

# Calibration and validation of an activated sludge model for greenhouse gases no. 1 (ASMG1): prediction of temperature-dependent N<sub>2</sub>O emission dynamics

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**Abstract** An activated sludge model for greenhouse gases no. 1 was calibrated with data from a wastewater treatment plant (WWTP) without control systems and validated with data from three similar plants equipped with control systems. Special about the calibration/validation approach adopted in this paper is that the data are obtained from simulations with a mathematical model that is widely accepted to describe effluent quality and operating costs of actual WWTPs, the Benchmark Simulation Model No. 2 (BSM2). The calibration also aimed at fitting the model to typical observed nitrous oxide (N<sub>2</sub>O) emission data, i.e., a yearly average of 0.5 % of the influent total nitrogen load emitted as N<sub>2</sub>O-N. Model validation was performed by challenging the model in configurations with different control strategies. The kinetic term describing the dissolved oxygen effect on the denitrification by ammonia-oxidizing bacteria (AOB) was modified into a Haldane term. Both original and Haldane-modified models passed calibration and validation. Even though their yearly averaged values were similar, the two models presented different dynamic N<sub>2</sub>O emissions under cold temperature conditions and control. Therefore, data collected in such situations can potentially permit model discrimination. Observed seasonal trends in N<sub>2</sub>O emissions are simulated well with both original and Haldane-modified models. A mechanistic explanation based on the temperature-dependent interaction between heterotrophic and autotrophic N<sub>2</sub>O pathways was provided. Finally, while adding the AOB denitrification pathway to a model with only heterotrophic N<sub>2</sub>O

production showed little impact on effluent quality and operating cost criteria, it clearly affected N<sub>2</sub>O emission productions.

**Keywords** Climate change · Mathematical modeling · Nitrous oxide · Process control · Temperature

## Introduction

Greenhouse gases (GHGs) are emitted from wastewater treatment plants (WWTPs). Among various kinds and sources of GHGs, nitrous oxide (N<sub>2</sub>O) is of importance due to its large global warming potential (GWP) which is 300 CO<sub>2</sub> equivalents for a time horizon of 100 years [1]. Consequently, the modeling of biological N<sub>2</sub>O production is particularly under debate. N<sub>2</sub>O is produced during nitrogen removal by both heterotrophs and autotrophs. General agreement has been reached on the mechanism of heterotrophic denitrification that is now modeled as a four-step process with N<sub>2</sub>O as intermediate [2–5]. The Activated Sludge Model for Nitrogen (ASMN) proposed by Hiatt and Grady [5] is considered state-of-the-art. Ammonia-oxidizing bacteria (AOB) are also able to produce nitric oxide (NO) and N<sub>2</sub>O [6]. Different experiments and models are still being proposed to study its mechanisms and also to understand the effects of dissolved oxygen (DO), nitrite (NO<sub>2</sub><sup>-</sup>), ammonia (NH<sub>4</sub><sup>+</sup>), hydroxylamine, etc. [7–10].

Benchmarking models, i.e., BSM1 and BSM2, provide a platform to compare the performance of nitrogen removal treatment plants and especially with different control strategies. Implementation of early N<sub>2</sub>O models has already been carried out in the Benchmark Simulation Model No. 2 (BSM2) framework and some scenarios for N<sub>2</sub>O emission mitigation were already discussed [11, 12].

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However, in general, little literature can be found on how well calibrated/validated these BSM models are in view of their use. Still, their development has been based on the combined knowledge of tens of experienced process engineers and modelers and their behavior is widely accepted to be realistic [13]. For the GHG extensions of these models, however, this is less the case. For one thing, the knowledge base has not matured as it has for that of traditional N-removal processes. One particular difficulty is that there is no comprehensive full-scale measured data available for calibration or validation of the new N<sub>2</sub>O models. However, the authors feel that they do not need to wait for such complete data sets to start the reflections on potential process optimizations (e.g., to reduce N<sub>2</sub>O emissions) using models that encapsulate the current insights in the relevant processes. Evidently, before using these models for comparison or testing control strategies, it is still meaningful to make these benchmarking models yield behavior that is as realistic as possible in terms of, on the one hand, traditional performance criteria, e.g., effluent quality and operation cost, and on the other hand N<sub>2</sub>O emissions. This is the basic goal of this paper.

In this contribution, an Activated Sludge Model for GHG No. 1 (ASMG1) was built by combining ASMN [5] and the aerobic AOB denitrification model proposed by Mampaey et al. [9], called original ASMG1. Furthermore, a modification was made to the DO kinetic term of this aerobic AOB denitrification model, called modified ASMG1. Calibration and validation was done for both original and modified ASMG1. Calibration and validation was intended to agree with, on the one hand, the regular BSM2 simulation results, i.e., effluent quality and operation cost, obtained with the existing BSM2 model which implements ASM1 [14], and, on the other hand, to match overall N<sub>2</sub>O emission data from literature reports [15, 16]. Therefore, in this paper, instead of relying on real plants or real measurement data sets, “calibration” is defined as: under certain operation conditions, the parameter values are tuned to match the simulation results of a new model with the results of a former, well-established model, generally accepted to provide a good description of reality. A similar approach has been adopted for the so-called surrogate modeling approach, although the objective there was different, i.e., calibrate a simpler model on the basis of data simulated with a reference model so as to gain calculation time [17, 18]. “Validation” is defined as: under operation conditions that differ from the “calibration” conditions, the simulation results of the new model are compared with the results of the former model. This paper is also meant to inspire future model calibration and validation of this type of models. It provides valuable experience on calibrations of ASMs and the proposed calibration procedure can be modified to use actual data from real plants. Moreover,

certain clues are given on how the still not completely elucidated submodel regarding AOB denitrification can influence the modeling results of the whole ASMG1 model.

## Model implementation and calibration/validation approach

### ASMG1 models and implementation

Two ASMG1 models (Table 1) are discussed in this paper. The original ASMG1 consists of ASMN [5] which extends ASM1 by including 2-step nitrification, 4-step denitrification, and an aerobic AOB denitrification model proposed by Mampaey et al. [9] which assumes that DO has a positive effect on N<sub>2</sub>O production and ammonia donates electrons for nitrite and NO reductions.

The concept of the AOB denitrification model of Mampaey et al. [9] agreed with general ideas in terms of ammonia being used as electron donor [7, 8], and using this model no components (such as hydroxylamine) need to be added to the basis provided by ASMN. One of the most debated aspects regarding the AOB denitrification model is the role of DO [7–10]. Therefore, in the modified ASMG1, a modification was made on the DO kinetic term of the original ASMG1. Some recent research suggests that for N<sub>2</sub>O production by AOB denitrification, a maximum rate occurs at relatively low DO conditions [8, 10]. This behavior may be explained by the hypothesis that a low DO stimulates N<sub>2</sub>O production, while high DO inhibits it, meaning that the influence of DO can be expressed by Haldane kinetics [19]. This kinetic approach is in accordance with and is a simplification of the model proposed by Ni et al. [10]. In the latter model, the production of hydroxylamine is stimulated by DO, while the N<sub>2</sub>O production from hydroxylamine is inhibited by DO. In this paper, the intermediate hydroxylamine is not considered to keep the model simple and does not introduce a component that is hard to measure at full-scale. The overall effect of DO was described by the DO kinetic term defined in Eq. (1):

**Table 1** Two ASMG1–BSM2 models

	Original ASMG1–BSM2	Modified ASMG1–BSM2
ASMN	Hiatt and Grady	Hiatt and Grady
AOB denitrification	Mampaey A	Modified Mampaey
Reduction factor on nitrite reduction	Yes	Yes
Reduction factor on NO reduction to N <sub>2</sub> O	No	Yes
DO kinetics	Monod	Haldane

$$DO_{Haldane} = \frac{S_O}{K_{SO\_AOB\ den.} + \eta_{Haldane} \cdot S_O + S_O^2/K_{IO\_AOB\ den.}} \tag{1}$$

where  $\eta_{Haldane}$ ,  $K_{SO\_AOB\ den.}$  and  $K_{IO\_AOB\ den.}$  are the kinetic parameters.

