub> O emission from the step-feed WWTP would be largely mitigated if 30% of the returned sludge were returned to the second step to reduce its biomass nitrogen loading rate

(continued on next page)

Table 1 (continued)

Study	Studied WWTP	Size	Configuration	Model used	Software	N <sub>2</sub> O emission	Main pathway	Remarks
Practical study by Ni et al. (2013)	2 WWTPs in Perth, Australia	4 ML/day and 120 ML/day	Oxidation Ditch and SBR	ASMN	AQUASIM	EF <sub>N2O</sub> = 0.52% of the influent TN-load	NH <sub>2</sub> OH oxidation pathway was found dominant	Only NH <sub>2</sub> OH oxidation pathway was included for N <sub>2</sub> O production during nitrification

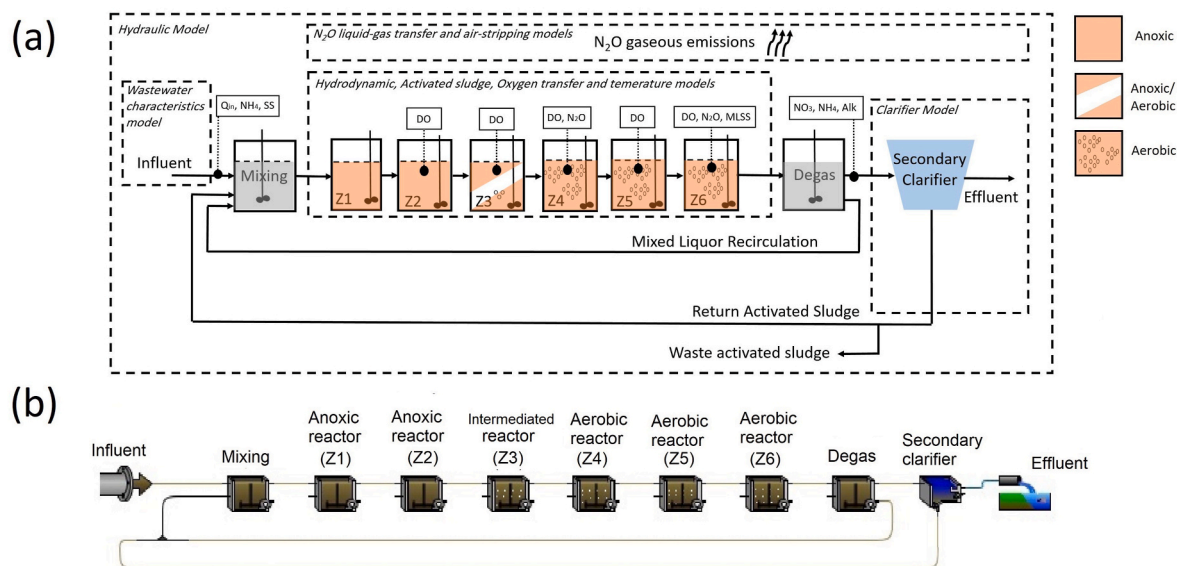


Fig. 1. Configuration of a single activated sludge line at Viikinmäki WWTP: (a) Schematic diagram, (b) GPS-X layout.

pattern of the suspended solids (SS) measurement (Blomberg et al., 2018).

### 2.2.3. Hydraulic model

The hydraulic model of the bioreactor is based on the modified Ludzack-Ettinger (pre-denitrification) process configuration. The model describes the bioreactor compartments and clarifier dimensions, specific liquid flow rates such as, influent wastewater, mixed liquor recirculation (MLR), return activated sludge (RAS) and mixed liquor flow rates between the bioreactor compartments (Fig. 1).

### 2.2.4. Hydrodynamic model of the bioreactors

Hydrodynamic models describe the flow patterns inside in the bioreactor compartments. In the absence of tracer measurements, the dispersion coefficient ( $E_L$ ) can be approximated using the following empirical relationship (Murphy and Boyko, 1970):

$$\frac{E_L}{W^2} = 3.118(q_A)^{3.346} \quad (1)$$

where  $q_A$  is the air flow rate per unit reactor volume ( $s^{-1}$ ) and  $W$  is the width of the reactor (m).

With the known  $E_L$ , one of the following hydrodynamics models can be selected: a plug-flow reactor (when  $E_L$  is close to 0), a completely mixed reactor ( $E_L$  greater than 4) or a tank-in-series (TIS), which consists of series of identical completely mixed reactors. The latter model is favorable in the case of deviations from an ideal flow patterns. In order to determine the number of the reactors, the Peclet number ( $Pe$ ) should be calculated using Eq. (2) (Makinia and Zaborowska, 2019):

$$Pe = \frac{uL}{E_L} \text{ in the axial direction} \quad (2)$$

where  $u$  is the mean velocity along a reactor (m/s) and  $L$  is the reactor's length (m).

Finally, the equivalent number of the completely mixed tanks ( $N$ ) can be found from the following formula (Laurent et al., 2014):

$$N = \frac{Pe}{2} \quad (3)$$

Potier et al. (2005) proposed an empirical relationship between the actual equivalent number of reactors ( $N$ ) and the mean hydraulic residence time (HRT) (Fig. S1 in the SI). By estimating the mean HRT, it would be possible to validate number  $N$  based on the empirical relationship. Table S3 in the SI provides the data and assumptions used for determining the hydrodynamic model of the reactors.

### 2.2.5. Biokinetic model of the bioreactor

The biokinetic model was developed as an extension of the International Water Association (IWA) ASM2d (Henze et al., 2000). The ASM2d-N<sub>2</sub>O model expanded with the N<sub>2</sub>O module was proposed by Zaborowska et al. (2019). In the conceptual model shown in Fig. 2a, three N<sub>2</sub>O production pathways were considered, including the final product of autotrophic denitrification mediated by AOB, an intermediate product of NH<sub>2</sub>OH oxidation by AOB and denitrifying heterotrophic bacteria (DHET) denitrification. For all the N<sub>2</sub>O production pathways, the conceptual model proposed by Lu et al. (2018) was adopted. The model comprised three enzymatic reactions mediated by AOB: (i) NH<sub>4</sub><sup>+</sup> oxidation to N<sub>2</sub>O, (ii) NH<sub>4</sub><sup>+</sup> oxidation to nitrite (NO<sub>2</sub><sup>-</sup>), (iii) NO<sub>2</sub><sup>-</sup> reduction to N<sub>2</sub>O, and three sequential reactions mediated by DHET: (i) NO<sub>3</sub><sup>-</sup> reduction to NO<sub>2</sub><sup>-</sup>, (ii) NO<sub>2</sub><sup>-</sup> reduction to N<sub>2</sub>O, (iii) N<sub>2</sub>O reduction to nitrogen gas (N<sub>2</sub>). In the DHET pathway it is important to account for the simultaneous production and consumption of N<sub>2</sub>O (Fig. 2b). Further details, including the process rate equations and stoichiometric matrices, are available in the SI (Tables S4 and S5).

