

Comparison of Different Modeling Approaches to Better Evaluate Greenhouse Gas Emissions From Whole Wastewater Treatment Plants

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ABSTRACT: New tools are being developed to estimate greenhouse gas (GHG) emissions from wastewater treatment plants (WWTPs). There is a trend to move from empirical factors to simple comprehensive and more complex process-based models. Thus, the main objective of this study is to demonstrate the importance of using process-based dynamic models to better evaluate GHG emissions. This is tackled by defining a virtual case study based on the whole plant Benchmark Simulation Model Platform No. 2 (BSM2) and estimating GHG emissions using two approaches: (1) a combination of simple comprehensive models based on empirical assumptions and (2) a more sophisticated approach, which describes the mechanistic production of nitrous oxide (N₂O) in the biological reactor (ASMN) and the generation of carbon dioxide (CO₂) and methane (CH₄) from the Anaerobic Digestion Model 1

(ADM1). Models already presented in literature are used, but modifications compared to the previously published ASMN model have been made. Also model interfaces between the ASMN and the ADM1 models have been developed. The results show that the use of the different approaches leads to significant differences in the N₂O emissions (a factor of 3) but not in the CH₄ emissions (about 4%). Estimations of GHG emissions are also compared for steady-state and dynamic simulations. Averaged values for GHG emissions obtained with steady-state and dynamic simulations are rather similar. However, when looking at the dynamics of N₂O emissions, large variability (3–6 ton CO₂e day⁻¹) is observed due to changes in the influent wastewater C/N ratio and temperature which would not be captured by a steady-state analysis (4.4 ton CO₂e day⁻¹). Finally, this study also shows the effect of changing the anaerobic digestion volume on the total GHG emissions. Decreasing the anaerobic digester volume resulted in a slight reduction in CH₄ emissions (about 5%), but significantly decreased N₂O emissions in the water line (by 14%).

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KEYWORDS: activated sludge modeling; anaerobic digestion; benchmarking; global warming; model-based evaluation; nitrous oxide; plant-wide model; sustainability; whole plant modeling

Abbreviations: AD, anaerobic digester; ADM1, anaerobic digestion model No. 1; AER, aerobic section; ANOX, anoxic section; AOO, ammonia oxidizing bacteria; ASM1, activated sludge model No. 1; ASMN, activated sludge model for nitrogen; BOD, biochemical oxygen demand (g m⁻³); C, carbon; CH₄, methane; CO₂, carbon dioxide; COD, chemical oxygen demand (g m⁻³); DO, dissolved oxygen (g m⁻³); FNA, free nitrous acid; GHG, greenhouse gas; GWP, global warming potential; H₂CO₃, carbonic acid; HCO₃⁻, bicarbonate; HRT, hydraulic retention time; IPCC, intergovernmental panel on climate change; K_a, ionization constant of the free nitrous acid equilibrium equation; K_{FNA}, inhibition constant for free nitrous acid (g N m⁻³); K_{1a}, volumetric oxygen transfer coefficient (day⁻¹); K_{0H3}, half-saturation coefficient for oxygen (g m⁻³); LGOP, local government operations protocol; N, nitrogen; N₂, nitrogen gas; N₂O, nitrous oxide; NO, nitric oxide; NO₂⁻, nitrite; NOO, nitrite oxidizing bacteria; PE, population equivalents; Q_w, waste flow rate (m³ day⁻¹); S_B, soluble biodegradable organics (g m⁻³); S_{N2}, dissolved nitrogen gas (g N m⁻³); S_O, dissolved oxygen (g m⁻³); SRT, sludge retention time; VSS, volatile suspended solids (g m⁻³); WWTP, wastewater treatment plant; X_{AOO}, ammonium oxidizing organisms (g m⁻³); X_{BA}, autotrophic biomass (g m⁻³); X_{CB}, particulate biodegradable organics (g m⁻³); X_{NOO}, nitrite oxidizing organisms (g m⁻³); X_{OH0}, ordinary heterotrophic organisms (g m⁻³).

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Introduction

The increasing demands for better effluent quality at lower operational costs have promoted the development of new technologies and the implementation of control concepts to improve the overall performance of wastewater treatment plants (WWTP). The increasing interest for greenhouse gas (GHG) emissions from wastewater treatment [carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O)]

leads to re-think the traditional engineering approaches by adding this new dimension to their evaluation. Therefore, new tools are needed to estimate the GHG emissions and evaluate different operation schemes that prevent or minimize their generation in WWTP.

Besides improving measurement techniques to reduce uncertainty related to GHG emissions (GWRC, 2011), different models are being developed which try to describe the GHG-related mechanisms involved in wastewater treatment. These models can be subdivided in three main groups. The first group corresponds to empirical models (e.g., IPCC, 2006; LGO, 2008; NGER, 2008) that are used to make inventories and that provide an order of magnitude of the production of GHGs. However, these models are based on strong assumptions and come along with high levels of uncertainty and variability (Pagilla et al., 2009). The second group includes simple comprehensive process models for wastewater and biosolids treatment (Bani Shahabadi et al., 2009; Bridle et al., 2008; Cakir and Stenstrom, 2005; Gori et al., 2011; Monteith et al., 2005). Finally, the third group of models consists of mechanistic models that dynamically describe the production of certain GHGs. In the liquid line, N_2O is generated during aerobic and anoxic processes and there have been attempts to provide detailed models for nitrification and denitrification by including the intermediates nitrite (NO_2^-), nitric oxide (NO), and N_2O (Hiatt and Grady, 2008; Mampaey et al., 2011; Ni et al., 2011, 2012; von Schulthess and Gujer, 1996; Yu et al., 2010). In the sludge line, the Anaerobic Digestion Model 1 (ADM1) proposed by Batstone et al. (2002) describes CH_4 and CO_2 emissions under anaerobic conditions.