The Haldane kinetics is presented in Fig. 1. The mathematical structure of this Haldane kinetics is a little different from the traditional structure [19]. The traditional Haldane kinetics never gets to 1 as its maximum, which is different from the Monod kinetics which approaches 1. The proposed modified Haldane kinetics, i.e., Eq. (1), sets 1 as its maximum value to agree with the Monod term. Therefore, in Eq. (1), the parameters can be calculated from the half-saturation DO concentrations,  $S_1$  and  $S_2$ , as usually done for Monod kinetics, while this is not possible for the traditional term:

$$\eta_{Haldane} = 1 - 2\sqrt{K_{SO\_AOB\ den.}/K_{IO\_AOB\ den.}} \tag{2}$$

$$K_{SO\_AOB\ den.} = \frac{S_1 \cdot S_2}{K_{IO\_AOB\ den.}} \tag{3}$$

$$K_{IO\_AOB\ den.} = \left(\sqrt{S_1} - \sqrt{S_2}\right)^2 \tag{4}$$

where  $S_1$  and  $S_2$  are the half-saturation DO concentrations ( $g/m^3$ ).

Besides the modification of the DO kinetic term, two different growth reduction factors,  $\eta_{AOB,1}$  and  $\eta_{AOB,2}$ , were multiplied, respectively, with the kinetic equations of the two AOB denitrification steps, i.e., nitrite reduction to NO (step 1) and NO reduction to  $N_2O$  (step 2), while in the original aerobic AOB denitrification model [9] only the step of nitrite reduction to NO uses the growth reduction factor. The use of the growth reduction factor for both steps is based on the consideration that the maximum growth rate of AOB can be different for denitrification and nitrification reactions.

In summary, the AOB denitrification model was modified as in Eq. (5), Eq. (1) replacing the Monod DO limitation term and multiplying the whole kinetic term by growth correction factors for the first and second step of AOB denitrification,  $\eta_{AOB,1}$  and  $\eta_{AOB,2}$

$$r_{AOB\ den.} = \mu_{AOB} \cdot (\eta_{AOB,1} \text{ or } \eta_{AOB,2}) \cdot DO_{Haldane} \cdot \left\{ \left( \frac{S_{NH}}{S_{NH} + K_{NH\_AOB\ den.}} \right) \cdot \left( \frac{S_{FNA}}{S_{FNA} + K_{FNA\_AOB\ den.}} \right) \text{ or } \frac{S_{NO}}{S_{NO} + K_{NO\_AOB\ den.}} \right\} \cdot X_{AOB} \tag{5}$$

where FNA is free nitrite acid,  $DO_{Haldane}$  is the DO kinetic term as defined in Eq. (1),  $\eta_{AOB}$  is the growth correction factor, and the multiplication term in curly brace is as the term in Mampaey et al. [9].

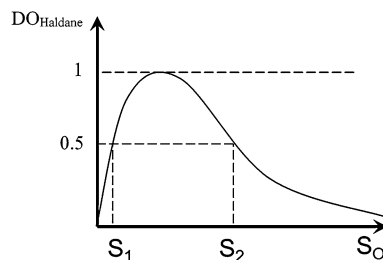
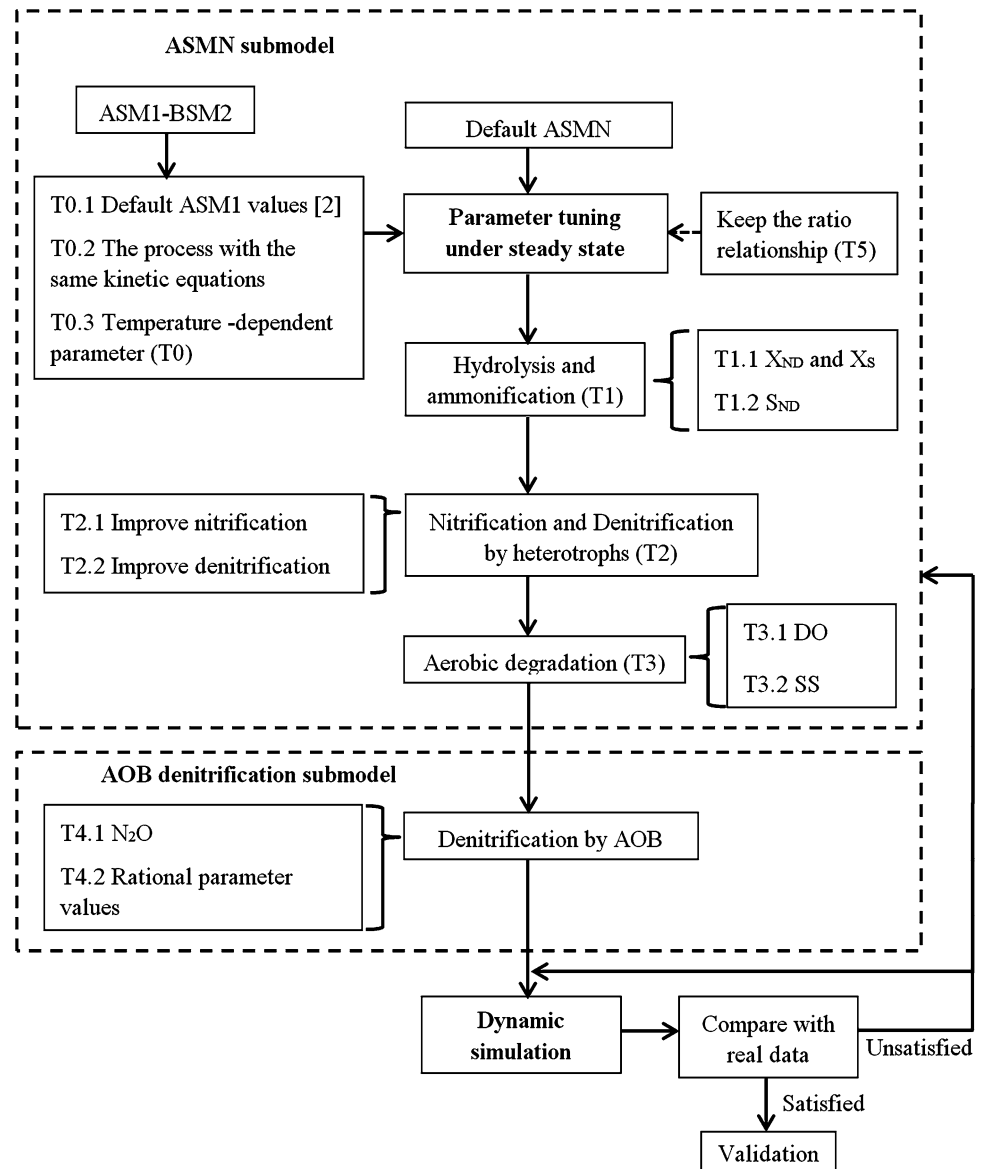