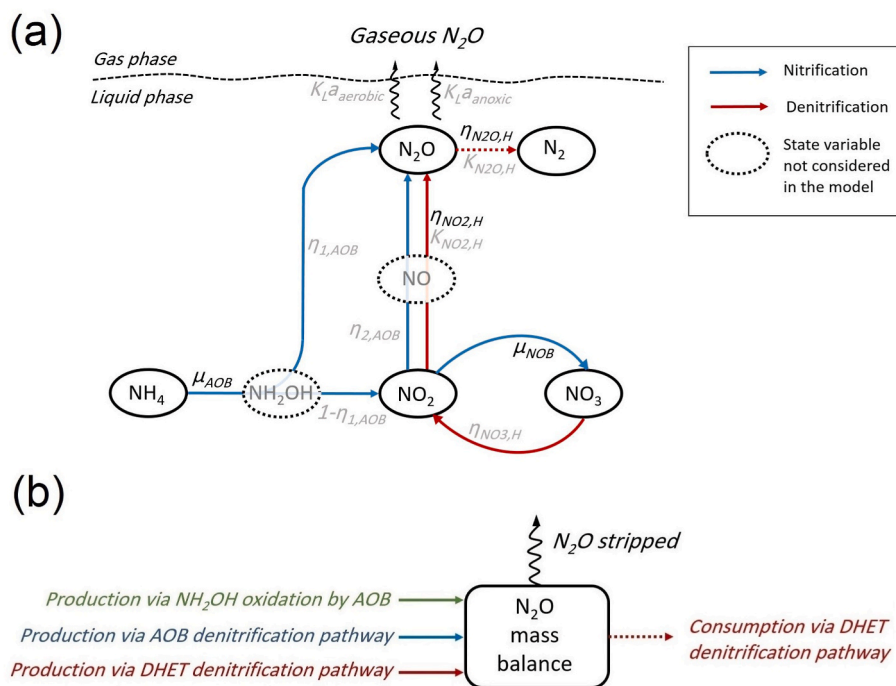


Fig. 2. (a) Mechanisms of  $\text{N}_2\text{O}$  production and consumption (the shown kinetic parameters were adjusted based on the process engineering approach and system engineering approach (only black)), (b) Overall  $\text{N}_2\text{O}$  mass balance in the reactor compartment.

### 2.2.6. $\text{N}_2\text{O}$ emission model

Two different  $\text{N}_2\text{O}$  emission models, described in the SI (section S.1.1) were used separately for the aerated and non-aerated (anoxic) compartments, both developed originally by Schulthess and Gujer (1996). These models were previously applied to predict  $\text{N}_2\text{O}$  emissions in full-scale bioreactors (Baresel et al., 2016). Two methods for the oxygen mass transfer coefficient ( $K_{L,a}$ ) calculations were investigated and compared in this study (see: SI section S.2 for details). The first method comprised  $K_{L,a}$  estimation based on the oxygen transfer rate (OTR) in the

reactor under field conditions. Alternatively,  $K_{L,a}$  was estimated based on the superficial gas velocity in the reactor (method 2). Finally, in the stripping formulae for the aerobic compartments,  $K_{L,a \text{ aerobic}}$  was estimated based on the OTR approach (Marques et al., 2016), which induced 10–20% increase in emissions compared to Foley et al. (2010) empirical method. Stripping was incorporated directly in GPS-X whereas in Blomberg et al. (2018) it was calculated using macros. The direct calculation in GPS-X resulted in lower predicted emissions. For the anoxic compartments, the saturation-induced liquid-gas transfer for  $\text{N}_2\text{O}$

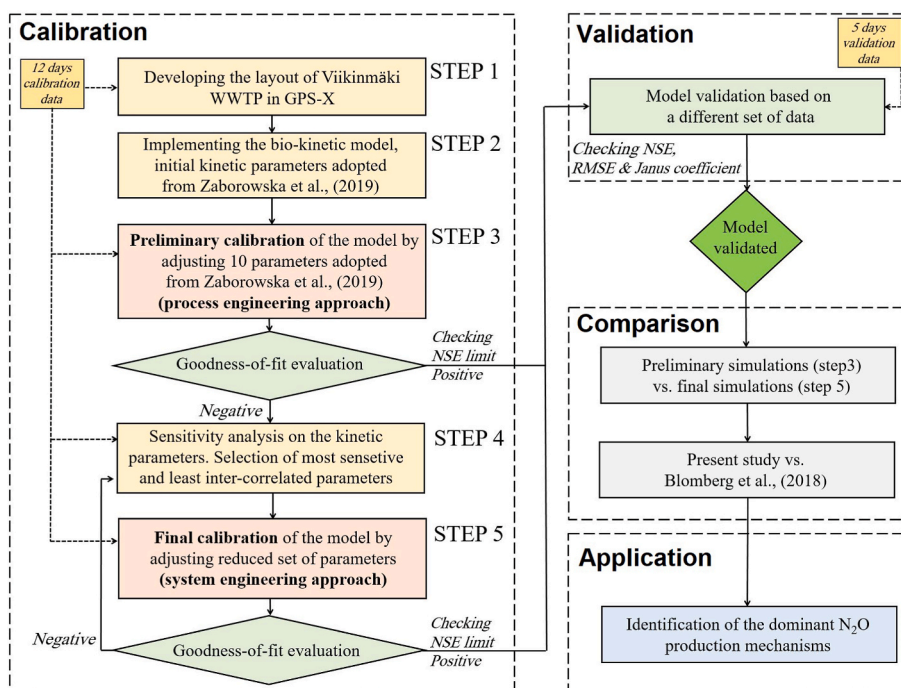


Fig. 3. Systematic step-wise approach to model calibration, validation, comparison and utilization used in the present study.

( $K_{1A}^{\text{anoxic}}$ ) was assumed at  $2 \text{ d}^{-1}$  which has widely been used in the literature (Foley et al., 2010; Schulthess and Gujer, 1996; Zaborowska et al., 2019).

The  $\text{N}_2\text{O}$  EF (%) in this study was determined based on the percentage ratio of absolute modeled  $\text{N}_2\text{O}$  emitted from the exhaust channel (kg  $\text{N}_2\text{O}$ ) to the total influent TN-load (kg TKN) and calculated as:

$$EF_{\text{N}_2\text{O}} = \frac{\text{Total } \text{N}_2\text{O emissions}}{\text{Influent TN - load}} \cdot 100\% \quad (4)$$

Moreover, the  $\text{N}_2\text{O}$  EFs functional units are occasionally reported in the literature based on other ratios, such as,  $\text{N}_2\text{O}$  emitted to the atmosphere to total removed load of nitrogen or  $\text{NH}_4^+\text{-N}$ .