These process-based models have to account for changes in influent load, temperature, and operating conditions, because they influence the production of GHGs. For instance, these changes can result with NO_2^- accumulation or low dissolved oxygen (DO) levels, which increase the N_2O production rates (Kampschreur et al., 2008; Rassamee et al., 2011; Wunderlin et al., 2012). Performing estimations based on averaged data or single emission factors, which do not account for these system changes, can lead to over or underestimations of GHG emissions.

The main objective of this study is to demonstrate the importance of using process-based models within a plant-wide context to better evaluate GHG emissions from WWTPs. It contributes to the field by comparing factors and simple comprehensive models with process-based models, identifying errors in current model implementations, and comparing steady-state and dynamic simulation results.

Methods

Wastewater Treatment Plant Under Study

The WWTP under study is the IWA Benchmark Simulation Model Platform No. 2 (BSM2) proposed by Jeppsson et al.

(2007) and redefined in Nopens et al. (2010). The benchmark is a simulation environment defining a plant layout, a simulation model, influent loads, test procedures, and evaluation criteria (Spanjers et al., 1998). For each of these items, compromises were pursued to combine plainness with realism and accepted standards (Gernaey et al., 2012). The virtual plant is designed for an average influent dry-weather flow rate of $20,648 \text{ m}^3 \text{ day}^{-1}$ and an average biodegradable COD in the influent of 592 g m^{-3} , serving a population of 80,000 Population Equivalents (PE). The BSM2 plant contains a primary clarifier, an activated sludge unit, a secondary clarifier, a sludge thickener, an anaerobic digester (AD), a storage tank, and a dewatering unit. Its hydraulic retention time (HRT; based on average dry weather flow rate and total tank volume—that is, primary clarifier (900 m^3) + biological reactor ($12,000 \text{ m}^3$) + secondary clarifier ($6,000 \text{ m}^3$)—of $18,900 \text{ m}^3$) is 22 h. The activated sludge unit is a modified Ludzack–Ettinger configuration consisting of five tanks in series. Tanks 1 (ANOX1) and 2 (ANOX2) are anoxic, while tanks 3 (AER1), 4 (AER2), and 5 (AER3) are aerobic. AER3 and ANOX1 are linked by means of an internal recycle.

The airflow supplied to the aerobic tanks is controlled to maintain a concentration of $2 \text{ g O}_2 \text{ m}^{-3}$ in AER1 and AER2. In AER3 the airflow is set to half the value of AER2. Two waste flow rates in the secondary clarifier are imposed depending on the time of the year in order to maintain sufficient biomass activity in the system during the winter period ($Q_W = 300 \text{ m}^3 \text{ day}^{-1}$). For the rest of the simulation time the waste flow is set to $450 \text{ m}^3 \text{ day}^{-1}$.

Estimation of Greenhouse Gas Emissions

WWTPs generate on-site (or direct) GHG emissions, including N_2O from secondary treatment and CH_4 from the sludge processing, together with biogenic and non-biogenic CO_2 emissions (both in the secondary treatment and the sludge processing). Following a life-cycle approach, the CO_2 generated during the production of energy and chemicals used in the WWTPs are also considered together with the sludge disposal and reuse CO_2 emissions (off-site or indirect emissions). The following categories of emissions are thus considered: (i) direct secondary treatment; (ii) sludge processing; (iii) net power; (iv) embedded GHG emissions from chemical use; and finally (v) sludge disposal and reuse. To deal with the different nature of the generated GHGs (CO_2 , CH_4 , and N_2O), they are converted in units of CO_2 equivalent (CO_2e) by using the global warming potential (GWP) values over 100 years (for CH_4 the GWP is 25 and for N_2O 298; IPCC, 2007). Two modeling approaches are compared to estimate GHG emissions in this study (the Bridle and the BSM2G), which differ in the calculation of N_2O emissions from the secondary treatment and in the calculation of CO_2 and CH_4 emissions from sludge processing, as reflected in Table I and Figure 1. The first approach uses a single factor for N_2O estimation and a

Table 1. Type of models used in the Bridle and the BSM2G for estimating GHG emissions.

	GHG emissions	Bridle	BSM2G
Direct secondary treatment	Biomass respiration	Simple comprehensive	Simple comprehensive
	BOD oxidation	Simple comprehensive	Simple comprehensive
	Credit nitrification	Simple comprehensive	Simple comprehensive
	N ₂ O emissions	Empirical factors	ASMN
Sludge processing GHG emissions		Simple comprehensive	ADM1
Net power	Power aeration	Simple comprehensive	Simple comprehensive
	Non-power aeration emissions	Simple comprehensive	Simple comprehensive
	Credit power GHG emissions	Simple comprehensive	Simple comprehensive
Embedded GHG emissions from chemical use		Empirical factor	Empirical factor
Sludge disposal and reuse GHG emissions		Simple comprehensive	Simple comprehensive

simple model of the AD. The second approach uses process-based models for N₂O and CH₄ estimation.