Fig. 1 The kinetic relationship between  $S_O$  and  $DO_{Haldane}$

The modeling and simulation software used is WEST (MIKEbyDHI.com). All ASMG1 models were implemented in the BSM2 whole plant configuration, called original or modified ASMG1–BSM2, respectively, and were run under the same conditions as described in the BSM2 finalization paper which uses ASM1 [14], named ASM1–BSM2. BSM2 describes a whole plant with a water line that includes a primary settler, activated sludge system with 2 anoxic zones (ASU1 and ASU2) and 3 aerobic zones (ASU3, ASU4 and ASU5), a secondary clarifier and a sludge line with a thickener, anaerobic digester and sludge dewatering. Compared to ASM1, ASMG1 does no longer have the variables  $S_{NO}$  (oxidized nitrogen) and  $X_{BA}$  (autotrophic organisms) and new variables were added, i.e., nitrate ( $NO_3^-$ ),  $NO_2^-$ , NO,  $N_2O$ , dinitrogen ( $N_2$ ), AOB and NOB. Therefore, to connect the activated sludge and anaerobic digester sections of the model, new interface models, which transfer components between ASMG1 and ADM1 instead of those of ASM1 and ADM1, were to be used. Since the same set of new variables had already been introduced in the earlier work of Corominas et al. [20], the reader is referred to their detailed description of the interface model.

The paper describing ASM1–BSM2 [14] compares the plant performance in open loop, i.e., without any controller active, and with the performance obtained for three control strategies, i.e., the 1-DO control strategy, the 2-DO control strategy and the cascade control strategy. In the 1-DO control strategy, the DO concentration of the second aerobic zone (ASU4) is maintained by manipulating the oxygen transfer coefficients ( $K_{la}$ ) of all three aerobic zones. In the 2-DO control strategy, the third aerobic zone (ASU5) is controlled individually by a DO controller, while the aeration in the two other reactors (ASU3 and ASU4) is controlled on the basis of the DO concentration of ASU4. In the cascade control system, the first two aerobic zones use the same strategy as in the 2-DO control strategy, but the DO setpoint of the aeration controller of ASU5 is controlled by an ammonia controller, yielding the so-called  $NH_4^+$ -DO cascade control set-up. These ASM1–BSM2 reference results of the open loop and these three control strategies were used to calibrate and validate the ASMG1–BSM2 models. The simulation results in terms of

**Fig. 2** The calibration procedure and the sub-targets of each step



indexes of effluent quality and operation cost for the ASMG1s–BSM2 were evaluated by exactly the same method as used for evaluating the ASM1–BSM2 with the extensions for the new oxidized nitrogen components according to [11]. The evaluation starts from days 245 to 609, day 245 being the 1st of July.

#### Calibration and validation objectives

The ASMG1–BSM2 models were calibrated in open loop and on literature data of yearly  $N_2O$  emissions. It was then validated with the data of the three control strategies of ASM1–BSM2 [14]. The objectives of model calibration thus include fitting the  $N_2O$  emission factor, the effluent quality and the operation cost. Given the fact that BSM2 is a virtual plant, no real  $N_2O$  data are available, but a

realistic value of  $N_2O$  emission can be obtained from literature. For plants with a modified Ludzack–Ettinger (MLE) process, the  $N_2O$  emission factor is in the range of 0.1–1 % of the influent total nitrogen (TN) load [15, 16]. Therefore, for BSM2 which is also a MLE plant, 0.5 % was chosen as the  $N_2O$  emission factor to be reached after model calibration. Effluent quality, including the effluent quality index (EQI) and the yearly averaged effluent concentrations, and the operation cost index (OCI) should agree with the results given in the finalized ASM1–BSM2 [14]. The validation only considered the effluent quality and OCI criteria because no  $N_2O$  emission factor values are currently available for plants running with such controllers.

The difference between the original and modified AOB denitrification model was further explored in terms of  $N_2O$  by comparing their sludge production rates and dynamic

N<sub>2</sub>O emissions. Finally, in open loop, the results of implementing only ASMN into BSM2, termed ASMN–BSM2, were compared with those of the ASMG1s–BSM2 to further evaluate the contribution of the AOB denitrification model in the integrated ASMG1 model.

### Calibration procedure

First, the simulation was run using the default parameter values suggested in the papers of Hiatt and Grady [5] and Mampaey et al. [9] to clarify the gaps with the calibration targets. Then the calibration was done following the procedure illustrated in Fig. 2. This procedure gives the calibration approach and the targets of each step, denoted with “T”. The parameters were tuned under steady-state conditions to make the steady-state results of ASMG1–BSM2 similar to those of ASM1–BSM2 [13]; then the parameter set was used in simulations under dynamic conditions to see whether the results agreed as well. If the dynamic simulation gives good results, the model is subjected to validation; otherwise, the calibration has to be repeated.

The calibration first focuses on adjusting the ASMN parameters and then moves on to the AOB denitrification parameters, because ASMN includes most processes overall (nitrification, denitrification, etc.). In terms of N<sub>2</sub>O emissions, the objective is to obtain a N<sub>2</sub>O emission of ASMN–BSM2 lower than 0.5 % of the influent TN load because it can be expected that some of the overall N<sub>2</sub>O emission will be produced by AOB denitrification. Also, the bioreactor mixed liquor nitrite concentrations of the calibrated ASMN–BSM2 should be low because nitrite is a reactant for N<sub>2</sub>O production through the AOB pathway that will only be evaluated in the next step of the calibration.

The concentrations of particulate biodegradable organic nitrogen ( $X_{ND}$ ), slowly biodegradable substrate ( $X_S$ ) and soluble biodegradable organic nitrogen ( $S_{ND}$ ) were targeted first because they are the sources of readily biodegradable substrate ( $S_S$ ) and ammonia which serve in other process steps. Then the parameter tuning was taken to simulate the nitrogen removal process well, i.e., following Corominas et al. [21] first the ammonia oxidation and nitrite oxidation process and then the denitrification processes, so as to satisfy the nitrate and nitrite concentrations and ultimately the N<sub>2</sub>O gas flux.