### 2.3. Model application procedure

The proposed model was calibrated and validated using a systematic step-wise protocol as shown in Fig. 3. In step 1, the process layout of the Viikinmäki WWTP was developed, considering the influent characteristics, and the assumed hydraulic and hydrodynamics models. In step 2, the bio-kinetic model was implemented with the values of kinetic parameters adopted from Zaborowska et al. (2019). In step 3, preliminary calibration was performed based on the process engineering approach adjusting 10 parameters adopted from Zaborowska et al. (2019). The target variables selected for calibration were the concentrations of  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_3^-\text{-N}$ , alkalinity, liquid  $\text{N}_2\text{O}$  and gaseous  $\text{N}_2\text{O}$ . Subsequently, the preliminary predictions were evaluated based on the goodness-of-fit criteria. The model results would be approved if both Nash-Sutcliffe coefficient (NSE) and root mean square error (RMSE) limit conditions were satisfied, i.e.  $\text{NSE} > 0.3$  and  $\text{RMSE} < 0.5$  (the limits adopted from Dai et al. (2017)).

In the case of unsatisfactory results after step 3, the final calibration would be performed based on the system engineering approach. Therefore, local sensitivity analysis (LSA) was carried out in step 4 in order to determine the most influential kinetic parameters. Subsequently, a correlation matrix between the detected influential parameters was determined to eliminate highly correlated parameters and minimize the number of adjusted parameters during the final calibration stage.

In step 5, the reduced set of parameters was estimated using the optimizer utility in GPS-X based on the Nelder-Mead simplex method with the maximum likelihood objective function. If the predictions could not pass the goodness-of-fit criteria, then further calibration should be done by repeating steps 4 and 5 until achieving the satisfactory results.

On the other hand, if the calibrated model passed the test, it would be validated based on another data set. During the validation phase, the model was evaluated based on the same criteria as for calibration and further verified the Janus coefficient. If the model was validated successfully, the final results could be compared with the preliminary results and the previous modelling study performed on Viikinmäki WWTP by Blomberg et al. (2018). The validated model was further applied for  $\text{N}_2\text{O}$  formation pathways analysis.

### 2.4. LSA and correlation matrix

In order to evaluate model uncertainty and reduce the number of adjusted parameters, LSA was carried out (equation (5)) using a 'one-variable-at-a-time' (OAT) approach by adjusting a perturbation value  $\Delta x_j$  of 10% ( $\pm 5\%$  of the adjusted value). Different perturbation values,  $\Delta x_j$ , have been reported in the literature ranging from 0.01 to 100% with 10% is being most frequently used in the literature since assuming  $\Delta x_j$ , too small will result in numerical inaccuracies and on the other hand,  $\Delta x_j$  should not be too large because then the nonlinearity of the model will affect the sensitivity calculations (Makinia and Zaborowska, 2019).

$$S_{ij} = \left| \frac{\Delta y_{ij} \cdot x_j}{y_i \cdot \Delta x_j} \right| \quad (5)$$

where the  $S_{ij}$  coefficient is the ratio of the percentage change ( $\Delta y_{ij} / y_i$ ) in the  $i$ th output variable ( $y_i$ ) to the percentage change ( $\Delta x_j / x_j$ ) in the  $j$ th model parameter ( $x_j$ ). The kinetic parameters were classified as extremely influential when  $S_{ij} \geq 2$ .

The tool used for sensitivity analysis was the GPS-X simulation platform (Hydromantis, Canada) which only supports the LSA. Previously reported studies, e.g. Cosenza et al. (2013), favoured global sensitivity analysis (GSA) over LSA due to the fact that GSA accounts for the interactions between kinetic coefficients simultaneously and examining different parameter values as the combinations of them. To overcome this deficiency of LSA, in the present study, the LSA was combined with the correlation matrix analysis of kinetic parameters in the calibration process. Consequently, the interactions between parameters for each target variable were considered. Furthermore, by developing the correlation matrix of the adjusted parameters, the number of the calibrated parameters were reduced by overlooking the highly correlated pairs of parameters. Zhu et al. (2015) proposed to classify parameters as highly correlated if the correlation coefficient of a pair of parameters is high enough ( $r > 0.9$ ). Then optimization can be done by adjusting only the most influential kinetic parameter.

### 2.5. Goodness-of-fit evaluation

In order to evaluate the efficiency of model predictions, appropriate goodness-of-fit measures should be determined in the calibration and validation stage of the modelling study. Verification of goodness-of-fit of the models after calibration was determined using both NSE and RMSE criteria. The mean absolute error (MAE) was examined in addition to the RMSE. Finally, the Janus coefficient was calculated in order to validate the model. Those criteria are described in more detail in the SI (section S.3). Al-Hazmi et al. (2021) compared NSE and RMSE and found a poor correlation among them. Therefore, it was recommended to evaluate the model with more than one criterion to improve evaluation of the prediction accuracy.

### 2.6. Model comparison

When comparing the two models applied for the Viikinmäki WWTP, the main conceptual difference refers to the approach for nitrogen conversion pathways and intermediates of nitrification and denitrification. In terms of  $\text{N}_2\text{O}$  production by AOB, the present model considers the 3-step two-pathway model, including  $\text{NH}_2\text{OH}$  oxidation and denitrification by AOB (Fig. 2). In contrast, the previous model (Blomberg et al., 2018) neglected the role of autotrophic denitrification. In terms of  $\text{N}_2\text{O}$  production and consumption by heterotrophs, the present model applies 3-step heterotrophic denitrification, while the previous model considered the additional intermediate (NO).

In general, similar emission models were applied as an extension to ASMs in both studies. The identical equations were used for the air-stripped  $\text{N}_2\text{O}$  emission (aerobic compartments) and saturation-induced liquid-gas transfer for  $\text{N}_2\text{O}$  (anoxic compartments). However, for the aerobic compartments, different methods were proposed for calculations of the mass transfer coefficient for oxygen and  $\text{N}_2\text{O}$ . In the present model, following the approach of (Zaborowska et al., 2019), the  $K_{1A}$  of oxygen was estimated based on the OTR of the reactor at field conditions to maintain the DO at the desired set-point. In the previous model,  $K_{1A}$  was determined from an empirical formula based on the superficial gas velocity in the reactor. Both methods are described in detail in the SI (see: Section S.2).

## 3. Results and discussion

### 3.1. Hydrodynamic model

With the known dimensions and average air flow rate in the reactors,

the  $E_L$  coefficient,  $E_L$ , and  $Pe$  number, were estimated at 11.7 m<sup>2</sup>/s and 16.2, respectively. The hydrodynamics of the reactors was described by the TIS model and the actual number of the equivalent tanks was  $N = 8$ . The  $N$  number was then validated with the known mean residence time (120 min) and the empirical relationship of Potier et al. (2005) (Fig. S1).

