

## Challenges encountered when expanding activated sludge models: a case study based on N<sub>2</sub>O production

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### ABSTRACT

It is common practice in wastewater engineering to extend standard activated sludge models (ASMs) with extra process equations derived from batch experiments. However, such experiments have often been performed under conditions different from the ones normally found in wastewater treatment plants (WWTPs). As a consequence, these experiments might not be representative for full-scale performance, and unexpected behaviour may be observed when simulating WWTP models using the derived process equations. In this paper we want to highlight problems encountered using a simplified case study: a modified version of the Activated Sludge Model No. 1 (ASM1) is upgraded with nitrous oxide (N<sub>2</sub>O) formation by ammonia-oxidizing bacteria. Four different model structures have been implemented in the Benchmark Simulation Model No. 1 (BSM1). The results of the investigations revealed two typical difficulties: problems related to the overall mathematical model structure and problems related to the published set of parameter values. The paper describes the model implementation incompatibilities, the variability in parameter values and the difficulties of reaching similar conditions when simulating a full-scale activated sludge plant. Finally, the simulation results show large differences in oxygen uptake rates, nitrification rates and consequently the quantity of N<sub>2</sub>O emission ( $G_{N_2O}$ ) using the different models.

**Key words** | carbon footprint, greenhouse gas emissions, good modelling practice, model upgrade, model coupling

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### NOMENCLATURE

|            |  |                   |   |
|------------|--|-------------------|---|
| AOB        | Ammonia-oxidizing bacteria   | $K_{I9FNA}$       | Free nitrous acid inhibition coefficient for ASMN process no. 9 [g N/m <sup>3</sup> ]   |
| ASMs       | Activated Sludge Models  | $K_{La}$          | Volumetric oxygen transfer coefficient [1/d]  |
| ASM1       | Activated Sludge Model No. 1   | $K_{NH_2OH, AOB}$ | $S_{NH_2OH}$ affinity constant for AOB [g N/m <sup>3</sup> ]                            |
| ASM2       | Activated Sludge Model No. 2   | $K_{NH_4, AOB}$   | $S_{NH_4}$ affinity constant for AOB [g N/m <sup>3</sup> ]                              |
| ASM2d      | Activated Sludge Model No. 2d  | $K_{NH_4}$        | Half-saturation coefficient for $S_{NH_4}$ [g N/m <sup>3</sup> ]                        |
| ASM3       | Activated Sludge Model No. 3   | $K_{NO_2, AOB}$   | $S_{NO_2}$ affinity constant for AOB [g N/m <sup>3</sup> ]                              |
| ASMN       | Activated Sludge Model for Nitrogen  | $K_{NO, AOB}$     | $S_{NO}$ affinity constant for AOB [g N/m <sup>3</sup> ]                                |
| $b_{AOB}$  | Decay rate of ammonia oxidizing bacteria [1/d]                                   | $K_{NOH}$         | Half-saturation coefficient for $S_{NOH}$ [g N/m <sup>3</sup> ]                         |
| BSM1       | Benchmark Simulation Model No. 1   | $K_{NOH, AOB}$    | $S_{NOH}$ affinity constant for AOB [g N/m <sup>3</sup> ]                               |
| COD        | Chemical oxygen demand   | $K_{OA1}$         | Half-saturation coefficient for $S_{O_2}$ [g COD/m <sup>3</sup> ]                       |
| GHG        | Greenhouse gas   | $K_{S1, O_2}$     | Model A: $S_{O_2}$ affinity constant for $S_{NH_4}$ oxidation [g COD/m <sup>3</sup> ]   |
| $G_{N_2O}$ | Quantity of generated nitrous oxide emissions per day [kg N <sub>2</sub> O-N/d]  | $K_{S2, O_2}$     | Model A: $S_{O_2}$ affinity constant for $S_{NH_2OH}$ oxidation [g COD/m <sup>3</sup> ] |
| $K_{FA}$   | Half-saturation coefficient for $S_{FA}$ [g N/m <sup>3</sup> ]                   |                   | Model C: $S_{O_2}$ affinity constant for process C-1 [g COD/m <sup>3</sup> ]            |
| $K_{FNA}$  | Half-saturation coefficient for $S_{FNA}$ [g N/m <sup>3</sup> ]                  |                   |   |
| $K_{I9FA}$ | Free ammonia inhibition coefficient for ASMN process no. 9 [g N/m <sup>3</sup> ] |                   |   |