The selection of parameters for calibration was based on expert knowledge [22]. Some parameter values were initialized based on ASM1–BSM2 [13], since some processes in ASMG1 have the same kinetic equations as in ASM1, including hydrolysis, ammonification and heterotrophic aerobic organic degradation. It is important to acknowledge that ASMN was proposed for high-strength wastewater in terms of nitrogen load [5], while the BSM2 plant treats typical municipal wastewater. Hence, some of

the parameters in ASMG1–BSM2 should use the commonly accepted values, i.e., the default ASM1 [2], instead of the ASMN defaults. Besides absolute values, for some parameters a fixed ratio relationship was adopted, e.g., the half-saturation coefficients for oxygen and substrate ( $K_{OH}$  and  $K_S$ ) in the aerobic heterotrophic growth and anoxic denitrification, and the growth factor of each denitrification step. The nitrogen conversion in each step can then be adjusted through manipulation of the ratios.

Although the calibration procedure described above was only applied to the BSM2 virtual plant, it has a general application potential which the authors believe can be used for real plant calibration.

## Results

### Calibration

Table 2 gives the results of ASMN–BSM2 before and after calibration. Compared to the results obtained when using default ASMN parameters, the N<sub>2</sub>O emission factor of the calibrated ASMN–BSM2 was significantly reduced to below 0.5 %. This thus gave the possibility of achieving the pursued N<sub>2</sub>O emission factor around 0.5 % by adding AOB denitrification (ASMG1–BSM2). Also, the nitrite concentrations were cut down by the calibration (Table 2)

**Table 2** Open loop BSM2 results obtained with ASMN with default and calibrated parameters

	Default ASMN–BSM2 <sup>a</sup>	Calibrated ASMN–BSM2
N <sub>2</sub> O emission factor <sup>b</sup>	6.42 %	0.36 %
Effluent quality		
Av. $S_{NO_3}$ (g N/m <sup>3</sup> )	7.62	8.40
Av. $S_{NH}$ (g N/m <sup>3</sup> )	3.78	1.82
Av. TN (g N/m <sup>3</sup> )	13.01	12.05
Av. TSS (g COD/m <sup>3</sup> )	14.73	14.93
Av. COD (g COD/m <sup>3</sup> )	48.48	48.55
Av. BOD5 (g COD/m <sup>3</sup> )	2.97	2.86
EQI	6,649	5,737
OCI	8,729	9,116
Average nitrite concentration in each ASU		
ASU1	1.07	0.15
ASU2	0.79	0.11
ASU3	1.52	0.24
ASU4	1.77	0.22
ASU5	1.92	0.17

<sup>a</sup> Results calculated using default parameters given in Hiatt and Grady [5]

<sup>b</sup> N<sub>2</sub>O emission factor is expressed as the percentage of influent TN load emitted as N<sub>2</sub>O-N

**Table 3** Tuned parameters of the ASMN submodel and corresponding target of each parameter tuning

Parameter	Unit	Default parameters of ASMN <sup>a</sup>	Calibrated parameters of ASMN	Sub-target
$b_{AOB}$	$d^{-1}$	0.055	0.028	T0.3
$b_{NOB}$	$d^{-1}$	0.055	0.028	T0.3
$b_H$	$d^{-1}$	0.232	0.3	T0.3
$k_a$	$l/(mg \text{ biomass COD} \cdot d)$	0.1136	0.07	T0.3, T1.1, T1.2
$K_{FA}$	mg N/l	0.0075	0.004	T2.1
$K_{FNA}$	mg N/l	0.0001	$10^{-6}$	T2.1
$k_h$	mg COD/(mg biomass COD · d)	1.275	2.89	T0.3
$K_{110FA}$	mg N/l	0.2	0.5	T2.1
$K_{110FNA}$	mg N/l	0.04	0.1	T2.1
$K_{15NO}$	mg N/l	0.075	0.2	T2.2
$K_{N2O}$	mg N/l	0.05	0.02	T2.2
$K_{NO}$	mg N/l	0.05	0.04	T2.2
$K_{NO2}$	mg N/l	0.2	0.3	T2.2
$K_{NO3}$	mg N/l	0.2	1.5	T2.2
$K_{OH}$	mg O <sub>2</sub> /l	0.1	0.2	T0.1, T0.2, T5
$K_{OH1}$	mg O <sub>2</sub> /l	0.1	0.2	T0.1, T0.2, T5
$K_{OH2}$	mg O <sub>2</sub> /l	0.1	0.2	T2.2, T5
$K_{OH3}$	mg O <sub>2</sub> /l	0.1	0.2	T2.2, T5
$K_{OH4}$	mg O <sub>2</sub> /l	0.1	0.2	T2.2, T5
$K_{OH5}$	mg O <sub>2</sub> /l	0.1	0.2	T2.2, T5
$K_{S1}$	mg COD/l	20	15	T3.1, T3.2
$K_{S5}$	mg COD/l	40	30	T2.5
$K_X$	mg COD/mg biomass COD	0.15	0.1	T0.2, T1.1
$\eta_{g2}$	–	0.28	0.3	T2.2
$\eta_{g3}$	–	0.16	0.3	T2.2
$\eta_{g4}$	–	0.35	0.6	T2.2
$\eta_{g5}$	–	0.35	0.8	T2.2
$\eta_h$	–	0.4	0.8	T0.2, T1.1
$Y_H$	mg biomass COD formed/mg COD removed	0.6	0.67	T0.1, T3.1, T3.2

<sup>a</sup> Reference temperature is 15 °C and the parameter values are from [5]

and this will also reduce the N<sub>2</sub>O production potential by AOB when using the ASMG1–BSM2 model.

Table 3 lists the values of the ASMN submodel parameters that were changed from the defaults and states the calibration target that was used to tune each parameter. Table 4 lists the parameters of the AOB denitrification models used in the subsequent calibration step. The calibration results of the original and modified ASMG1–BSM2 are given in Table 5. Similar results as ASM1–BSM2 in terms of effluent quality and operating costs are obtained and their N<sub>2</sub>O emission factors are around 0.5 %, indicating that both models thus pass the calibration.

Before validation is started (Fig. 2), the next step consists of evaluating the model's performance by comparing the results obtained by dynamic simulation with observed data (in our case, from the original ASM1–BSM2). Figure 3a compares the DO, NO<sub>3</sub><sup>−</sup> and NH<sub>4</sub><sup>+</sup> concentrations in ASU4 in open loop simulated by the original

ASMG1–BSM2, the modified ASMG1–BSM2 with the original ASM1–BSM2. The results show that the three models behave very similarly, except for NO<sub>3</sub><sup>−</sup> probably because ASM1 has only one oxidized N species (NO<sub>x</sub>), while the ASMG1 models model several NO<sub>x</sub> components. This result demonstrates that the ASMG1 models are also adequate for dynamic simulation in open loop despite the fact that the model calibration objectives only considered yearly averaged values. It also allows moving on to the validation step.