For comparison, in the literature, the equivalent number of tanks ranged from 5 to 20 (Potier et al., 2005). Typical aeration reactors have shown mixing patterns to be equivalent to 3–12 tanks (Makinia and Zaborowska, 2019).

### 3.2. Evaluation of kinetic parameters

The initial values of kinetic parameters were adopted from Zaborowska et al. (2019) (Table S6 in the SI). The preliminary calibration of those 10 kinetic parameters was carried out based on the process engineering approach. Due to unsatisfactory results (NSE lower than 0 for N<sub>2</sub>O liquid concentration), re-calibration (final calibration) was necessary following the systematic protocol (Fig. 3).

#### 3.2.1. LSA

The results of LSA performed on the set of 10 parameters, which were adjusted during preliminary calibration, are shown in Fig. 4. The target variables for sensitivity of each parameter were the concentrations of NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N, alkalinity, liquid N<sub>2</sub>O in the last aerobic compartment and accumulative N<sub>2</sub>O emissions from the anoxic and aerobic compartments. The total sensitivity of the parameters, considering all five defined target variables, were determined. The N<sub>2</sub>O reduction factor for DHET ( $\eta_{N2O,H}$ ), NO<sub>2</sub><sup>-</sup> reduction factor for DHET ( $\eta_{NO2,H}$ ) and AOB maximum specific growth rate ( $\mu_{AOB}$ ) were most influential with the highest  $S_{ij} = 4.4, 3.3$  and  $2.5$ , respectively. Due to the controlled alkalinity at Viikinmäki WWTP, alkalinity was excluded from the further optimization step. Moreover, since the N<sub>2</sub>O emission model was highly influenced by the liquid N<sub>2</sub>O concentration, the sensitivity coefficients for both targets (liquid and gaseous N<sub>2</sub>O) were similar (Fig. 4). For the remaining three target variables (NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N and liquid N<sub>2</sub>O), the set of four most influential parameters, i.e.  $\eta_{N2O,H}$ ,  $\eta_{NO2,H}$ ,  $\mu_{AOB}$  and maximum specific growth rate of NOB ( $\mu_{NOB}$ ), was used for optimization.

#### 3.2.2. Correlation matrix

Table 2 shows the correlation between pairs of the adjusted parameters. In the present study, there was a high correlation (the absolute value > 0.9) between the NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> reduction factors for DHET ( $\eta_{NO3,H}$  and  $\eta_{NO2,H}$ ). Due to this high correlation and higher influence of

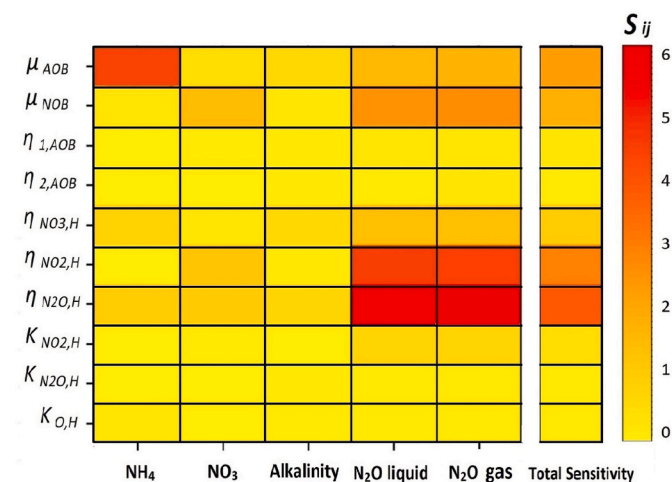


Fig. 4. Sensitivity coefficients of the adjusted parameters during model calibration.

Table 2  
Correlation matrices of the parameters with the highest overall  $S_{ij}$ .

$\mu_{AOB}$	1				
$\mu_{NOB}$	-0.71	1			
$\eta_{NO3,H}$	-0.68	0.29	1		
$\eta_{NO2,H}$	0.86	-0.90	-0.98	1	
$\eta_{N2O,H}$	-0.36	0.89	0.82	-0.90	1
	$\mu_{AOB}$	$\mu_{NOB}$	$\eta_{NO3,H}$	$\eta_{NO2,H}$	$\eta_{N2O,H}$

$\eta_{NO2,H}$  in comparison with  $\eta_{NO3,H}$  (Fig. 4),  $\eta_{NO2,H}$  was selected for the final calibration. Furthermore,  $\eta_{NO2,H}$  also showed high correlations (0.9) with  $\mu_{NOB}$  and  $\eta_{N2O,H}$ . This high correlation refers to NO<sub>2</sub><sup>-</sup> related processes during heterotrophic denitrification. While NO<sub>2</sub><sup>-</sup> is reduced to N<sub>2</sub>O ( $\eta_{NO2,H}$ ), N<sub>2</sub>O is subsequently reduced to N<sub>2</sub> gas ( $\eta_{N2O,H}$ ). Both processes, i.e., N<sub>2</sub>O production and consumption, occur simultaneously.

All the adjusted parameters in this study (Table S6) fall within the range reported in the literature (Zaborowska et al., 2019). The most influential parameters were adjusted during both preliminary and final calibration. The remaining coefficients showed a smaller influence or were highly correlated with one of the most influential parameters. Therefore,  $\eta_{NO3,H}$  was excluded during the final calibration. The reduced set of parameters adjusted during final calibration is shown in Fig. 5.

### 3.3. Simulation results of inorganic nitrogen compounds

Model predictions were first fitted to the measured NH<sub>4</sub><sup>+</sup>-N concentrations by adjusting only the most influential parameter ( $\mu_{AOB}$ ). Fig. 6a and c present the model predictions for NH<sub>4</sub><sup>+</sup>-N concentrations in the last aerobic compartment (bioreactor effluent) during the final calibration and validation steps. The model predictions were able to follow the NH<sub>4</sub><sup>+</sup>-N dynamics in both calibration and validation periods