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|                                     |   |
|-------------------------------------|---|
|                                     | Model C: S <sub>O<sub>2</sub></sub> affinity constant for process C-2 [g COD/m <sup>3</sup> ] |
| $K_{S3,O_2}$                        | Model C: S <sub>O<sub>2</sub></sub> affinity constant for process C-3 [g COD/m <sup>3</sup> ] |
| $i_{\text{Charge},\text{NH}_4}$     | Charge of NH <sub>4</sub> <sup>+</sup> [charge/g N]   |
| $i_{\text{Charge},\text{NO}_2}$     | Charge of NO <sub>2</sub> <sup>-</sup> [charge/g N]   |
| $i_{\text{N},\text{AOB}}$           | Nitrogen content in ammonia-oxidizing bacteria [g N/g COD]                                    |
| $MW_{\text{N}}$                     | Molar weight of nitrogen [g/mol]  |
| $MW_{\text{O}}$                     | Molar weight of oxygen [g/mol]  |
| $\eta_{\mu_{\text{AOB},\text{Ax}}}$ | Anoxic reduction factor [-]   |
| N <sub>2</sub> O                    | Nitrous oxide   |
| NO                                  | Nitric oxide  |
| NOH                                 | Nitroxyl  |
| OHO                                 | Ordinary heterotrophic organisms  |
| $q_{\text{AOB},1,\text{max}}$       | Specific maximum rate of R1 in model C (1/d)  |
| $q_{\text{AOB},2,\text{max}}$       | Specific maximum rate of R2 in model C (1/d)  |
| $q_{\text{AOB},3,\text{max}}$       | Specific maximum rate of R3 in model C (1/d)  |
| $q_{\text{AOB},4,\text{max}}$       | Specific maximum rate of R4 in model C (1/d)  |
| $S_{\text{ALK}}$                    | Alkalinity [mol HCO <sub>3</sub> <sup>-</sup> /m <sup>3</sup> ]                               |
| $S_{\text{FA}}$                     | Free ammonia [g N/m <sup>3</sup> ]  |
| $S_{\text{FNA}}$                    | Free nitrous acid [g N/m <sup>3</sup> ]   |
| $S_{\text{O}_2}$                    | Dissolved oxygen [g O <sub>2</sub> /m <sup>3</sup> ]  |
| $S_{\text{N}_2\text{O}}$            | Dissolved nitrous oxide [g N/m <sup>3</sup> ]   |
| $S_{\text{N}_2}$                    | Dissolved dinitrogen [g N/m <sup>3</sup> ]  |
| $S_{\text{NH}_2\text{OH}}$          | Dissolved hydroxylamine [g N/m <sup>3</sup> ]   |
| $S_{\text{NH}_4}$                   | Dissolved ammonium [g N/m <sup>3</sup> ]  |
| $S_{\text{NO}}$                     | Dissolved nitric oxide [g N/m <sup>3</sup> ]  |
| $S_{\text{NO}_2}$                   | Dissolved nitrite [g N/m <sup>3</sup> ]   |
| $S_{\text{NO}_3}$                   | Dissolved nitrate [g N/m <sup>3</sup> ]   |
| $S_{\text{NOH}}$                    | Dissolved nitroxyl radical [g N/m <sup>3</sup> ]  |
| $S_{\text{S}}$                      | Readily biodegradable substrate [g COD/m <sup>3</sup> ]                                       |
| WWTP                                | Wastewater treatment plant  |
| $X_{\text{AOB}}$                    | Ammonia-oxidizing biomass [g COD/m <sup>3</sup> ]   |
| $X_{\text{NOB}}$                    | Nitrite oxidizing biomass [g COD/m <sup>3</sup> ]   |
| $X_{\text{OHO}}$                    | Heterotrophic biomass [g COD/m <sup>3</sup> ]   |
| $X_{\text{P}}$                      | Inert products from biomass decay [g COD/m <sup>3</sup> ]                                     |
| $X_{\text{S}}$                      | Slowly biodegradable substrate [g COD/m <sup>3</sup> ]  |
| $Y_{\text{AOB}}$                    | Yield of ammonia-oxidizing bacteria [g cell COD formed/g N oxidized]                          |
| $\mu_{\text{A1}}$                   | Maximum specific growth rate of AOB [1/d]   |
| $\mu_{\text{AOB},\text{AMO}}$       | Maximum ammonia mediated oxidizing reaction rate [1/d]  |

$\mu_{\text{AOB},\text{HAO}}$  Maximum hydroxylamine oxidoreductase mediated oxidizing reaction rate [1/d]

## INTRODUCTION

The Activated Sludge Model No. 1 (ASM1) (Henze *et al.* 2000) describes organic carbon and nitrogen removal processes in activated sludge systems and has been successfully applied to simulate a large number of wastewater treatment plants (WWTPs). The realistic results obtained in the early years promoted intensive research to improve and further expand the scope and phenomena included in ASM1, e.g. by including the description of bacterial storage, two-step nitrification, four-step denitrification and biological phosphorus removal. In this way, ASM1 evolved into ASM2, ASM2d and finally ASM3 as well as many other versions (Henze *et al.* 2000). This trend led to an increased number of state variables, biochemical processes and model parameters in the models. These extensions improved the level of detail, the realism and predictive capabilities of the developed models. However, they also increased the difficulties regarding model selection, simulation, parameter identification and validation (Vanrolleghem *et al.* 2003).

Extending standard activated sludge models (ASMs) with additional processes is not always a straightforward task. Engineers may encounter multiple problems when trying to incorporate additional model equations that are normally generated from batch experiments. Most of the time, these batch experiments were performed under well controlled conditions and their performance has been evaluated for short periods of time. Different conditions can lead to different microbial communities in activated sludge (Lu *et al.* 2014). The resulting model equations focus on the phenomena of interest, and therefore only describe part of the existing processes of the system under investigation.

The objective of this paper is to illustrate with a simple case study the difficulties encountered when upgrading an ASM with additional processes. The starting point for the case study is a modified version of the ASM1 (Henze *et al.* 2000), with two-step nitrification and four-step denitrification (Hiatt & Grady 2008), that is upgraded with nitrous oxide (S<sub>N<sub>2</sub>O</sub>) formation during nitrification performed by ammonia-oxidizing bacteria (X<sub>AOB</sub>). Four different model structures – based on either formation of S<sub>N<sub>2</sub>O</sub> as the final product of nitrifier denitrification with nitrite (S<sub>NO<sub>2</sub></sub>) as the terminal electron acceptor or on generation of S<sub>N<sub>2</sub>O</sub> as a

by-product of oxidation of hydroxylamine ( $S_{\text{NH}_2\text{OH}}$ ) to  $S_{\text{NO}_2}$  (Ni *et al.* 2013) – have been implemented in the Benchmark Simulation Model No. 1 (BSM1) (Copp 2002). The paper details the general issues that need to be considered for model extension and also provides specific examples.