#### Validation and model discrimination

The validation was done for the three control strategies proposed in the finalized ASM1–BSM2. Table 6 gives the validation results of the calibrated original and modified ASMG1–BSM2. According to Table 6, the two ASMG1 models pass validation, indicating good model transferability

**Table 4** Tuned parameters of the two AOB denitrification submodels and corresponding target of each parameter tuning

Parameter	Unit	Default parameters of original AOB den. model <sup>a</sup>	Calibrated parameters of original AOB den. model	Calibrated parameters of modified AOB den. model	Sub-target
$K_{FNA\_AOB\ den.}$	mg N/l	0.002	0.0006	0.0006	T4.2
$K_{SO\_AOB\ den.}$	mg O <sub>2</sub> /l	0.5	1	–	T4.1
$K_{SO\_mod. AOB\ den.}$	mg O <sub>2</sub> /l	–	–	11.40	T4.1
$K_{IO\_mod. AOB\ den.}$	mg O <sub>2</sub> /l	–	–	0.035	T4.1
$\eta_{AOB1}$	–	0.028	0.5	0.5	T4.1
$\eta_{AOB2}$	–	1	0.5	0.5	T4.1

den. denitrification

<sup>a</sup> Parameter values are from [9]

**Table 5** Calibration results of ASMG1–BSM2 in open loop

	Finalized ASMG1–BSM2 <sup>a</sup>	Calibrated original ASMG1–BSM2	Calibrated modified ASMG1–BSM2
N <sub>2</sub> O emission factor <sup>b</sup>	–	0.49 %	0.50 %
Effluent quality			
Av. S <sub>NO<sub>3</sub></sub> (g N/m <sup>3</sup> )	7.47	7.32	7.30
Av. S <sub>NH</sub> (g N/m <sup>3</sup> )	1.65	1.51	1.55
Av. TN (g N/m <sup>3</sup> )	11.20	10.71	10.74
Av. TSS (g COD/m <sup>3</sup> )	15.90	15.63	15.63
Av. COD (g COD/m <sup>3</sup> )	50.06	49.51	49.51
Av. BOD5 (g COD/m <sup>3</sup> )	2.77	2.82	2.82
EQI	5,661	5,400	5,422
OCI	9,208	9,104	9,104

<sup>a</sup> Results are from the BSM2 finalization paper of Nopens et al. [13]

<sup>b</sup> Calibration objective of the N<sub>2</sub>O emission factor (% of influent TN load emitted as N<sub>2</sub>O-N) is 0.5 %

of the indexes listed in Table 6. These results thus suggest that the extrapolation power of the models in terms of traditional performance criteria is quite important, especially given the important change these controllers make to the DO dynamics that significantly affect the nitrification/denitrification processes.

To better reveal the actual difference between the two models, Table 7 compares the average N<sub>2</sub>O production rates by the different bacterial groups and the average N<sub>2</sub>O emission rates. Under each scenario, little difference was observed between both models for the average total net production rate and the average N<sub>2</sub>O emission rate. However, under 1-DO and 2-DO control strategies, the modified ASMG1–BSM2 simulated significantly more AOB-produced N<sub>2</sub>O but at the same time also a higher N<sub>2</sub>O removal by heterotrophs leading to the same net production rate as the original ASMG1–BSM2. In theory, this significant difference could be used to discriminate between the two models. A recently proposed method

based on the isotopic signature of N<sub>2</sub>O could, for instance, be used to assess the N<sub>2</sub>O production by the different pathways, but there still remains difficulties to partition N<sub>2</sub>O sources, e.g., under low DO conditions [23].

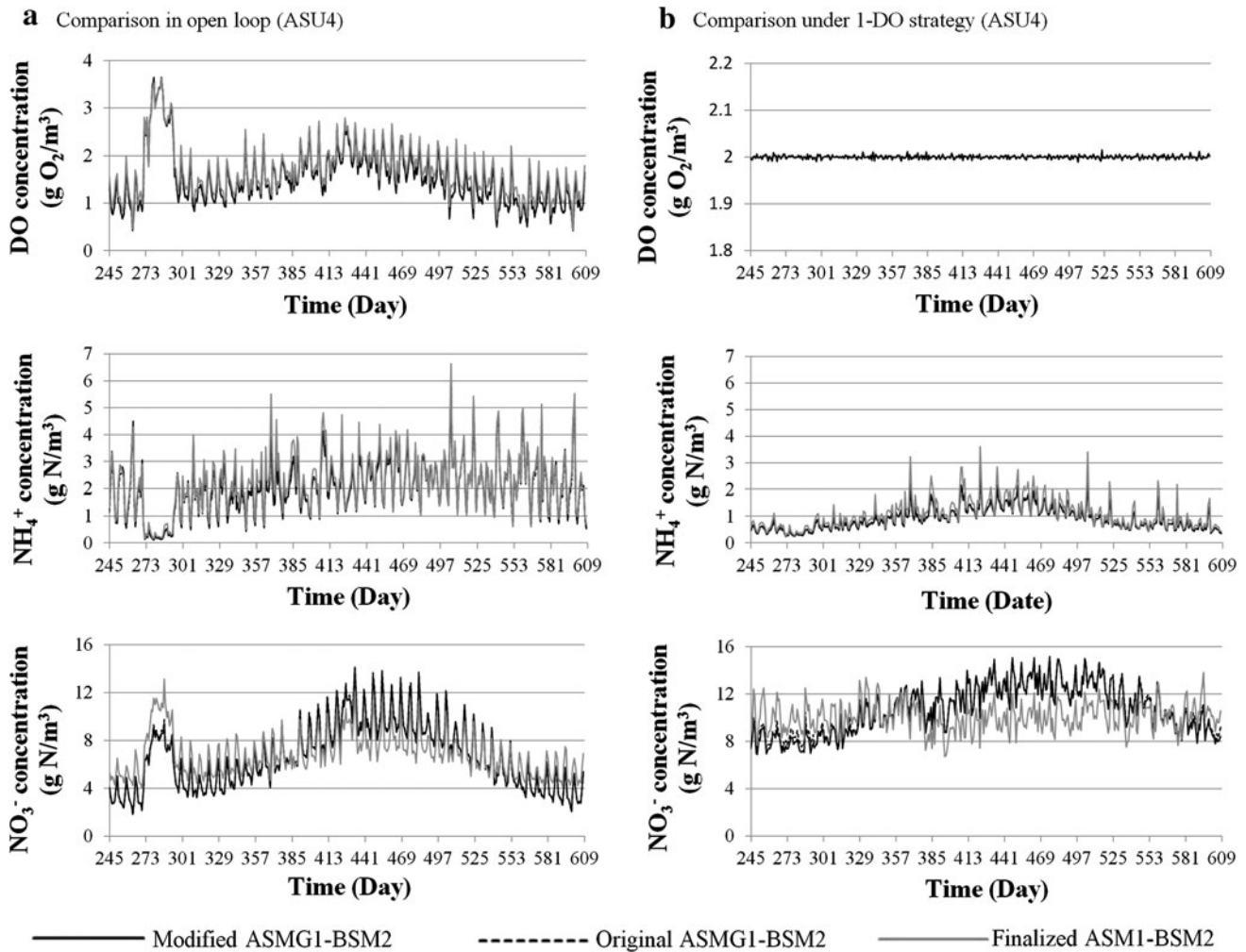
But dynamic results can be considered as an alternative source of information for model discrimination. Indeed, Fig. 4 compares the sum of dynamic N<sub>2</sub>O emissions from the three aerobic tanks during the two warmest weeks and the two coldest weeks for the two models. The dynamic data show that the two calibrated models present little difference in open loop, while for the controlled systems during the coldest weeks significantly lower N<sub>2</sub>O emissions are obtained when using the modified ASMG1–BSM2 compared to the original ASMG1–BSM2. According to Table 6, the yearly averaged N<sub>2</sub>O emission factors of the modified ASMG1–BSM2 and the original ASMG1–BSM2 are similar, which means that during the intermediate temperature periods, more N<sub>2</sub>O is emitted by the modified ASMG1–BSM2 than the original ASMG1–BSM2. Generally, the models differ a lot in terms of dynamic N<sub>2</sub>O emissions under control strategies, which suggest that observations under dynamic conditions could be exploited for model discrimination.