Modeling Approach 1 (Based on Bridle et al., 2008)

Figure 1 presents the GHG emissions computed in this approach. The inputs of the model are influent characteristics (flow and concentrations), operating conditions [e.g., sludge retention time (SRT), HRT], process variables [DO and mixed liquor suspended solids concentration in the reactors, volatile suspended solids (VSS), and flow at the influent and effluent of the AD], energy and chemicals consumed, obtained from averaging the results of the simulations run for the WWTP under study. A description of the models is provided below.

Direct Secondary Treatment

The GHG emissions from the activated sludge section include the CO₂ generated from (1) biomass respiration and (2) BOD oxidation, (3) the CO₂ credit from nitrification and (4) the N₂O generated from nitrogen removal. The first two processes are estimated following the methodology proposed by Monteith et al. (2005) using the factors 1.947 kg CO₂ (kg biomass respired endogenously)⁻¹ and

1.1 kg CO₂ (kg O₂ consumed for BOD degradation)⁻¹, respectively. The credit from nitrification (as CO₂ is consumed by nitrifiers to fulfil their carbon requirements) is calculated using the factor 0.308 kg of CO₂ consumed (kg N nitrified)⁻¹ (calculated from Tchobanoglous et al., 2003) instead of the factor 4.49 kg of CO₂ consumed (kg N nitrified)⁻¹ suggested by Bridle et al. (2008). The latter was taken from a wrongly balanced nitrification reaction given by Parker et al. (1975). N₂O emissions are estimated using the empirical factor 0.004 kg N₂O (kg N fed to aeration)⁻¹ applied by Bridle et al. (2008).

Sludge Processing

The emissions of GHG during sludge treatment are mainly generated in the AD. Direct biogas CO₂ and CH₄ emissions are quantified by using the following procedure: (a) calculation of the difference between VSS that enter and that leave the anaerobic digestion; (b) calculation of mass of biogas produced in the AD, assuming that 1 kg of sludge produces 1 kg of biogas; (c) estimation of the CH₄ and CO₂ mass produced, assuming that the CH₄ in the biogas is 65% by volume and the remainder of the biogas is CO₂; and (d) calculation of the CO₂ generated by burning CH₄ to CO₂.

Chemicals

This refers to the embedded CO₂ in the production of some chemicals used in the plants. In the present study, the emissions associated with the production of the external carbon source were calculated by using the emission factor of 1.54 g CO₂ g methanol as COD⁻¹ (Dong and Steinberg, 1997).

Sludge Disposal and Reuse

Only carbon mineralization to CO₂ is considered (CH₄ and N₂O emission factors per ton of VSS applied in the field are not included). CO₂ emissions associated with trucking of bio-solids are quantified by multiplying the truck movements by the distance to the reuse (150 km to agriculture, 20 km to compost, and 144 km to forestry). The CO₂ emissions by mineralization are calculated based on the sludge mass times the carbon concentration (using an

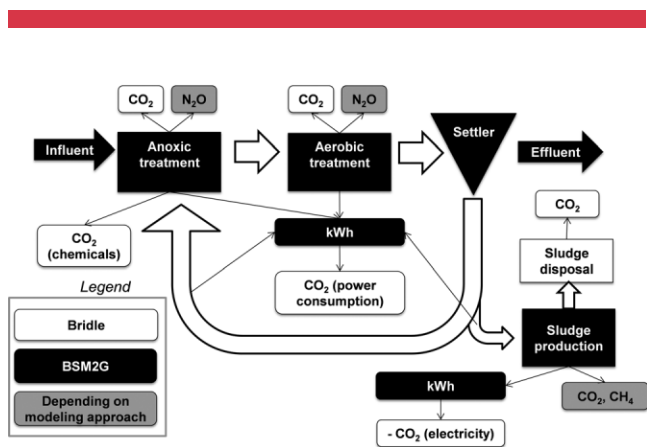


Figure 1. Boundaries for the case study.

empirical equation) times the factor of CO₂ to carbon. In this case study it is assumed that 38% of sludge goes to agriculture, 45% to a compost site, and 17% to forestry (Bridle et al., 2008).

Net Power

This refers to the difference between the energy consumption and the energy credit. The total energy consumption is quantified using the operational cost index defined by Nopens et al. (2010). This index includes the different energy consumptions in the plant, such as aeration, pumping, mixing, and heating (kWh day⁻¹). The credit refers to the electricity generated by the turbine and it is calculated by using a factor for the energy content of the CH₄ gas (50.014 MJ (kg CH₄)⁻¹) and assuming a 43% efficiency for electricity generation. The factor 0.94 kg CO₂ kWh (Bridle et al., 2008) was applied to convert energy into CO₂ emissions.