## METHODS

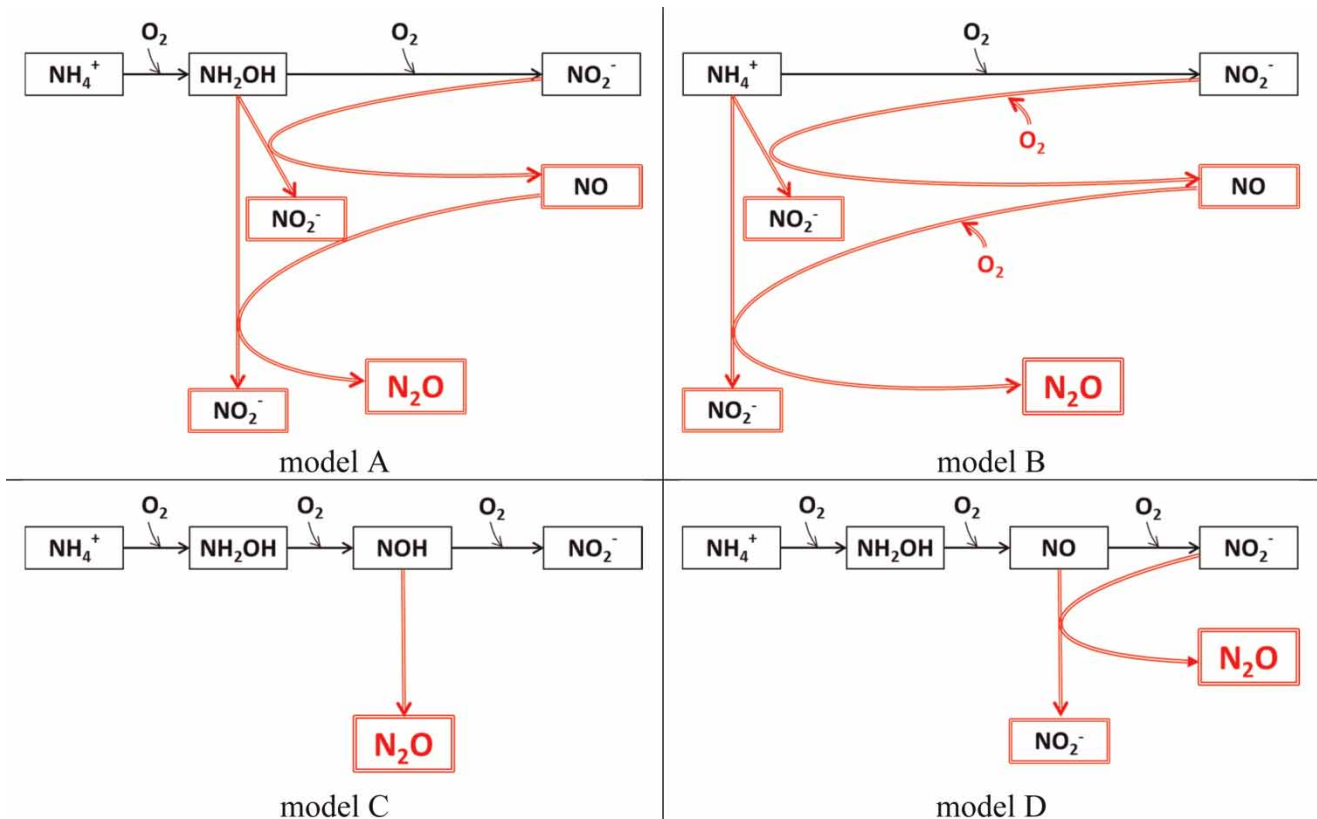
### WWTP under study

The BSM1 is the WWTP under study and the plant layout is a modified Ludzack–Ettinger configuration. Tanks 1 and 2 are anoxic, while tanks 3–5 are aerobic. An internal recycle sends part of the effluent of tank 5 back to tank 1. The activated sludge unit is followed by a secondary settler. A part of the sludge separated in the settler is returned to the first anoxic reactor to ensure a reasonable sludge age. The remaining part leaves the plant through the sludge line. The standard BSM1 input is used with additional influent concentration of 13.3 g N<sub>2</sub>/m<sup>3</sup>.

The ASM1 (Henze *et al.* 2000) extended with a two-step nitrification and four-step denitrification according to the activated sludge model for nitrogen (ASMN) of Hiatt & Grady (2008) and adjusted as explained in Corominas *et al.* (2012) is selected as the biochemical model for the activated sludge units. This model already includes N<sub>2</sub>O production by ordinary heterotrophic organisms (OHO). The 10-layer Takács model (Takács *et al.* 1991) based on the double exponential settling velocity function is used to represent the settling process. Further details about the different BSMs can be found in Gernaey *et al.* (2014).

### Investigated mathematical models

Four different models describing  $S_{\text{N}_2\text{O}}$  formation by  $X_{\text{AOB}}$  (Ni *et al.* 2013) were incorporated in the ASM framework that was implemented in BSM1. It is important to note that these models expanded the first nitrification step, nitrification, in which ammonium ( $S_{\text{NH}_4}$ ) is converted into nitrite ( $S_{\text{NO}_2}$ ) by AOB ( $X_{\text{AOB}}$ ), resulting in a more detailed



**Figure 1** | Overview of the four different models that predict N<sub>2</sub>O production by AOB. Model A is based on the nitrifier denitrification pathway using hydroxylamine as an intermediate of the first step of nitrification. Model B is also based on the nitrifier denitrification pathway; however it excludes hydroxylamine as an intermediate. Model C describes the chemical breakdown of radical NOH and model D expresses the biological reduction of NO. The full colour version of this figure is available online at <http://www.iwaponline.com/wst/toc.htm>.

nitritation model. The four models are shown in Figure 1 with the component N<sub>2</sub>O depicted in thicker, grey lines (red in online version of paper), as the focus is on that nitrogen component.

- Models A and B: Nitrous oxide (S<sub>N<sub>2</sub>O</sub>) is produced by X<sub>AOB</sub> as a result of the nitrifier denitrification pathway. In model A, nitrifier denitrification with nitrite (S<sub>NO<sub>2</sub></sub>) as the terminal electron acceptor produces nitric oxide (S<sub>NO</sub>) and subsequently S<sub>N<sub>2</sub>O</sub> by consuming hydroxylamine (S<sub>NH<sub>2</sub>OH</sub>) as the electron donor (Ni et al. 2011). In model B, the same nitrifier denitrification pathway is followed as in model A except that the electron donor used is S<sub>NH<sub>4</sub></sub> and not S<sub>NH<sub>2</sub>OH</sub> (Mampaey et al. 2013). Another important difference between the two models is the consumption of oxygen during nitrifier denitrification in model B, while model A assumes no consumption of oxygen and even incorporates an inhibitory effect of oxygen. Furthermore, model A takes no biomass growth into account during nitrifier denitrification, while model B assumes growth of AOB for the same process.
- Models C and D: S<sub>N<sub>2</sub>O</sub> is produced as a product of incomplete oxidation of S<sub>NH<sub>2</sub>OH</sub> to S<sub>NO<sub>2</sub></sub>. In model C the S<sub>N<sub>2</sub>O</sub> production is due to the chemical decomposition of the unstable radical S<sub>NOH</sub>, an intermediate of S<sub>NH<sub>2</sub>OH</sub> oxidation (Law et al. 2012). In this model, nitritation is split into a three-step process with S<sub>NH<sub>2</sub>OH</sub> and S<sub>NOH</sub> as intermediates. All three of these steps consume oxygen. During the nitrification and the chemical decomposition of S<sub>NOH</sub>, no biomass growth is modelled as it is assumed that too few electrons are released during the processes (Law et al. 2012). In contrast, model D assumes that S<sub>N<sub>2</sub>O</sub> is produced from the reduction of S<sub>NO</sub>, an intermediate of the aerobic oxidation of S<sub>NH<sub>2</sub>OH</sub> (Ni et al. 2013). This model assumes biomass growth during nitrification but not during the biological reduction of S<sub>NO</sub>.