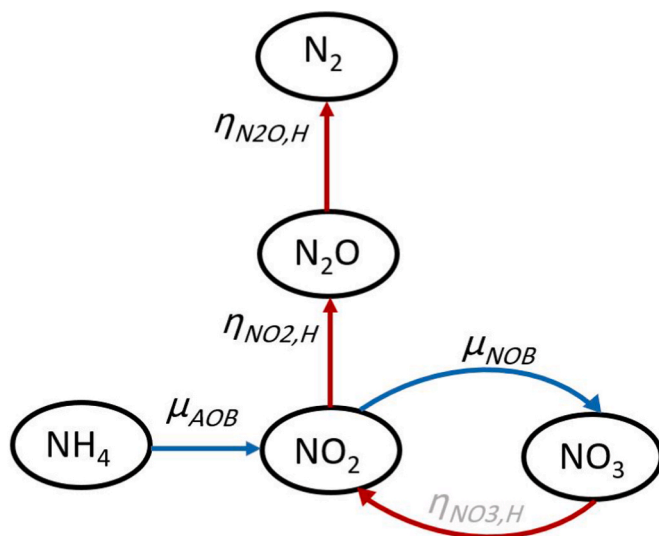
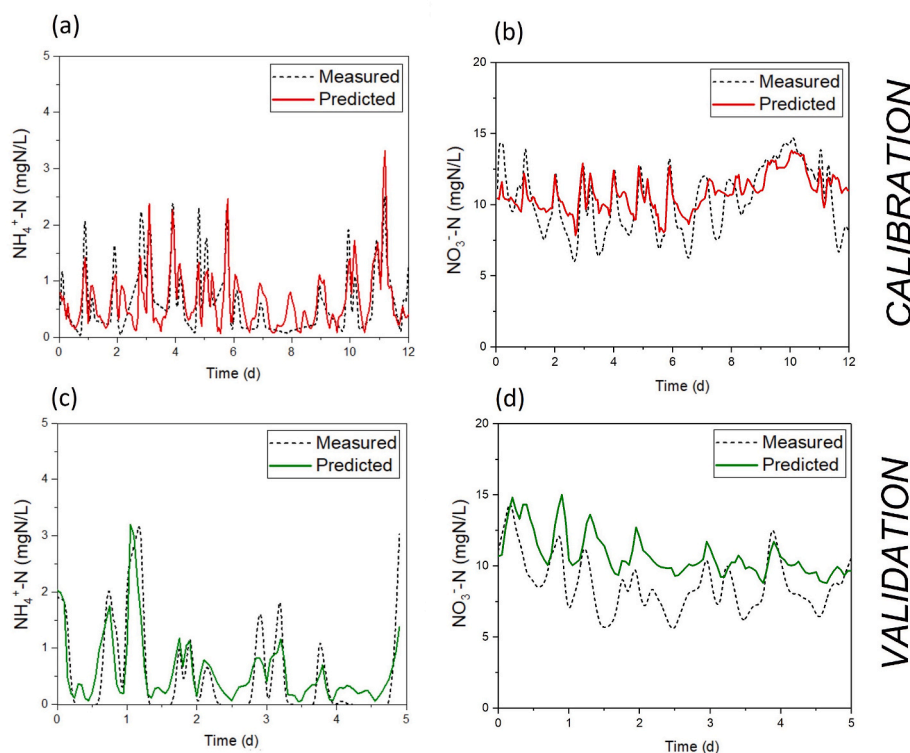


Fig. 5. Kinetic parameters adjusted during final calibration (based on system engineering approach).



**Fig. 6.** Predicted (solid line) and measured (dashed line) in the last aerobic compartment (bioreactor effluent): (a)  $\text{NH}_4^+\text{-N}$  and (b)  $\text{NO}_3^-\text{-N}$ , concentrations during calibration (red), (c)  $\text{NH}_4^+\text{-N}$  and (d)  $\text{NO}_3^-\text{-N}$ , concentrations during validation (green).

**Table 3**

Goodness-of-fit of the model predictions expressed as the NSE, MAE, RMSE and Janus coefficients.

Parameter	Goodness-of-fit measure	This study		Blomberg et al. (2018) calibration
		Calibration	Validation	
$\text{NH}_4^+\text{-N}$	NSE	0.55	0.67	0.28
	RMSE	0.39	0.48	0.50
	MAE	0.30	0.36	0.37
	Janus		1.49	
$\text{NO}_3^-\text{-N}$	NSE	0.47	0.10	-0.27
	RMSE	1.66	1.87	2.58
	MAE	1.37	1.51	2.08
	Janus		1.12	
Liquid $\text{N}_2\text{O}$	NSE	0.35	-0.17	0.26
	RMSE	0.02	0.03	0.03
	MAE	0.02	0.03	0.02
	Janus		1.33	
$\text{N}_2\text{O}$ emission	NSE	0.33	0.30	-0.95
	RMSE	0.41	0.38	0.70
	MAE	0.31	0.27	0.62
	Janus		0.82	

and passed the goodness-of-fit tests for all the criteria (Table 3).

In the final calibration,  $\mu_{\text{NOB}}$  and  $\eta_{\text{NO}_2, \text{H}}$  were adjusted to predict the  $\text{NO}_3^-\text{-N}$  concentrations in the last aerobic compartment. Fig. 6b and d show the  $\text{NO}_3^-\text{-N}$  predictions in the final calibration and validation steps, respectively. The  $\text{NO}_3^-\text{-N}$  concentration dynamics is directly related to denitrification, and thereby, to the variations in the influent organic load. The plant received less organic load during the weekends (days 9–11 during calibration and days 3–5 during validation) which resulted from a smaller amount of industrial wastewater in that period.

### 3.4. Simulation results of $\text{N}_2\text{O}$ production and emission

Fig. 7 presents the dynamic predictions of liquid  $\text{N}_2\text{O}$  and  $\text{N}_2\text{O}$  emissions from the bioreactor. In terms of the liquid  $\text{N}_2\text{O}$  concentration, the model accurately predicted the behavior for the last aerobic zone (Z6), while the predictions were less accurate for the first aerobic zone (Z4). This behavior could be attributed to sudden surges in the liquid  $\text{N}_2\text{O}$  concentration which occurred in the preceding intermediate zone (Z3). Regarding the  $\text{N}_2\text{O}$  emission model, the dynamics of the measured  $\text{N}_2\text{O}$  emissions were captured while maintaining the base level of those emissions in both calibration and validation periods (Fig. 7c and f).

Based on the model predictions of  $\text{N}_2\text{O}$  emission during the calibration period (Fig. 7c), the calculated EF was 0.94% of the influent TN-load. The latest Intergovernmental Panel on Climate Change (IPCC) guidelines recommended the EF of 1.6% of the influent TN-load which is the average of the available literature data (IPCC, 2019). The EF reported by IPCC (2019) is frequently used as an empirical model in the CF assessments to predict the released  $\text{N}_2\text{O}$  from wastewater. The difference of the specific modeled  $\text{N}_2\text{O}$  EF in the present study and the IPCC (2019) empirical EF, would result in approximately 10 kg  $\text{N}_2\text{O}/\text{d}$  difference in the predicted emission rate. This means that, in comparison to the mechanistic models, the empirical model would overestimate 952 ton  $\text{CO}_2$  equivalent annually.

Foley et al. (2010) reported 1.57% of the removed N-load EF, which is the reference  $\text{N}_2\text{O}$  EF applied in CF calculation tools, e.g. (CFCT, 2014). For comparison, the reported  $\text{N}_2\text{O}$  EFs for other processes are typically higher than those for nitrification/denitrification, e.g. 6% of the removed  $\text{NH}_4^+\text{-N}$  load for nitrification (Gustavsson and La Cour Jansen, 2011), and 3% of the removed N-load for partial nitrification/anammox (Kampschreur et al., 2009).