Modeling Approach 2 (BSM2G)

The approach suggested by Bridle et al. (2008) is used only to estimate the GHG emissions from secondary treatment (biomass respiration, BOD oxidation, and credit nitrification; Fig. 1) and the GHG emissions from sludge disposal and reuse. The other GHG emissions, CH₄ and N₂O, are obtained from the process-based models. This second modeling approach uses the models described in the standard BSM2 but with the Activated Sludge Model No. 1 (ASM1) replaced by the ASMN model (Hiatt and Grady, 2008) to provide N₂O emission data, with few modifications to account for the necessities of this work (see below). The widely recognized ADM1 (Batstone et al., 2002) using default parameter values described by Gernaey et al. (2012) is used to estimate CH₄ and CO₂ emissions from sludge processing. A full description of models and parameter values are provided in the Supplementary Material.

ASMN Model

The ASMN model (Hiatt and Grady, 2008) is the current available model that integrates the existing knowledge on N₂O production under anoxic conditions. The model incorporates four-step denitrification [sequential reduction of nitrate to nitrogen gas (N₂), via NO₂⁻, NO, and N₂O], using individual reaction-specific parameters. It also considers two nitrifying populations—ammonia oxidizing organisms (AOO) and nitrite oxidizing organisms (NOO)—using free ammonia and free nitrous acid (FNA), respectively, as their substrates. The effect of temperature on microbial growth is implemented with the Ratkowsky equation (Ratkowsky et al., 1983).

Modifications Compared to Hiatt and Grady (2008)

The modeled processes of NO₂⁻ reduction to NH₄⁺ and the mixotrophic growth of the nitrite oxidizing bacteria are not included in this study. The state variables salt, biodegradable AOB inhibitor, and priority pollutant are considered neither.

- The parameter values suggested by Hiatt and Grady (2008) were used, except for the K_{FNA} that was reduced from 1×10^{-4} (used for high nitrogen loads) to $1 \times 10^{-6} \text{ gm}^{-3}$ (used for low nitrogen loads) to get reasonable NOB growth in the modeled system.
- In order to account for seasonal variability, liquid–gas saturation constants, kinetic parameters, transfer coefficients, and equilibrium reactions are temperature dependent. Stripping equations for the gases were implemented as in Foley et al. (2010).
- S_{N_2} is added as state variable in order to close the mass balance for nitrogen.

Errors/Typos by Hiatt and Grady (2008) That Were Corrected

The equations and the continuity were checked with the method of Hauduc et al. (2009). The following errors/typos were found in the original publication:

- The inhibition term for oxygen in the equation for anoxic growth of heterotrophs is $K_{OH}/(K_{OH_3} + S_O)$ and it should be $K_{OH_3}/(K_{OH_3} + S_O)$.
- The temperature-dependent coefficient that was used to calculate the FNA concentration should have been calculated by $K_a = e^{-(2,300/(273+T))}$ (Anthonisen et al., 1976) and not by $K_a = e^{-(2,300(273+T))}$.
- The value for converting the temperature from degrees Celsius to Kelvin was rounded by Hiatt and Grady (2008). The conversion factor 273 was changed to 273.15 which is more accurate.
- The continuity check revealed that the composition coefficients used in the stoichiometric matrix by Hiatt and Grady (2008) were rounded. In order to minimize the error in the continuity one should use the numbers expressed as fractions (e.g., 64/14 instead of 4.57).
- FNA calculation should be equal to $S_{NO_2}(1/(1+K_a \times 10^{pH}))$ instead of $S_{NO_2}(1/(K_a + 10^{pH}))$ by Hiatt and Grady (2008). Note that the equation given by Anthonisen et al. (1976), $S_{NO_2}(1/(K_a \times 10^{pH}))$, is a missprint. A sensitivity analysis showed that this error has rather small impact under the typical WWTP conditions, which is probably the reason why the error remained undetected so far.

ASMN–ADM1 Interfaces

The interfaces presented by Nopens et al. (2009) have been modified to link ASMN and ADM1, by considering COD, N,

and charge balances for all oxidized nitrogen compounds. At the activated sludge side 5 new variables are defined compared to the ASM1 model used in BSM2: NO_2^- , NO , N_2O , N_2 , and an additional autotrophic biomass ($X_{\text{BA}2}$). In the ASM–ADM interface this additional biomass is treated as the other biomasses and converted in carbohydrates, lipids, protein, and inerts. At the other end of the digester, no autotrophs are coming back in the ADM–ASM interface.

The additional nitrogen species are treated as follows at the ASM–ADM interface: the negative COD content of NO_2^- , NO , N_2O is subtracted from the COD pool with an associated loss of substrate (S_{B} , X_{CB} , X_{OHO} , X_{AOO} , and X_{NOO} in that order, according to the notation presented by Corominas et al., 2010). The COD subtraction by reduction of the different species to N_2 is: NO_2^- ($24/14 \text{ g}(-\text{COD}) \text{ g N}^{-1}$), NO ($16/14 \text{ g}(-\text{COD}) \text{ g N}^{-1}$), and N_2O ($8/14 \text{ g}(-\text{COD}) \text{ g N}^{-1}$). The corresponding nitrogen is captured as N_2 that is not considered in ADM1 (it is assumed that N_2 is stripped). For the charge balance, only NO_2^- needs to be considered additionally at the ASM-side of the interface with an assumed charge $\alpha_{\text{NO}_2}^{\text{ch}} = -1 \text{ mole}^{-1}$ (considered independent of pH for simplicity). At the ADM–ASM interface no oxidized nitrogen species are to be considered.