Oxygen is needed for all processes except the biological reduction from S<sub>NO</sub> to S<sub>N<sub>2</sub>O</sub>.

Stripping equations are implemented for S<sub>N<sub>2</sub>O</sub>, S<sub>NO</sub> and S<sub>N<sub>2</sub></sub> as given by Foley et al. (2010) to estimate the quantity of N<sub>2</sub>O (generated by both AOB and OHO activities) emitted per day (G<sub>N<sub>2</sub>O</sub>). Nitrous oxide volumetric mass transfer coefficients are calculated from aeration intensity, represented as the volumetric oxygen transfer coefficient (K<sub>L</sub>a) combined with an empirical correlation between the molecular diffusivity of O<sub>2</sub> and N<sub>2</sub>O in water. The volumetric mass transfer coefficients of S<sub>NO</sub> and S<sub>N<sub>2</sub></sub> are calculated by the same approach as used for S<sub>N<sub>2</sub>O</sub>.

## RESULTS AND DISCUSSION

Note that the corrected model matrices for models A and C are included in the paper (Tables 1 and 2, respectively), whereas models B and D are included in an appendix to the paper (Tables A.1 and A.2, respectively; available online at <http://www.iwaponline.com/wst/070/347.pdf>).

### Mathematical model structure

Before implementing the four models presented above into the BSM1, the continuity of the stoichiometry and the consistency of the kinetic expressions were verified. The continuity check was carried out numerically by multiplying the stoichiometric matrix with the composition matrix (chemical oxygen demand (COD), nitrogen and charge). The resulting matrix should contain only zeros, or values near zero in case of rounding approximations (Hauduc et al. 2010). Kinetic expressions were checked carefully ensuring: (1) reactant limitation; (2) coherence in the switching functions; and (3) consistency in the rates (Hauduc et al. 2010). The results of

**Table 1** | Snapshot of the corrected process matrix for autotrophic N<sub>2</sub>O formation according to model A within the ASM context (full description of the process parameters can be found in Ni et al. (2013))

| Process | S <sub>O<sub>2</sub></sub>        | S <sub>NH<sub>4</sub></sub> | S <sub>NH<sub>2</sub>OH</sub> | S <sub>NO<sub>2</sub></sub> | S <sub>NO</sub> | S <sub>N<sub>2</sub>O</sub> | X <sub>AOB</sub> | S <sub>ALK</sub>  | rate  |
|---------|-----------------------------------|-----------------------------|-------------------------------|-----------------------------|-----------------|-----------------------------|------------------|---|---|
| A-1     | -1.14                             | -1                          | 1                             |                             |                 |                             |                  | -1 * i <sub>Charge_NH4</sub>                                      | $\mu_{AOB,AMO} \frac{S_{O_2}}{K_{S1,O_2,AOB} + S_{O_2}} \frac{S_{NH_4}}{K_{NH_4,AOB} + S_{NH_4}} X_{AOB}$   |
| A-2     | $-\frac{2.29 - Y_{AOB}}{Y_{AOB}}$ | $-i_{NAOB}$                 | $-\frac{1}{Y_{AOB}}$          | $\frac{1}{Y_{AOB}}$         |                 |                             | 1                | $-i_{NAOB} * i_{Charge_NH4} + \frac{1}{Y_{AOB}} * i_{Charge_NO2}$ | $\mu_{AOB,HAO} \frac{S_{O_2}}{K_{S2,O_2,AOB} + S_{O_2}} \frac{S_{NH_2OH}}{K_{NH_2OH,AOB} + S_{NH_2OH}} \frac{S_{NH_4}}{K_{NH_4} + S_{NH_4}} X_{AOB}$          |
| A-3     |                                   |                             |                               | -1                          | -3              | 4                           |                  | -3 * i <sub>Charge_NO2</sub>                                      | $\mu_{AOB,HAO} \frac{K_{1,O_2,AOB}}{K_{1,O_2,AOB} + S_{O_2}} \frac{S_{NO_2}}{K_{NO_2,AOB} + S_{NO_2}} \frac{S_{NH_2OH}}{K_{NH_2OH,AOB} + S_{NH_2OH}} X_{AOB}$ |
| A-4     |                                   |                             |                               | -1                          | 1               | -4                          | 4                | 1 * i <sub>Charge_NO2</sub>                                       | $\mu_{AOB,HAO} \frac{K_{1,O_2,AOB}}{K_{1,O_2,AOB} + S_{O_2}} \frac{S_{NO_2}}{K_{NO_2,AOB} + S_{NO_2}} \frac{S_{NH_2OH}}{K_{NH_2OH,AOB} + S_{NH_2OH}} X_{AOB}$ |
| ASMN-12 |                                   |                             |                               |                             |                 |                             | -1               |   | $b_{AOB} X_{AOB}$   |

**Table 2** | The corrected process matrix for autotrophic N<sub>2</sub>O formation according to model C (full description of the process parameters can be found in Ni *et al.* (2013))