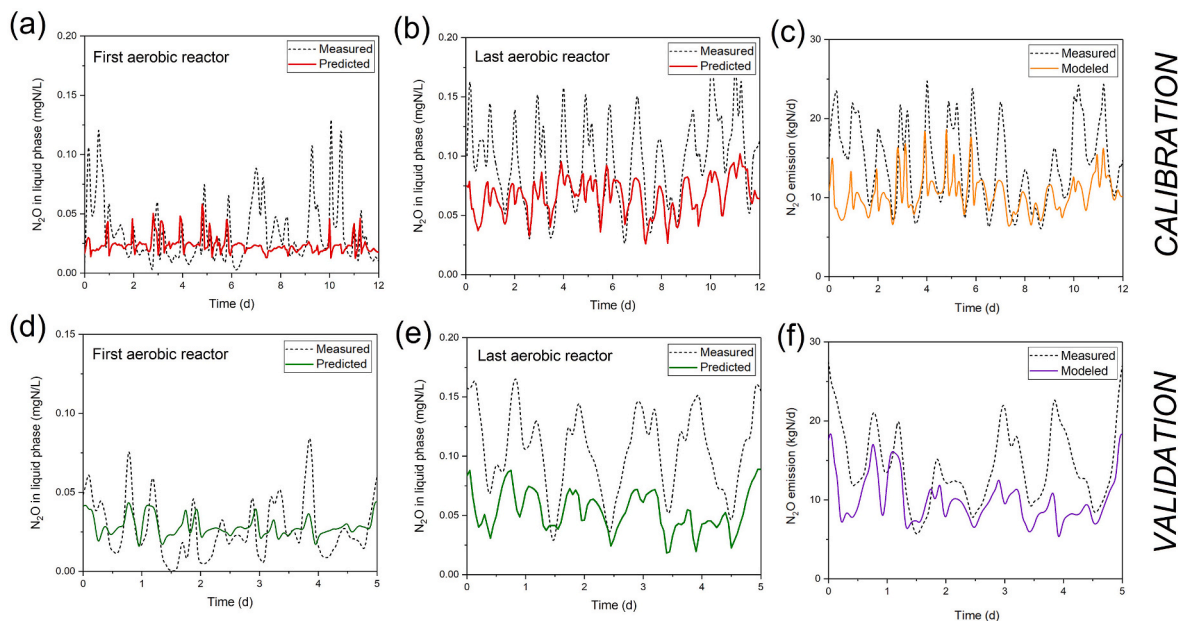


Fig. 7. Predicted (solid line) and measured (dashed line): (a) liquid N<sub>2</sub>O concentration in the first aerobic zone (Z4), (b) liquid N<sub>2</sub>O concentration in the last aerobic zone (Z6), (c) total N<sub>2</sub>O emissions from the biological reactor during calibration; (d) liquid N<sub>2</sub>O concentration in Z4, (e) liquid N<sub>2</sub>O concentration in Z6, (f) total N<sub>2</sub>O emissions from the biological reactor during validation.

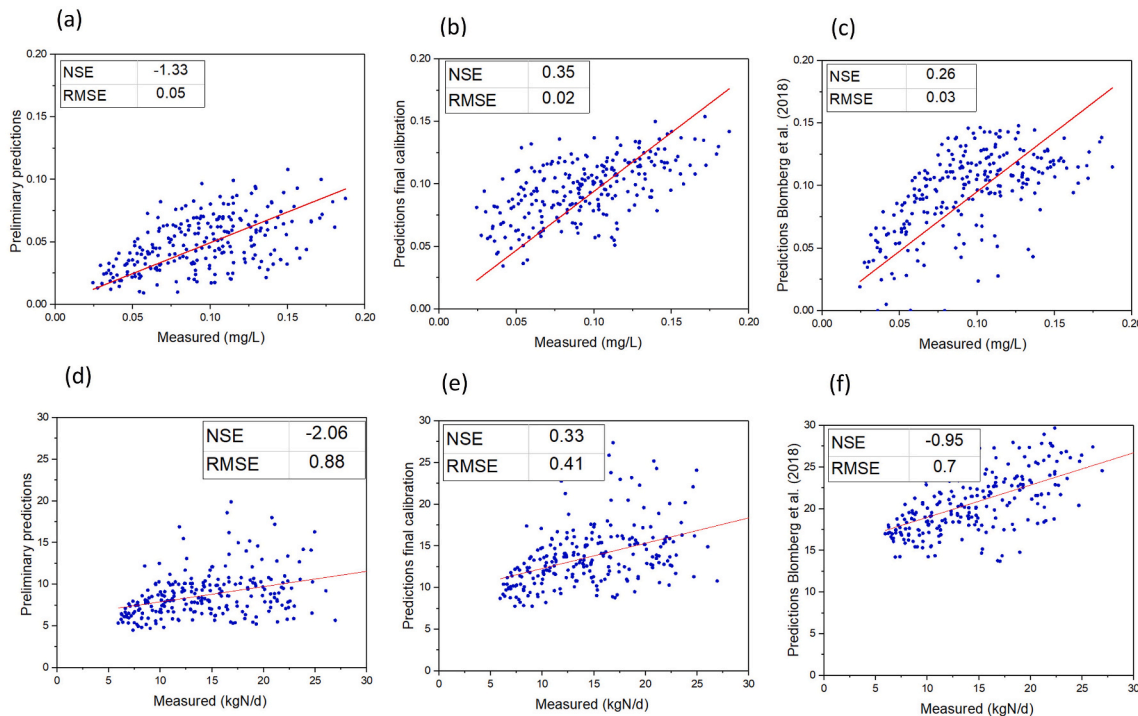


Fig. 8. Model predictions vs. measured data for liquid N<sub>2</sub>O concentration in the last aerobic zone (Z6) for: (a) preliminary calibration, (b) final calibration (with the reduced set of parameters), (c) predictions by Blomberg et al. (2018); and model predictions vs. measured data for N<sub>2</sub>O gas emissions for: (d) preliminary calibration, (e) final calibration, (f) predictions by Blomberg et al. (2018).

### 3.5. Comparison of model predictions

#### 3.5.1. Comparison of preliminary and final simulation results

The measured data against model predictions for N<sub>2</sub>O liquid concentration in the last aerobic compartment (Z6) and overall N<sub>2</sub>O emission are shown in Fig. 8. By optimizing the reduced set of 4 parameters, the model could equally well predict the N<sub>2</sub>O emissions, in comparison with the case of adjusting 10 parameters during the preliminary

calibration. Fig. 8b shows that the NSE and RMSE coefficients for the liquid N<sub>2</sub>O concentration were significantly improved in comparison with the preliminary simulations (Fig. 8a). During the preliminary simulations, the liquid N<sub>2</sub>O concentration was underestimated and thus the negative NSE was achieved. This issue was overcome after the final calibration using the system engineering approach when the acceptable goodness-of-fit measure was achieved (NSE = 0.35).