Simulation Procedure (Steady-State and Dynamic Simulations)

The simulations have been performed in WEST^(R) (mikebyDHI.com, Belgium; Vanhooren et al., 2003), running a steady-state simulation (200 days) followed by a dynamic simulation of 609 days. Only the data generated during the last 364 days (52 weeks) of the dynamic simulation are used for the calculation of GHGs.

Table II. GHG emissions ($\text{kg CO}_2\text{e day}^{-1}$) estimated for different models, influent types, and anaerobic digester volumes (dynamic means averaged over a year).

Model	Bridle (A1)	BSM2G (A2)	BSM2G (A3)	Bridle (A1)	BSM2G (A2)	BSM2G (A3)
Influent	Steady-state	Steady-state	Dynamic	Steady-state	Steady-state	Dynamic
Anaerobic digester volume (m^3)	Large volume	Large volume	Large volume	Small volume	Small volume	Small volume
Biomass respiration	3,785	3,785	3,936	3,825	3,825	3,981
BOD oxidation	4,361	4,361	4,515	4,462	4,462	4,625
Credit nitrification	−247	−247	−242	−244	−244	−239
N_2O emissions	1,359	4,432	4,277	1,354	3,905	3,692
Total direct secondary treatment emissions	9,258	12,331	12,487	9,398	11,948	12,059
CO_2 emissions from digesting	1,756	1,631	1,617	1,723	1,582	1,568
CH_4 emissions from digesting	3,261	3,123	3,093	3,200	2,976	2,944
Total sludge processing GHG emissions	5,017	4,754	4,710	4,923	4,558	4,512
Power	5,919	5,919	6,031	5,701	5,701	5,821
Credit power	−6,659	−6,376	−6,317	−6,534	−6,078	−6,012
Total net power GHG emissions	−787	−457	−286	−886	−376	−191
Total embedded GHG emissions from Chemicals	2,053	2,053	2,053	2,053	2,053	2,053
Total sludge disposal and reuse GHG emissions	4,013	4,013	3,956	4,145	4,145	4,081
Total GHG emissions (GHG total)	19,554	22,694	22,920	19,633	22,328	22,514

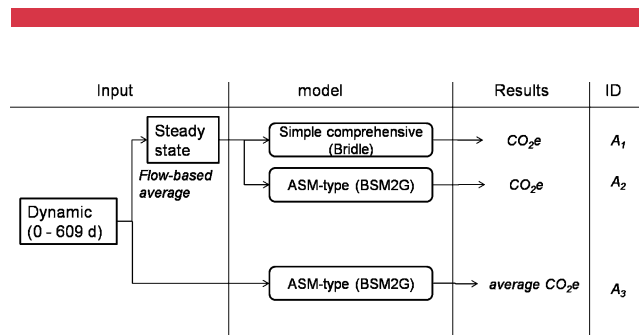


Figure 2. Degrees of freedom evaluated in this study (input data and model type).

Results

The performed comparison of different approaches to estimate GHGs considers three key points: (i) the use of different model approaches [simple comprehensive (Bridle et al., 2008) vs. process-based Activated Sludge Models (ASMN & ADM1)]; (ii) the type of input data fed to the models (flow-based averaged data or dynamic data; Fig. 2); and (iii) the evaluation of changes in GHG emissions as a result of changing the process configuration. In this case, two AD volumes are evaluated.

Comparison of a Simple Comprehensive and a Process-Based Model (Bridle and BSM2G)

The GHG estimations from the simple comprehensive (Bridle) and the process-based modeling approach (BSM2G) are presented in Table II. The results show large differences in the direct secondary treatment emissions (about 30%), in the net power emissions (about 50%), and small differences in the sludge processing emissions (about

6%). Evidently, no differences are observed in the total embedded GHG emissions from chemicals and the total sludge disposal and reuse GHG emissions because the same GHG calculation models are used.

The direct secondary treatment emissions are higher in the BSM2G model mainly due to higher N_2O emissions. For the simulated influent wastewater/operating conditions and using the default ASMN parameter values (Hiatt and Grady, 2008), the estimated N_2O emissions expressed as a percentage of incoming nitrogen is 1.4% (on a yearly average basis). On the other hand, the factor used in Bridle is around 0.4%. The comparison of several studies that provide ranges for this factor shows a large variability. GWRC (2011) provides a range between 0.42% and 6.1%, whereas Ahn et al. (2010) gives an even larger range (0.01–1.8% of N_2O emissions) for several configurations and operating conditions. When looking at MLE configurations (the same as BSM2G), the percentages range from 0.3% to 1.2% by Foley et al. (2010) and from 0.06% to 0.07% by Ahn et al. (2010). Besides the variability in different measuring campaigns, the selection of the sampling period also influences the obtained results. As shown in Figure 3, several sampling periods result in different mean and standard deviations for this factor. One year sampling (case A) compared to 1 day (cases B, C, G, and H), whole summer (D) or winter (E) gives different mean and standard deviation values. One day sampling (as conducted in Ahn et al., 2010) is not representative for the whole year. The examples B and C show that depending on the selection of the sampling day (B corresponds to day 385 of the simulation and C to day 286), the results can change significantly.