| Process | S <sub>O2</sub>                        | S <sub>NH4</sub>            | S <sub>NH2OH</sub> | S <sub>NOH</sub> | S <sub>NO2</sub>    | S <sub>N2O</sub> | X <sub>AOB</sub> | S <sub>ALK</sub>   | rate   |
|---------|--|-----------------------------|--------------------|------------------|---------------------|------------------|------------------|--|--|
| C-1     | $-\frac{1}{2} * 2 * \frac{MW_O}{MW_N}$ | -1                          | 1                  |                  |                     |                  |                  | $-1 * i_{charge,NH4}$  | $q_{AOB,1,max} \frac{S_{O2}}{K_{S1,O2,AOB} + S_{O2}} \frac{S_{NH4}}{K_{NH4,AOB} + S_{NH4}} X_{AOB}$  |
| C-2     | $-\frac{1}{2} * 2 * \frac{MW_O}{MW_N}$ |                             | -1                 | 1                |                     |                  |                  |  | $q_{AOB,2,max} \frac{S_{O2}}{K_{S2,O2,AOB} + S_{O2}} \frac{S_{NH2OH}}{K_{NH2OH,AOB} + S_{NH2OH}} X_{AOB}$  |
| C-3     | $-\frac{1}{2} * 2 * \frac{MW_O}{MW_N}$ |                             |                    | -1               | 1                   |                  |                  | $1 * i_{charge,NO2}$   | $q_{AOB,3,max} \frac{S_{O2}}{K_{S3,O2,AOB} + S_{O2}} \frac{S_{NOH}}{K_{NOH,AOB} + S_{NOH}} X_{AOB}$  |
| C-4     |  |                             |                    | -1               |                     | 1                |                  |  | $q_{AOB,4,max} \frac{S_{NOH}}{K_{NOH} + S_{NOH}}$  |
| ASMN-9  | $-\frac{3.43 - Y_{AOB}}{Y_{AOB}}$      | $-\frac{i_{NAOB}}{Y_{AOB}}$ |                    |                  | $\frac{1}{Y_{AOB}}$ |                  | 1                | $\left( -i_{NAOB} - \frac{1}{Y_{AOB}} \right) * i_{charge,NH4} + \frac{1}{Y_{AOB}} * i_{charge,NH4}$ | $\hat{\mu}_{A1} X_{AOB} \frac{S_{FA}}{K_{FA} + S_{FA} + S_{FA}^2/K_{I9FA}} \frac{S_{O2}}{K_{O2} + S_{O2}} \frac{K_{I9FNA}}{K_{I9FNA} + S_{FNA}}$ |
| ASMN-12 |  |                             |                    |                  |                     |                  | -1               |  | $b_{AOB} X_{AOB}$  |

these two analyses revealed four different types of problems: (1) ‘inconsistencies’; (2) ‘gaps’; (3) ‘typing errors’; and (4) ‘coupling problems’.

### Inconsistencies

The first problem was related to the kinetic rate expression of nutrient (ammonium) limitation in the autotrophic growth process. This term was missing in models A, C and D, which could induce negative ammonium concentration values, especially during long-term simulations. The kinetic rates were modified in models A, C and D to include switching functions. Table 1 shows an example of the corrected kinetics of rate A-2 (grey shaded) of model A.

Another inconsistency is how AOB growth is (mathematically) represented in the different models. For example, model A has growth included in only one process, namely the reduction of S<sub>NH<sub>2</sub>OH</sub>, while model B has included AOB growth in all three processes (Table 1 and Table A.1). Thermodynamically speaking, it is difficult to assess in which process the energy is used for growth and thus in which process the growth should be modelled. This can be done by choosing one process as is done in model A, or by dividing the growth accordingly over the different processes as is shown in model B. In model D the growth was modelled in two processes which lead to an overestimation of the growth of AOB as the growth was not equally divided. Therefore the matrix was adjusted to remove the growth of AOB in process D-3 by dividing the  $\mu_{AOB,HAO,1}$  by the yield of AOB (see Table A.2).

### Gaps

The second problem concerned the correct descriptions of alkalinity (S<sub>ALK</sub>) to guarantee the continuity in ionic charge of the biological processes and thereby the possibility to predict potential pH changes. The effect of the different charged compounds on S<sub>ALK</sub> was taken into account in models A, B, C and D. No alkalinity limitations were assumed in the models. Table 1 shows the calculated stoichiometric coefficients for S<sub>ALK</sub> to balance charges for model A in the dashed box.

### Typing errors

Typing errors were found in models A and D in the publication of Ni *et al.* (2013). In the stoichiometry matrices of these models, S<sub>NH<sub>4</sub></sub> was modelled as being produced instead of consumed as nutrient during growth of X<sub>AOB</sub>. In Table 1, the correct sign is included to describe growth-related uptake of S<sub>NH<sub>4</sub></sub> by X<sub>AOB</sub> (in the box).

### Coupling challenges

There were three different challenges encountered with the models when trying to couple them with the ASMN. The first challenge is related to process omission, the second to the units used and the last to the structure of the model.

Models A, B and D describe the first step of nitrification and the corresponding growth of X<sub>AOB</sub>. However, the models do not include the decay of these bacteria. In the



work of Ni *et al.* (2013) the models were used to describe batch experiments, and therefore absence of decay rates was indeed not an issue due to the limited duration of the experiments (hours). However, when extending the simulation time to weeks, which is required when simulating an activated sludge plant, this assumption could lead to unrealistic concentration values. In order to correct this situation, the ASMN (Hiatt & Grady 2008) decay rates were used. Table 1 shows an example for model A, which includes the decay of AOB (ASMN-12) and its rate (shown in bold). In addition, the whole ASM is assumed to be based on the death–regeneration principle (not shown in the table). Thus, one fraction of the decayed biomass is transformed to inert products ( $X_P$ ) and the other part becomes biodegradable organic material ( $X_S$ ) that may potentially be hydrolysed.

Model C had no biomass growth associated with nitrification due to a low consumption of electrons (Law *et al.* 2012). Therefore the nitrification process of ASMN could not be replaced by the nitrification of model C, as was done for the other three models. An option to include AOB growth may be to use the  $X_{AOB}$  growth of ASMN (Hiatt & Grady 2008). This can be seen in Table 2 where the  $X_{AOB}$  growth (ASMN-9) and  $X_{AOB}$  decay (ASMN-12) are added to the model (bold). However, such an addition could lead to an unrealistic high consumption of  $S_{NH_4}$  as this consumption is included twice. Another possibility to overcome the exclusion of biomass growth could be to include growth of AOB in the process equations of model C. There is a possibility to add biomass growth to C-2 or C-3 or both (Table 2). If this inclusion were to be done, the stoichiometric matrix should be adjusted in those processes to include the yield of the AOB and also the rates ( $q_{AOB}$ ) should be divided by the yield of AOB in order to represent maximum growth rates. However, the yield of AOB was not used for the estimation of parameters as model C has no biomass growth included. Also it is uncertain if C-2 and C-3 or only one of those processes should have biomass growth modelled. Due to these uncertainties and in order to stay as close to the original model as possible, it was decided to use the processes of ASMN for the  $X_{AOB}$  growth even though the  $S_{NH_4}$  consumption could be unrealistically high.