For the N<sub>2</sub>O emissions, the model predictions were less accurate.

After the preliminary calibration, the emissions were underestimated which resulted in a negative NSE (Fig. 8d). The stripping model was highly influenced by the liquid  $N_2O$  concentration. Therefore, due to the underestimation of liquid  $N_2O$  (Fig. 8a), the gaseous emissions were also underestimated. This issue was overcome during the final simulation and the model could better predict the emissions with  $NSE = 0.33$  (Fig. 8e).

### 3.5.2. Comparison of simulation results with the previous study

The previous modelling study was performed by Blomberg et al. (2018) who applied another model on the same set of data for the calibration and validation periods. The extended ASM3 model was implemented considering  $NH_2OH$  oxidation and heterotrophic denitrification pathways. It was reported that the model was able to predict the liquid  $N_2O$  concentration accurately, while regarding the emissions, the model was capturing the dynamics of the measured  $N_2O$ . However, the base level of the model predictions was higher in comparison with the measured emissions.

Fig. 8b and c show that both modelling studies, i.e. (Blomberg et al., 2018) and the present study, could equally well predict the biological  $N_2O$  productions in the liquid phase. In terms of  $N_2O$  emissions, the model predictions were improved in this study (Fig. 8e) in comparison with the study of Blomberg et al. (2018) (Fig. 8f) based on the different implementation of stripping as described in section 2.2.6. A similar comparison of the simulation results for other nitrogen compounds is available in the SI (Figs. S2 and S3 for  $NH_4^+-N$  and  $NO_3^--N$  concentrations, respectively). Furthermore, the OTR method employed, in this study for determination of the  $K_{La}$  of oxygen, enhanced the model predictions of  $N_2O$  emissions (see: Fig. S7 in the SI).

Good prediction accuracy was confirmed by the low values of MAE and RMSE obtained for all the targets (Table 3). The MAE values were found very similar for the calibration and validation periods. In order to further evaluate the validated model, the Janus coefficient was calculated for all four analyzed target variables ( $NH_4^+-N$ ,  $NO_3^--N$ , liquid  $N_2O$

and  $N_2O$  emission). The results showed that the Janus coefficient remained close to 1 in all the cases. This indicates that the model prediction accuracy in the validation period was similar to the calibration period.

### 3.6. Model application - identifying the dominant $N_2O$ formation pathway

The continuous  $N_2O$  production and consumption rates in the anoxic, intermediate and aerobic compartments are presented in Fig. 9. Fig. 9a shows the  $N_2O$  consumption and production rates in the last anoxic compartment (Z2). In that compartment, the average  $N_2O$  production rate by DHET was 76 mg N/L/d, producing 97% of the total amount of  $N_2O$ , while the remaining production was through the AOB denitrification pathway. Simultaneously, over 99% of the produced  $N_2O$  was consumed in Z2, leaving the emitted  $N_2O$  rate as low as 0.08 mg N/L/d. The model prediction revealed that DHET served as a net  $N_2O$  sink in the anoxic compartment.

On the other hand, in the last aerobic compartment (Z6) (Fig. 9b), the average  $N_2O$  production rate by DHET was reduced to 13 mg N/L/d (78% share of the total production rate). The relatively high contribution of DHET to  $N_2O$  production in the aerobic compartment can be justified by the high biomass concentration of DHET (1295 mg COD/L) vs. AOB (78 mg COD/L). At the same time, the specific rate of  $NO_2^-$  heterotrophic reduction to  $N_2O$  was estimated at  $0.02 d^{-1}$  in comparison with  $0.1 d^{-1}$  for the AOB nitrification pathway.

In the aerobic compartment, the share of the  $NH_2OH$  oxidation pathway in the total  $N_2O$  production increased to 20%. As a consequence, the rate of stripped  $N_2O$  increased to 1.4 mg N/L/d making it 17 times greater compared to the anoxic compartment. This is clearly demonstrated in Fig. 9c showing the  $N_2O$  production and emission rates in the intermediate zone (Z3). During the aeration periods, the share of the  $NH_2OH$  oxidation pathway increased and consequently higher amounts of  $N_2O$  were emitted. Within all the zones (Fig. 9d), the aerobic

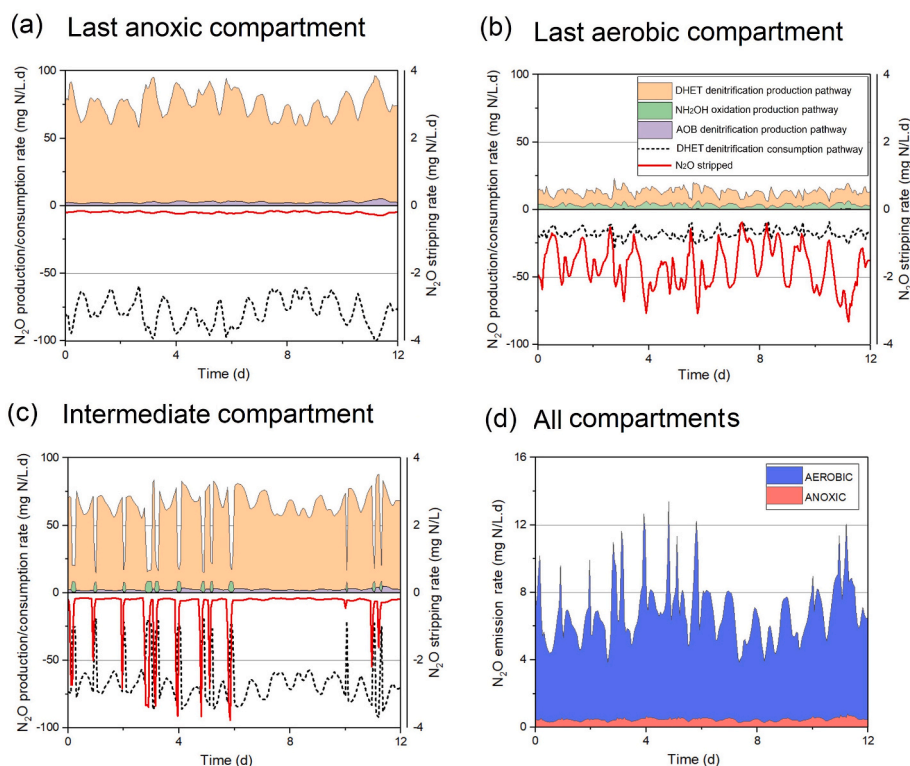


Fig. 9. Model predictions of  $N_2O$  production, consumption and emission rates in the selected compartments: (a) last anoxic zone, (b) last aerobic zone, (c) intermediate zone and (d) the  $N_2O$  emission rate for the whole bioreactor.

compartments contributed on average to over 93% of the emitted  $N_2O$ , while the remaining 7% resulted from the  $N_2O$  liquid-gas transfer in the non-aerated zones.