As in the calibration step with dynamic model evaluation, Fig. 3b compares the DO, NO<sub>3</sub><sup>–</sup> and NH<sub>4</sub><sup>+</sup> concentrations in ASU4 under the 1-DO control strategy simulated by the original ASMG1–BSM2, the modified ASMG1–BSM2 and the original ASM1–BSM2. Again, the three models show very similar dynamics except for NO<sub>3</sub><sup>–</sup>, as discussed above.

## Discussion

### Calibration and validation method

The calibration and validation procedure proposed in this paper was applied to fit a model using the virtual data provided



**Fig. 3** Comparison of daily averaged dynamic results of ASU4 obtained with the original, the modified ASMG1–BSM2 and the finalized ASMI–BSM2 in open loop (a) and with 1-DO strategy (b)

by the benchmarking model, but the procedure can generally be applied to calibrate/validate full-scale plants. The particularity of the approach to calibrate/validate a new model is that it took advantage of the knowledge consolidated in a widely accepted model. Such model is used to generate data that represent reality in such a way that it is acceptable for a new model to be calibrated/validated on these virtual data. In fact, this calibration/validation concept exploits the fact that when different models are used for the same system (plant or reactor), they should give similar results. In this case, these are the traditional plant performance indices, i.e., the effluent quality and the operation cost.

Importantly, it is believed by the authors that the proposed calibration procedure provides expert guidance on how an ASMG1 model could be calibrated for a real plant. In ongoing work [24], this calibration method is applied to an actual plant.

Comparing the  $N_2O$  emissions from a steady-state simulation with those for a dynamic simulation (Fig. 5)

confirms that the steady-state  $N_2O$  emissions can be quite different from the average of  $N_2O$  emissions calculated under dynamic conditions [12]. This demonstrates that even though the calibration is based on average emissions, the model should be run dynamically to get the proper value to compare with.

In this paper, the averaged dynamic simulation results are used as objectives of the new model's calibration and validation. However, model calibration and validation objectives reflect the purpose of the model [25]. In most applications of the benchmarking models, different scenarios are evaluated and compared in terms of these yearly averaged index values [11, 14] and this was the underlying reason for the objectives adopted in this paper. Moreover, Fig. 3 demonstrates that the ASMG1 models calibrated using the yearly averaged values satisfactorily pass the comparison with the original ASMI–BSM2 model under dynamic conditions. However, while this holds for this case study, calibration and validation under dynamic conditions



**Table 6** Validation of calibrated ASMG1 in BSM2 control strategies

	1-DO control strategy			2-DO control strategy			Cascade control strategy		
	Finalized ASM1–BSM2 <sup>a</sup>	Original ASMG1–BSM2	Modified ASMG1–BSM2	Finalized ASM1–BSM2 <sup>a</sup>	Original ASMG1–BSM2	Modified ASMG1–BSM2	Finalized ASM1–BSM2 <sup>a</sup>	Original ASMG1–BSM2	Modified ASMG1–BSM2
N <sub>2</sub> O emission factor <sup>b</sup>	–	0.48 %	0.49 %	–	0.43 %	0.43 %	–	0.67 %	0.60 %
Effluent quality									
Av. S <sub>NO<sub>3</sub></sub> (g N/m <sup>3</sup> )	11.05	12.01	11.93	10.40	11.69	11.63	7.85	6.30	6.34
Av. S <sub>NH</sub> (g N/m <sup>3</sup> )	0.47	0.35	0.36	0.48	0.39	0.40	1.11	1.76	1.81
Av. TN (g N/m <sup>3</sup> )	13.53	14.17	14.10	12.89	13.90	13.84	10.94	9.82	9.91
Av. TSS (g COD/m <sup>3</sup> )	15.17	14.96	14.96	15.17	14.95	14.95	14.92	14.66	14.66
Av. COD (g COD/m <sup>3</sup> )	49.02	48.38	48.38	49.03	48.42	48.43	48.78	48.57	48.56
Av. BOD5 (g COD/m <sup>3</sup> )	2.79	2.82	2.82	2.79	2.83	2.83	2.74	2.87	2.87
EQI	5,577	5,557	5,545	5,447	5,517	5,509	5,274	5,210	5,250
OCI	9,450	9,467	9,461	9,348	9,353	9,350	8,052	8,043	8,045

<sup>a</sup> Results are from the BSM2 finalization paper [13]

<sup>b</sup> N<sub>2</sub>O emission factor is expressed as % of influent TN load emitted as N<sub>2</sub>O-N

**Table 7** Comparison of average heterotrophic and autotrophic N<sub>2</sub>O production rates and the emission rate for the two AOB models

Averaged process rate (g N/day)	Open loop		1-DO control		2-DO control		Cascade control	
	Original ASMG1–BSM2	Modified ASMG1–BSM2	Original ASMG1–BSM2	Modified ASMG1–BSM2	Original ASMG1–BSM2	Modified ASMG1–BSM2	Original ASMG1–BSM2	Modified ASMG1–BSM2
Net N <sub>2</sub> O produced	5,717	5,825	5,441	5,609	4,879	4,973	7,739	6,919
By heterotrophs	–2,763	–2,159	–2,086	–3,661	–2,070	–3,575	–2,521	–3,469
By AOB	8,480	7,984	7,526	9,270	6,949	8,547	10,260	10,388
N <sub>2</sub> O emission	–5,639	–5,753	–5,435	–5,605	–4,874	–4,969	–7,631	–6,812

may be needed in other cases, e.g., when applying the model for more detailed process optimization or peak performance [25].

**AOB denitrification model**

The N<sub>2</sub>O production by AOB is still under study and no model has been agreed upon yet [10]. This paper illustrates how this still unclear part of the N<sub>2</sub>O model may affect simulation results and may therefore help directing experimental work. Comparing the calibration results under open loop in Tables 2 and 5, once the ASMN parameters are set, the EQI and OCI of using only the ASMN submodel can give similar results as using the whole ASMG1, but the N<sub>2</sub>O emission factor obtained using ASMG1 was obviously larger than using ASMN. The results also show that compared to ASMN, adding the AOB denitrification submodel has only little influence on the average simulation values of effluent quality and OCI. This is quite different for its contribution to N<sub>2</sub>O production.