Related to sludge processing, the Bridle approach shows higher biogas production (about 5% for the large AD volume, see values in Table II). The total amount of sludge entering the digester is the same for both models. However, in the Bridle model it is assumed that the yield for biogas generation per mass of VSS is $1 \text{ kg biogas (kg VSS)}^{-1}$, whereas the BSM2G approach (using ADM1 model to

predict biogas production) leads to a lower yield of $0.94 \text{ kg biogas (kg VSS)}^{-1}$. The difference in this factor also propagates to the credit power (difference of 4%) and to the net power GHG emissions (difference of 42% amplified because of dividing by a lower number). Since the Bridle approach predicts a higher CH_4 production, the energy credit that can be obtained from its usage is also higher.

Comparison of Steady-State and Dynamic Simulations

The second goal of this study is to compare the estimations of GHGs calculated using steady-state or dynamic simulations for the process-based modeling approach. Average values in Table II show small differences in direct secondary treatment emissions (around 1%), sludge processing emissions (around 1%), and the total sludge disposal and reuse GHG emissions (about 1.5%). There is no difference in the total embedded GHG emissions from chemicals.

Even though the comparison between steady-state and averaged dynamic results did not show significant differences in this study for N_2O emissions (about 5%), large variability ($3\text{--}6 \text{ ton CO}_2\text{e day}^{-1}$) is observed in the dynamic results. This variability is due to changes in influent wastewater C/N ratio and temperature, things whose effects are not captured by a steady-state analysis ($4.4 \text{ ton CO}_2\text{e day}^{-1}$). The dynamic simulation results over 1 year show two types of variability (Fig. 4): (a) variability during the holiday season (days 280–310) explained by a temporary decrease of population and (b) variability between summer (days 245–375 and 520–609) and winter period (days 375–520) explained by temperature changes. During the holiday season, the decrease in N_2O emissions (Fig. 4a) and the increase of net power emissions (Fig. 4b) are explained by the lower nitrogen (decreasing N_2O emissions) and organic matter loads (decreasing biogas production). During the summer season, the modeled N_2O emissions are higher compared to the winter season. High temperatures in summer affect the growth of AOB and NOB and NO_2^- accumulates in the reactor. The presence of NO_2^- during denitrification leads to a lower denitrification rate and accumulation of NO and N_2O (Schulthess et al., 1995). Also, different wastage flow rates are applied in winter and summer to guarantee a sufficient SRT for nitrifiers to grow. In winter, the growth rates of nitrifiers are lower and therefore, the SRT is increased (by decreasing wastage flow rates). In summer, the growth is faster and then wastage flow rates can be increased. As a result, in winter, the waste load going to digesters is lower and CH_4 production is also lower. The reduced N load coming back from the return liquors explains the decrease in the production of N_2O . Moreover, the net power usage increases (Fig. 4b) as a result of lower biogas production and higher power consumption. The respiration in the reactors increases at longer SRTs and more power is required to maintain the DO set-point of 2 g m^{-3} . Hence, during the winter season the WWTP is producing less energy.

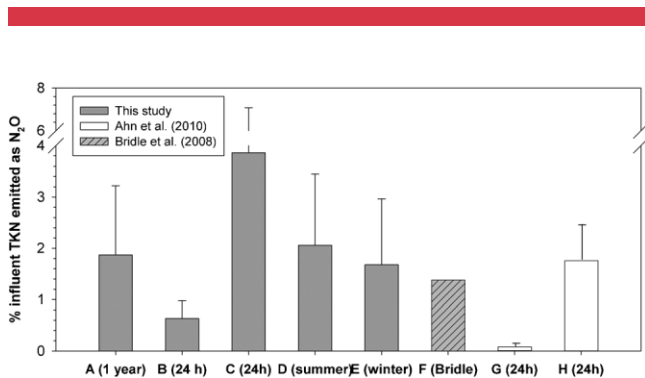


Figure 3. N_2O emissions expressed as % of influent TKN for this study at different sampling periods and for two other studies (mean value and standard deviations are provided).

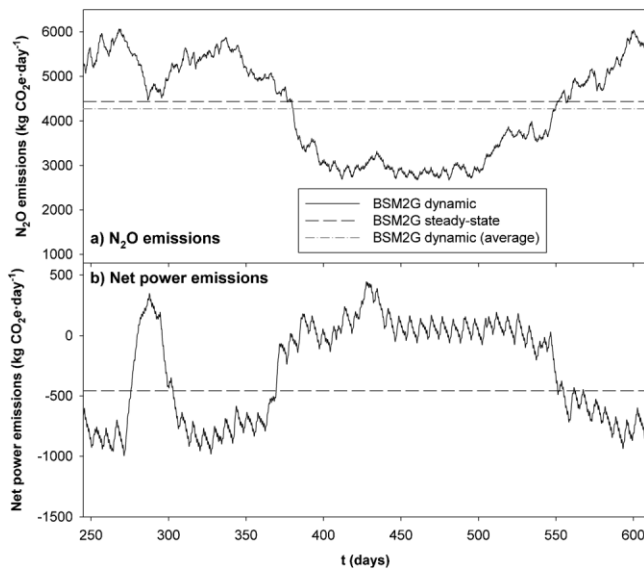


Figure 4. Comparison of dynamic and steady-state results for BSM2G: (a) N₂O emissions and (b) Net power emissions.