The contribution of the AOB denitrification pathway was found negligible and confirmed the assumption of the previous modelling study at Viikinmäki WWTP by Blomberg et al. (2018). In the  $N_2O$  model of Blomberg et al. (2018), the AOB denitrification pathway was excluded. Although that pathway was considered in the present study, the results showed that the share of the AOB denitrification pathway in  $N_2O$  production was marginal. In three aerobic compartments, the contribution of that pathway was lower than 2%. The highest share, 3.3% of the total  $N_2O$  production rate, was observed in the last anoxic compartment (Fig. 9a). The predictions of  $N_2O$  production pathways in the other zones are available in the SI (Fig. S4).

The results of this study are consistent with the modelling study of Sun et al. (2017) in terms of the highly descending order from oxic to anoxic tanks for the total  $N_2O$  flux. For the DHET denitrification pathway, both production and consumption rates must be taken into account to reflect the net  $N_2O$  production as shown in Fig. 2b. The study of Conthe et al. (2019) confirmed that denitrification could be an effective sink for  $N_2O$ , potentially scavenging a fraction of the  $N_2O$  produced by  $NH_4^+$  oxidation. Chen et al. (2020c) also pointed out that AOB were  $N_2O$  producers, while DHET were both producers and consumers.

The exact triggering operational and environmental conditions that govern  $N_2O$  production are still under extensive investigation. Table 1 summarizes the full-scale modelling studies, indicating different dominant pathways of  $N_2O$  emission under diverse operational conditions.

The previous modelling study of Blomberg et al. (2018) modeled the  $N_2O$  emissions from the aerobic bioreactors (with the average  $DO \approx 3$  mg  $O_2/L$ ), including the DHET denitrification and  $NH_2OH$  oxidation, and suggested that the latter pathway was the dominant contributor to  $N_2O$  emission. The  $NH_2OH$  oxidation pathway has been reported in the literature for the environments with higher  $DO$  concentrations (Ni et al., 2013; Peng et al., 2015). In contrast, the model of Zaborowska et al. (2019) revealed that the DHET denitrification pathway was predominant in terms of  $N_2O$  production in both anoxic and aerobic reactors. In this study, similar to the studies of Domingo-Félez et al. (2017) and Zaborowska et al. (2019), the model showed the highest  $N_2O$  production and consumption through the DHET denitrification pathway in both aerated and non-aerated compartments. The actual role of DHET denitrification in  $N_2O$  production in the aerobic zones with different  $DO$  levels should be investigated in depth in future studies including gene activity measurements. Data from the analyzed gene expression would help identify the key pathways and microbial groups responsible for nitrogen metabolism and  $N_2O$  production at specified conditions (Conthe et al., 2019).

Moreover, it was suggested that maintaining the  $DO$  levels between 1 and 2 mg  $O_2/L$  could minimize the overall  $N_2O$  production in the bioreactors. Massara et al. (2018) presented a model including all the biological pathways for  $N_2O$  production in a municipal WWTP with the  $A^2O$  (anaerobic-anoxic-aerobic) biological configuration. Based on theoretical simulations, it was revealed that with the  $DO$  below 1.8 mg  $O_2/L$ , the AOB prevailed over NOB and prompted the shift to decreasing  $NH_4^+$  concentration and  $NO_2^-$  accumulation. The authors reported that in the  $DO$  range of 0.8–1.8 mg  $O_2/L$ , the  $N_2O$  EF was 10% of the removed  $NH_4^+$ -N load, which mainly resulted from the AOB denitrification pathway. Chen et al. (2020b) reported that the  $DO$  concentration would need to be maintained above 2 mg  $O_2/L$  in aerobic phases to satisfy BNR removal and  $N_2O$  mitigation. When the  $DO$  concentration is lower than 2 mg  $O_2/L$ , the nitrification rate decreases and the intermediates, such as  $N_2O$  and  $NH_2OH$ , could accumulate in the liquid phase (Li et al., 2020).

### 3.7. Model limitations

Although mechanistic models are powerful tools to predict  $N_2O$  emission from WWTPs, there are limitations found in this comparative study:

- The different findings of the dominant  $N_2O$  production pathways have been based on the model predictions only. In order to validate those results, further detailed analysis would be necessary to obtain site specific data on the actual contributions of AOB and DHET which can be obtained by gene activity measurements.
- The data on both liquid  $N_2O$  concentration and  $N_2O$  emissions in full-scale WWTPs are still limited. Moreover, the developed model only predicted  $N_2O$  emissions in the activated sludge reactors, while other elements (e.g. secondary clarifiers) of the WWTP were not taken into account.

## 4. Conclusions

The direct confirmation of the validated model on another plant was not successful in Viikinmäki WWTP. Therefore, the novel calibration strategy, based on adjusting the most influential and least correlated kinetic coefficients, was developed and successfully applied, which could be exploited in future studies. This allowed to recalibrate the model by optimizing only four kinetic parameters. The re-calibrated model accurately predicted the behavior of both liquid  $N_2O$  in the bioreactor and  $N_2O$  emission in the exhaust channel. The estimated  $N_2O$  EF at the studied plant for the calibration period was 0.94% of the influent TN-load. This value falls in the low range of the reported  $N_2O$  EFs from the literature with the average of 1.6% of the influent TN-load. The difference between the predicted  $N_2O$  EF and the empirical EF would lead to 952 ton  $CO_2$  equivalent reduction of the annual CF of the plant. The model showed the highest  $N_2O$  production and consumption rates for DHET denitrification pathway in all the compartments. Furthermore, the DHET denitrification pathway was an effective sink for the produced  $N_2O$ , while  $NH_2OH$  oxidation was the second contributor to  $N_2O$  produced in the aerobic reactors. The contribution of the AOB denitrification pathway was found negligible. In overall, the aerobic zones contributed to over 93% of the emitted  $N_2O$ , while the remaining portion resulted from the  $N_2O$  liquid-gas transfer in the non-aerated zones.

### CRedit authorship contribution statement

**Mojtaba Maktabifard:** Formal analysis, Methodology, Visualization, Writing – original draft. **Kati Blomberg:** Data curation, Methodology. **Ewa Zaborowska:** Supervision, Methodology, Writing – review & editing. **Anna Mikola:** Conceptualization, Supervision, Writing – review & editing. **Jacek Małkinia:** Conceptualization, Funding acquisition, Project administration.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2021.130347>.

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