The second challenge was related to the units used in the different models and those in model C. The state variables of model C were defined in mmol/L units, while the ASM is based on g COD/m<sup>3</sup> and g N/m<sup>3</sup>. To be able to implement model C in an ASM context, the units have to be identical, and thus the model had to be rewritten and stoichiometry and parameter values needed to be converted.

This was done by calculating the amount of COD or N in the components per mol (Table 2, boxes).

The last challenge was encountered in the model structure and also found in model C. The structure of model C was based on the different steps occurring within the AOB cells and with a last process (C-5) closing the electron balance by taking only reduction of oxygen into account. When implementing this model in the ASM framework, the continuity of the processes could not be verified with process C-5 standing alone. Therefore this process was divided over the processes C-1, C-2 and C-3 in order to close the mass balance of each process (boxes). The implemented model can be seen in Table 2.

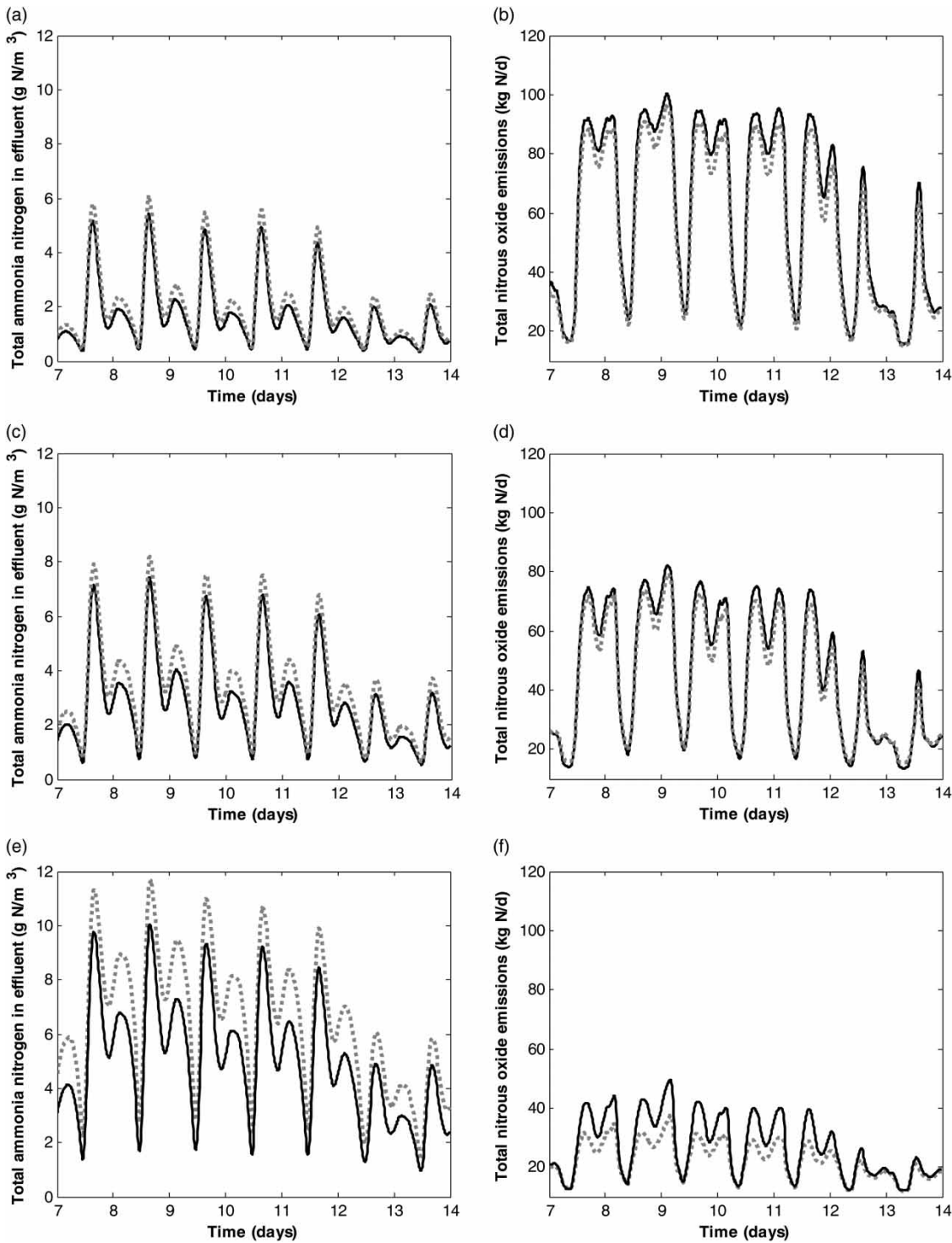
## Parameter values

### Parameter variability

The presented parameter sets for models A–D show high variability (Ni *et al.* 2013). For example, in model A the maximum hydroxylamine oxidoreductase mediated reaction rate ( $\mu_{AOB,HAO}$ ) shows 50% variation (from 0.092 to 0.183 1/h). Another example, and even more extreme, is the anoxic reduction factor ( $\eta_{r,AOB,AX}$ ) in model B, which changes from 0.0006 to 0.72 (a factor of 1200). The authors are aware that those parameters were estimated under different conditions of temperature, sludge retention time and feeding composition, and therefore correction factors must be adjusted by, for example, Arrhenius equations. Thus, Ni *et al.* (2013) fitted the parameter values to describe the data. However, in some cases the values could not fully represent the real situation. Furthermore, the parameters could also have been lumped, meaning they represent multiple parameters, which could explain the large variation of the values.

### Parameter compatibility

As mentioned at the beginning of the paper, some of the models describing the added phenomena are developed based on quite exceptional experimental situations (control, duration). It has been a concern for some years whether batch experiments can provide parameter values that are applicable to continuous long-term processes (Vanrolleghem & Keesman 1996; Checchi & Marsili-Libelli 2005). Another issue is linking a partial nitrification model with its subsequent processes such as decay of AOB and growth of nitrite-oxidizing bacteria (NOB) for which no parameter values have been obtained during the batch experiments. Inadequate decay rates for AOB or growth rates and affinity



**Figure 2** | The effluent concentration of total ammonia nitrogen and the total  $N_2O$  emissions of model A with a maximum growth rate for AOB of 2.928 1/d (black line) and 2.760 1/d (dashed line) in combination with different decay rates for AOB of 0.05 1/d ((a), (b)), 0.096 1/d ((c), (d)) and 0.15 1/d ((e), (f)).

constants for NOB may produce undesirable results and will require an extra calibration effort. An example of the effect of different parameter values is given in Figure 2. The decay rates were based on the minimum, default and maximum

value mentioned by Hiatt & Grady (2008). The maximum growth rates are based on the smallest and the largest value found in Ni *et al.* (2013). With these values, the largest variation in the results can be found.