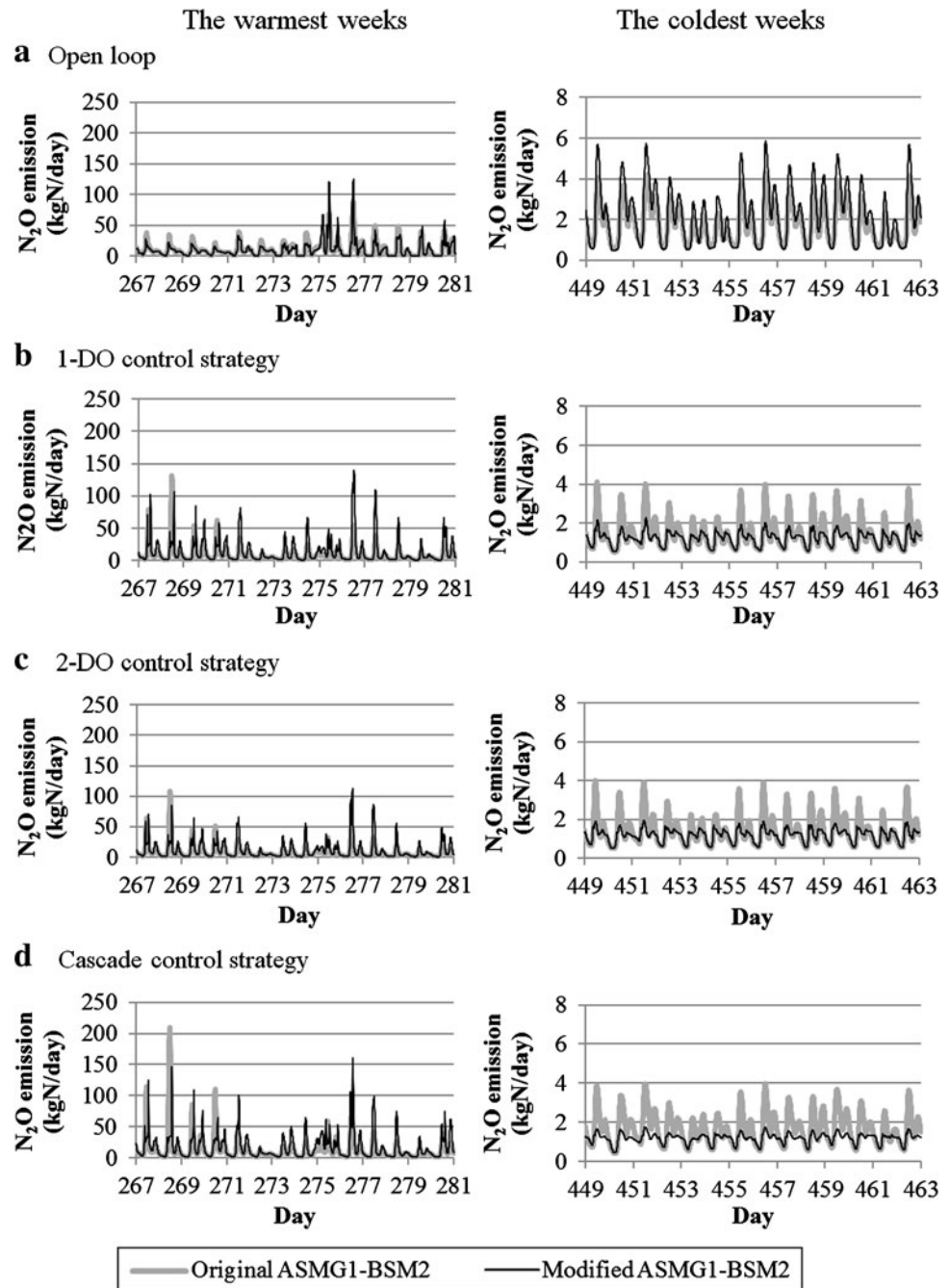
A new mathematical formulation of the Haldane kinetic term, Eq. (1), was used to describe the influence of DO in

the modified ASMG1–BSM2. Using this kinetics model structure has two advantages: its parameters can easily be obtained from half-saturation concentrations, and the maximum is kept at 1 as for Monod kinetics. This Haldane kinetic term has not been applied to the FNA and free ammonia (FA) inhibition terms in this paper. However, for the future, it is suggested to use this new kinetic term to also describe substrate inhibition.

**N<sub>2</sub>O emissions under different process conditions**

The relationship between N<sub>2</sub>O production and different process conditions has already been discussed [26]. Figure 4 presents the effect of temperature variation on the model’s response. Although the two ASMG1 models show different dynamic patterns of N<sub>2</sub>O emission under particular conditions (Fig. 4), they both simulated higher N<sub>2</sub>O emissions under warm conditions. The fact that this seasonality is what is generally observed in practice, e.g., [27], can be considered an important independent validation of these two models. The models allowed suggesting the following explanation. Increasing temperatures increase

**Fig. 4** Comparison of total dynamic  $N_2O$  emissions in the two warmest (a) and the two coldest weeks (b) in open loop and under the three tested control strategies

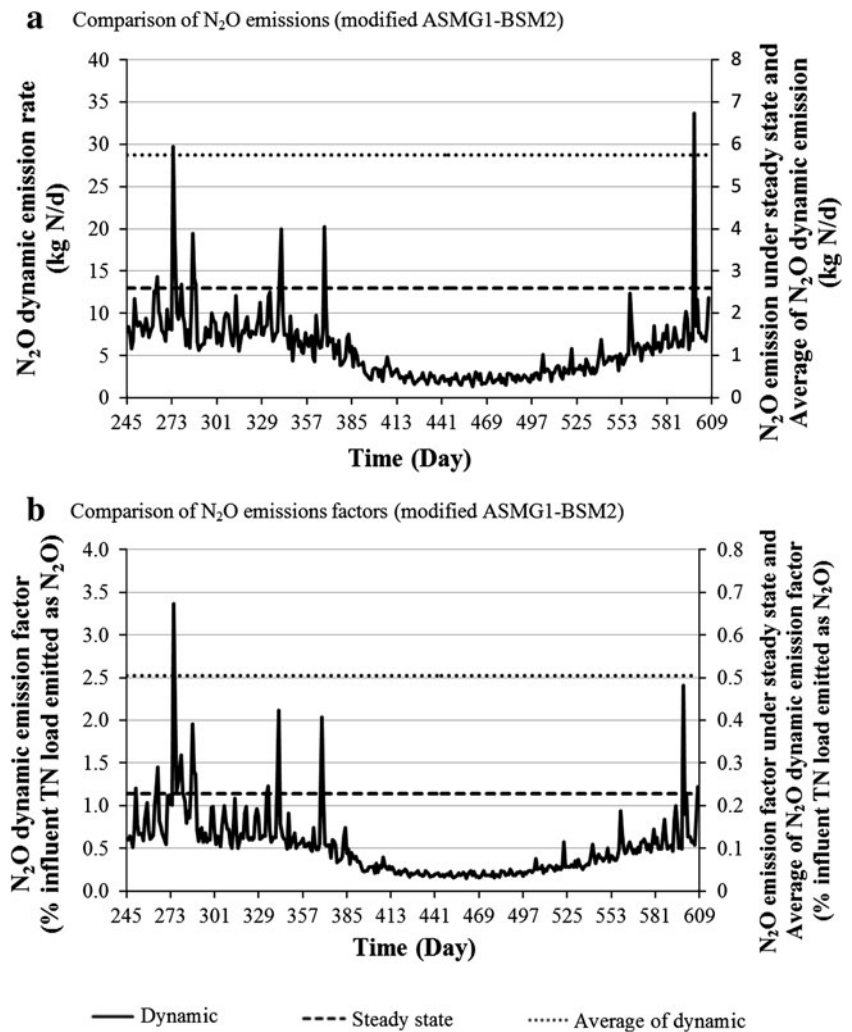


bioreaction rates, e.g., heterotrophic denitrification rates and AOB denitrification rates. Heterotrophs reduce NO to  $N_2O$ , but more importantly, they also reduce  $N_2O$  to  $N_2$ . Since the rates of both reactions increase with temperature, the net production rate by heterotrophs, which is equal to the difference of the two reaction rates, does not change too much over the year (Fig. 6a). However, AOB can only reduce NO to  $N_2O$  and are unable to further reduce  $N_2O$  to  $N_2$ . Hence, the increasing rate of AOB denitrifying NO to  $N_2O$  increases the pure accumulation of  $N_2O$  in warmer conditions. As a result, the total net  $N_2O$  production rate,