Comparison of Different Anaerobic Digester (AD) Retention Times

The simulation in which the AD volume was modified aims at investigating how a change in the system configuration is captured by more complex models while it is not by the simpler ones. In this example, a simulation was run with an AD volume reduced by 50% (3,400–1,700 m³). Table II shows a reduction of the N₂O emissions (about 14%, 4,277 kg CO₂e day⁻¹ vs. 3,692 kg CO₂e day⁻¹) with reduced AD volume only for the BSM2G approach. Figure 5 presents the N₂O and CH₄ emissions for BSM2G dynamic simulations. With smaller AD volumes, the hydraulic residence time decreases and volatile fatty acids naturally rise due to the overloading of the methanogens (Ahring et al., 1995). In the BSM2G with reduced AD volume, the supernatant that is recycled to the influent of the WWTP is richer in soluble biodegradable organic compounds, increasing by 10% at the inlet of the reactor. The fact that N₂O emissions decrease when increasing the C/N ratio has been demonstrated experimentally (Hanaki et al., 1992) and using model-based approaches (e.g., Flores-Alsina et al., 2011; Ni et al., 2011). The Bridle approach does not account for changes in the biodegradable organic compounds to estimate N₂O emissions and therefore smaller differences are observed compared to BSM2G (1,359 kg CO₂e day⁻¹ vs. 1,354 kg CO₂e day⁻¹ in reduced AD volume).

Another effect of the reduced AD volume is that a lower quantity of CH₄ emissions (down by 5%) is obtained by the BSM2G approach, whereas Bridle just predicts a change of 1% (see values in Table II). This difference between the approaches is explained by the more comprehensive ADM1

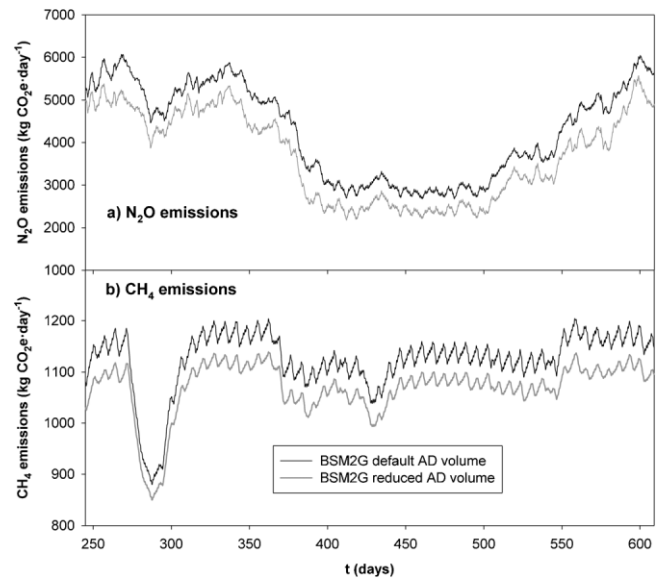


Figure 5. Comparison of GHG emissions for different anaerobic digester volumes for BSM2G: (a) N₂O emissions and (b) CH₄ emissions.

model that can handle changes in the residence time of the system. The decrease of CH₄ emissions also coincides with an increase in the total sludge disposal and reuse emissions (about 3%) because less VSS is transformed into soluble or gaseous compounds with the smaller AD volume.

Discussion and Perspectives

The objectives of a modeling study determine which units of the WWTP need to be modeled and in how much detail (Rieger et al., 2012). Objectives such as better understanding of GHG emissions under different operating conditions or defining control strategies to minimize them requires more complex model structures that include the whole plant in the system boundaries and need detailed process-based models. For instance, the work of Flores-Alsina et al. (2011) demonstrated that implementation of aeration, internal recycle, and suspended solids control strategies significantly influence the N₂O emissions.

The generation of GHGs is not a linear process and daily–weekly–seasonal variations and operating conditions affect their production and emission (Fig. 4). One of the main issues appears the estimation of N₂O which depends on the process conditions. Estimating them using a single factor would not capture variability in the emissions related to changes in process configuration, operating conditions (e.g., change of C/N ratio), and temperature (winter/summer), as demonstrated in this work. We could come up with many factors for many situations, but in the end it will be more efficient to run the process-based model. Thus, the use of dynamic process-based models helps to better evaluate GHG emissions.

Table III. Advantages and disadvantages of the two modeling approaches compared in this study.