Figure 2 shows how the  $S_{\text{NH}_4}$  concentration will change when different maximum growth rates and decay rates of the  $X_{\text{AOB}}$  are used. The effect of these different parameter values is even larger on the N<sub>2</sub>O emissions. From Figure 2 it can be concluded that according to model A the more AOB are present, the lower will be the ammonia concentration in the effluent and the higher the N<sub>2</sub>O emissions.

### Simulation results

The default parameter values of ASM1 (Henze *et al.* 2000) and ASMN (Hiatt & Grady 2008; Corominas *et al.* 2012) were used to simulate models A, B, C & D when possible and complemented with the estimated parameters from the experiments performed by Yang *et al.* (2009) and estimated by Ni *et al.* (2013). Dynamic simulation results of the (open loop) BSM1 plant are summarized in Table 3. Results show very different oxygen uptake rates, nitrification, denitrification and consequently N<sub>2</sub>O formation rates (from 21.32 to 175.20 kg N<sub>2</sub>O-N per day, equivalent to 2.1 and 17.5% of the total influent nitrogen load per day, see bold in Table 3), although the models in the literature show similar behaviour when fitting the data from the batch experiments. The difference in the N<sub>2</sub>O production between model A and model B is due to the different roles of oxygen in the AOB denitrification pathway. Model C predicts the lowest concentration of  $X_{\text{AOB}}$  as there are two processes consuming  $S_{\text{NH}_4}$  whereas only one of those has AOB growth associated. Thus a fraction of substrate is being consumed without growth of  $X_{\text{AOB}}$  (see section 'Coupling challenges').

Model D has the lowest emissions of the four models due to a more complete heterotrophic denitrification, as a result of higher NO consumption, which has an inhibitory effect on OHOs.

The discrepancies among the predictions of the different models are the result of both different parameter values and mathematical structures used to express the kinetic rates. It must be noted that processes related to NOB and OHO all have the same model structure and use identical parameter sets in all four models. Also note that model parameters have not been calibrated for the BSM1 system, which can contribute to the relatively high N<sub>2</sub>O emissions seen in Table 3 compared to Aboobakar *et al.* (2013) who reported only 0.036% N<sub>2</sub>O emissions of the total nitrogen influent. However, emission levels are still comparable with those reported by Kampschreur *et al.* (2009) for full-scale systems. The reader should also be aware that the focus of this paper is not to discuss how realistic these model predictions are, but rather to demonstrate the challenges encountered when extending ASMs with additional processes and reactions.

Regarding the production of N<sub>2</sub>O by AOB it is still unclear which pathway is the dominant pathway in full-scale WWTPs. A possibility can be that more than one of the mentioned pathways are active, which has been tested by Ni *et al.* (2014) by modelling oxidation and reduction processes separately. Also Wunderlin *et al.* (2012) mention that heterotrophic denitrification and nitrifier denitrification as well as hydroxylamine oxidation should be considered when studying strategies to avoid N<sub>2</sub>O emissions.

**Table 3** | Dynamic results of the AOB description of models A, B, C and D into the ASMN context simulated using BSM1 (parameter values can be found in appendix, available online at <http://www.iwaponline.com/wst/070/347.pdf>)

| Effluent conc.           | ASMN (Corominas <i>et al.</i> 2012) | AOB denitrification         |                               | Incomplete oxidation of hydroxylamine (NH <sub>2</sub> OH) |                             | Units  |
|--------------------------|-------------------------------------|-----------------------------|-------------------------------|--|-----------------------------|--|
|                          |                                     | Model A                     | Model B                       | Model C  | Model D                     |  |
| $S_{\text{O}_2}$         | 2.38                                | 2.51                        | 3.96                          | 5.42   | 2.52                        | g O <sub>2</sub> /m <sup>3</sup>                                   |
| $S_{\text{NH}_4}$        | 5.74                                | 2.86                        | 0.042                         | 2.31   | 3.35                        | g N/m <sup>3</sup>   |
| $S_{\text{NO}_3}$        | 16.71                               | 14.34                       | 2.99                          | 23.82  | 13.96                       | g N/m <sup>3</sup>   |
| $S_{\text{NO}_2}$        | 0.45                                | 1.81                        | 1.98                          | 0.0030   | 1.10                        | g N/m <sup>3</sup>   |
| $S_{\text{NO}}$          | 0.015                               | 0.019                       | 0.33                          | 0.0010   | 0.0020                      | g N/m <sup>3</sup>   |
| $S_{\text{N}_2\text{O}}$ | 0.11                                | 0.026                       | 0.098                         | 0.069  | 0.046                       | g N/m <sup>3</sup>   |
| $X_{\text{AOB}}^*$       | 83.53                               | 102.72                      | 95.16                         | 48.53  | 81.25                       | g COD/m <sup>3</sup>   |
| $X_{\text{NOB}}^*$       | 32.22                               | 30.38                       | 13.20                         | 29.22  | 30.52                       | g COD/m <sup>3</sup>   |
| $X_{\text{OHO}}^*$       | 2,148.96                            | 2,145.04                    | 2,097.12                      | 2,213.11   | 2,144.61                    | g COD/m <sup>3</sup>   |
| $G_{\text{N}_2\text{O}}$ | <b>21.32</b><br><b>2.1%</b>         | <b>68.42</b><br><b>6.8%</b> | <b>175.20</b><br><b>17.5%</b> | <b>70.13</b><br><b>7.0%</b>                                | <b>56.70</b><br><b>5.7%</b> | kg N <sub>2</sub> O-N/d<br>mass % N <sub>2</sub> O-N of N-influent |

\*Concentrations of  $X_{\text{AOB}}$ ,  $X_{\text{NOB}}$  and  $X_{\text{OHO}}$  are taken from the last reactor.