the sum of net production rates by heterotrophs and AOB, is higher during warm periods (Fig. 6b).

Concerning the different scenarios discussed in this paper, the cascade control strategy has clearly higher  $N_2O$  emissions than the other two control strategies and the open loop system. The cascade control has a tendency to decrease the DO concentrations in view of energy saving [11, 12]. According to the description in the “[ASMG1 models and implementation](#)”, this low DO level will directly stimulate AOB-produced  $N_2O$  through the Haldane term of the modified ASMG1. It may also induce a high

**Fig. 5** Comparison of daily averaged  $N_2O$  emissions in open loop under steady-state simulation and dynamic simulation with the modified ASMG1–BSM2



nitrite concentration which indirectly promotes AOB-produced  $N_2O$ . Both modified and original ASMG1 models predict such behavior. The way the models describe the relationship between  $N_2O$  production and DO concentrations agrees with experimental observation [8, 10, 26].

#### Future $N_2O$ measurement strategies

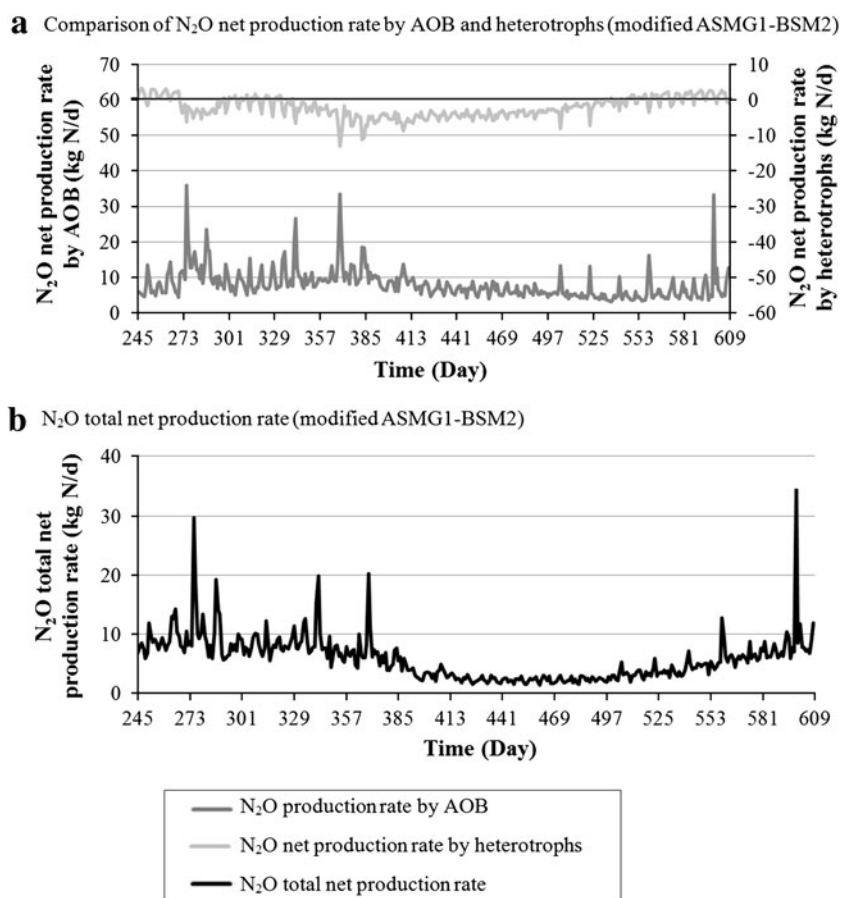
While the ASMG1 models do not show differences in terms of averaged measurement values, even for the different control strategies that bring the models in more extreme situations, the detailed dynamic results suggest that several short-term on-line measurements of  $N_2O$  emissions should be carried to help discriminate the models. This conclusion has practical consequences and is in an agreement with [27, 28] that demonstrated the usefulness of on-line high-frequency data for studying the process. Considering financial and other limitations, measurement campaigns for  $N_2O$  emissions could be designed to be spread over several short-term campaigns, e.g., every 1 or

2 weeks, over a whole year to cover different seasons. Then, by comparing the measurement data with the simulation results, the models can be further validated or falsified.

#### Conclusion

An ASMG1 model, as well as a modified ASMG1, were calibrated and validated using the BSM2 whole plant model that was considered to represent realistic plant behavior. Both ASMG1 models were successfully calibrated to meet requirements regarding a 0.5 %  $N_2O$  emission factor, effluent quality and operating costs. The validation of the model run under three control strategies was also successful according to the results of effluent quality and operational cost as published for the finalized ASMG1–BSM2 conditions [14]. Further evaluation on the calibrated ASMG1 models under dynamic conditions showed that they both can follow well the ASMG1–BSM2

**Fig. 6** Comparison of daily averaged dynamic  $N_2O$  production rates by different bacterial groups simulated with the modified ASMG1–BSM2 in open loop



dynamics. The proposed calibration procedure is also applicable to real plants and provides useful experience regarding future ASMG1 model calibration on full-scale data, e.g., obtained by spreading several short-term measurement campaigns over a whole year to cover the important seasonal variations in  $N_2O$  emissions.

Indeed, both ASMG1 models show more  $N_2O$  emissions in summer than in winter. This result was shown to be related to the temperature dependency of bacterial activity. The accumulation of  $N_2O$  in summer is mainly due to the increased AOB pathway activity, while the net  $N_2O$  production by heterotrophs does not change too much all year round.

The two ASMG1 models showed little difference for the average values of effluent quality, operating costs and net  $N_2O$  production and emission rates under each scenario, but a significant difference showed up when studying the  $N_2O$  reaction rates by the different bacterial groups and the dynamic  $N_2O$  emissions under control strategies and cold weather conditions. It is suggested to take advantage of the reported difference under dynamic conditions to achieve model discrimination. This encourages more dynamic  $N_2O$  data collection in view of model discrimination.

Finally, the comparison between the ASMN–BSM2 and ASMG1–BSM2 models (the latter including the AOB

denitrification process) revealed that little difference occurs at the level of effluent quality and operating cost. On the other hand, the  $N_2O$  emission factor was increased significantly when including AOB denitrification (ASMG1).

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