Another possibility could be that in different WWTPs different pathways are responsible for the N<sub>2</sub>O production. Another question that should be answered is how much detail is needed in the models to predict the N<sub>2</sub>O production; for example is the intermediate S<sub>NH<sub>2</sub>OH</sub> needed? Another important note is that the four models describe nitrification using different parameter values and with different stoichiometry and kinetics. Also this last issue contributes to the variation of the predicted N<sub>2</sub>O emissions.

## CONCLUSION

This case study demonstrates the problems that typically arise when expanding an ASM with additional processes. These problems were related to both the mathematical structure and the parameter values. The mathematical structure of the additional model equations should be checked for: (1) 'inconsistencies'; (2) 'gaps'; (3) 'typing errors'; and (4) 'coupling problems'. Regarding the parameter values, care must be taken when coupling different processes. The parameter values estimated during batch experiments may not be adequate for the continuous process and may not be compatible with the values of other parameters. Also, a large variation can be found in parameter values when fitting them to data from batch experiments. The different N<sub>2</sub>O-producing models mentioned in the case study demonstrate different behaviour as they are based on different assumptions regarding both nitrification and the autotrophic N<sub>2</sub>O production.

Finally, one should keep in mind that models are approximations, and therefore one should also have realistic expectations about their predictive capabilities and be aware of their inherent uncertainty.

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## REFERENCES

- Aboobakar, A., Cartmell, E., Stephenson, T., Jones, M., Vale, P. & Dotro, G. 2013 Nitrous oxide emissions and dissolved oxygen profiling in a full-scale nitrifying activated sludge treatment plant. *Water Research* **47** (2), 524–534.
- Cecchi, N. & Marsili-Libelli, S. 2005 Reliability of parameter estimation in respirometric models. *Water Research* **39** (15), 3686–3696.
- Copp, J. B. (ed) 2002 *The COST Simulation Benchmark: Description and Simulator Manual*. Office for Official Publications of the European Community, Luxembourg.
- Corominas, Ll., Flores-Alsina, X., Snip, L. & Vanrolleghem, P. A. 2012 Comparison of different modelling approaches to better understand and minimize greenhouse gas emissions from wastewater treatment plants. *Biotechnology and Bioengineering* **109** (11), 2855–2863.
- Foley, J., de Haas, D., Yuan, Z. & Lant, P. 2010 Nitrous oxide generation in full-scale biological nutrient removal wastewater treatment plants. *Water Research* **44** (3), 831–844.
- Gernaey, K. V., Jeppsson, U., Vanrolleghem, P. A. & Copp, J. B. (eds) 2014 *Benchmarking of Control Strategies for Wastewater Treatment Plants*. IWA Scientific and Technical Report No. 23, IWA Publishing, London, UK.
- Hauduc, H., Rieger, L., Takacs, I., Heduit, A., Vanrolleghem, P. A. & Gillot, S. 2010 A systematic approach for model verification: application on seven published activated sludge models. *Water Science and Technology* **61** (4), 825–839.
- Henze, M., Gujer, W., Mino, T. & van Loosdrecht, M. C. M. 2000 *Activated Sludge Models ASM1, ASM2, ASM2d and ASM3*. IWA Scientific and Technical Report No. 9, IWA Publishing, London, UK.
- Hiatt, W. C. & Grady Jr, C. P. L. 2008 An updated process model for carbon oxidation, nitrification, and denitrification. *Water Environment Research* **80** (11), 2145–2156.
- Kampschreur, M. J., Temmink, H., Kleerebezem, R., Jetten, M. S. M. & van Loosdrecht, M. C. M. 2009 Nitrous oxide emission during wastewater treatment. *Water Research* **43** (17), 4093–4103.
- Law, Y., Ni, B. J., Lant, P. & Yuan, Z. 2012 N<sub>2</sub>O production rate of an enriched ammonia-oxidising bacteria culture exponentially correlates to its ammonia oxidation rate. *Water Research* **46** (10), 3409–3419.
- Lu, H., Chandran, K. & Stensel, D. 2014 Microbial ecology of denitrification in biological wastewater treatment. *Water Research* **64**, 237–254.
- Mampaey, K. E., Beuckels, B., Kampschreur, M. J., Kleerebezem, R., van Loosdrecht, M. C. M. & Volcke, E. I. P. 2013 Modelling nitrous and nitric oxide emissions by autotrophic ammonium oxidizing bacteria. *Environmental Technology* **34** (12), 1555–1566.
- Ni, B. J., Ruscalleda, M., Pellicer-Nacher, C. & Smets, B. F. 2011 Modeling nitrous oxide production during biological nitrogen removal via nitrification and denitrification: extensions to the general ASM models. *Environmental Science and Technology* **45** (18), 7768–7776.

- Ni, B. J., Yuan, Z., Chandran, K., Vanrolleghem, P. A. & Murthy, S. 2013 Evaluating four mathematical models for nitrous oxide production by autotrophic ammonia-oxidizing bacteria. *Biotechnology and Bioengineering* **110** (1), 153–163.
- Ni, B. J., Peng, L., Law, Y., Guo, J. & Yuan, Z. 2014 Modeling of nitrous oxide production by autotrophic ammonia-oxidizing bacteria with multiple production pathways. *Environmental Science and Technology* **48** (7), 3916–3924.
- Takács, I., Patry, G. G. & Nolasco, D. 1991 A dynamic model of the clarification thickening process. *Water Research* **25** (10), 1263–1271.
- Vanrolleghem, P. A. & Keesman, K. J. 1996 Identification of biodegradation models under model and data uncertainty. *Water Science and Technology* **33** (2), 91–105.
- Vanrolleghem, P. A., Insel, G., Petersen, B., Sin, G., De Pauw, D., Nopens, I., Dovermann, H., Weijers, S. & Gernaey, K. 2003 A comprehensive model calibration procedure for activated sludge models. In: *Proceedings 76th Annual WEF Technical Exhibition and Conference 2003 (WEFTEC2003), October 11–15, Los Angeles, USA*.
- Wunderlin, P., Mohn, J., Joss, A., Emmenegger, L. & Siegrist, H. 2012 Mechanisms of N<sub>2</sub>O production in biological wastewater treatment under nitrifying and denitrifying conditions. *Water Research* **46** (4), 1027–1037.
- Yang, Q., Liu, X., Peng, C., Wang, S., Sun, H. & Peng, Y. 2009 N<sub>2</sub>O production during nitrogen removal via nitrite from domestic wastewater: main sources and control method. *Environmental Science and Technology* **43** (24), 9400–9406.

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