Description	Simple comprehensive	Dynamic process-based
Accuracy on the estimation of GHG emissions	Lower accuracy as averages any system variability	Higher accuracy as it considers variability in operating conditions, changes in the influent load, etc.
Usefulness for process understanding	Not useful as they rely on empirical factors, obtained after observations	Process-based models help to better understand underlying mechanisms behind GHG emissions
Appropriateness in a plant-wide model context	Limited success as it only partially captures structural modifications in the system configuration	Very appropriate
Model applicability	Process design	Process optimization, e.g., control
Model implementation	Simple	Complex
Computational power	Low computational power required	High computational power required

The implementation of simplified digester models to estimate CH₄ emissions is a suitable alternative in view of speeding up simulation calculations. This study demonstrated that differences in CH₄ emissions among the evaluated approaches were not significant (less than 5%). Nevertheless, the use of the ADM1 model captured changes in the N₂O emissions that were indirectly due to the change in the AD volume, demonstrating the importance of using a plant-wide model, interfacing activated sludge with anaerobic digestion process-based models.

Table III summarizes the advantages and disadvantages of using simple comprehensive or dynamic process-based models in relation to the (i) accuracy on the estimation of GHG emissions; (ii) usefulness for process understanding; (iii) appropriateness in a plant-wide model context; (iv) applicability; (v) model implementation; and (vi) computational power requirements.

The results on the estimations of GHGs obtained in this study should not be taken as absolute values. The goal of the BSM2G platform is to study the dynamic interactions between the sludge and liquid lines in the WWTP taking into account not only effluent quality and operating costs, but also the emitted GHGs. It is not to provide an exact estimation of GHG emissions in WWTPs. The use of plant-wide models is still under development and some gaps and limitations can be identified from the present study:

- The ASMN model simulation results have been checked against ASM1 results (Hiatt and Grady, 2008). However, there is still need to obtain complete experimental datasets and perform studies to calibrate and validate these models (see Ni et al., 2011 as an example of a calibration study).
- Recent studies show that N₂O can also be generated under aerobic conditions (Ahn et al., 2010; Huijie and Chandran, 2010; Mampaey et al., 2011; Ni et al., 2011; Yu et al., 2010). Therefore, the ASM model used here should be updated to account for the new processes involved in the aerobic generation of N₂O once consensus is achieved (Ni et al., 2012).
- CO₂ emissions from endogenous respiration and BOD oxidation (direct secondary treatment) have been calculated according Monteith et al. (2005). To have these calculations done dynamically, one approach would

be to use the calculated oxygen uptake rates to estimate the CO₂ emissions as presented by Hellinga et al. (1996). An alternative would be to add CO₂ as an additional state variable in the ASM, but then one should also include the acid–base equilibria with H₂CO₃ and HCO₃⁻ and a pH calculation module (Grau et al., 2007). A dynamically calculated pH would also improve the realism of the description of the N₂O dynamics as pH significantly affects the related bioprocesses due to the weak acid substrates involved.

- In this study, the CH₄ generated in the AD that remains in the liquid phase is assumed to be removed before it enters the anoxic reactor. An alternative would be to consider that CH₄ enters the anoxic reactor where can be oxidized through denitrification (Hu et al., 2009).
- The N₂O emission from land applications of sludge can be significant as reported by Inubushi et al. (2000) when having anaerobic or anoxic conditions. Therefore, this should also be included in the evaluation, given the pursued life-cycle perspective.

Different approaches are used in current practice to estimate GHG emissions. This results in different values and makes the comparison between practical studies difficult. This is, for instance, the case for the estimation of N₂O. Overall, there is further research to be conducted on developing process-based models to describe GHG emissions and an effort should be made to benchmark the methods used for their estimation.

Conclusions

This work demonstrates that using a simplified approach compared to the use of ASMN and ADM1 models, resulted in large differences for N₂O emissions (a factor of 3) and small differences in CH₄ emissions (about 4%). Even though the comparison between steady-state and dynamic results using BSM2G (averaging yearly data) did not show significant differences in this study (about 5%), large variability (3–6 ton CO₂e day⁻¹) is observed in the dynamic simulation results due to changes in influent wastewater C/N ratio and temperature, things that are not captured in a

steady-state analysis. Finally, wastewater and sludge treatment processes influence each other and therefore proper estimation of GHG emissions should be performed according a plant-wide modeling approach. The modification of the AD volume, using the ADM1 model interfaced with the ASMN, resulted in a slight reduction in CH₄ emissions (about 5%), but significantly decreased N₂O emissions in the water line (by 14%) due to changes in the C/N ratio.

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References

- Ahn JH, Kim S, Park H, Rahm B, Pagilla K, Chandran K. 2010. N₂O emissions from activated sludge processes, 2008–2009: Results of a national monitoring survey in the United States. *Environ Sci Technol* 44:4505–4511.
- Ahring BK, Sandberg M, Angelidaki I. 1995. Volatile fatty acids as indicators of process imbalance in anaerobic digestors. *Appl Microbiol Biotechnol* 43:559–565.
- Anthonisen AC, Loehr RC, Prakasam TBS, Srinath EG. 1976. Inhibition of nitrification by ammonia and nitrous-acid. *J Water Pollut Control Fed* 48(5):835–852.
- Bani Shahabadi M, Yerushalmi L, Haghight F. 2009. Impact of process design on greenhouse gas (GHG) generation by wastewater treatment plants. *Water Res* 43:2679–2687.
- Batstone DJ, Keller J, Angelidaki I, Kayuznyi SV, Pavlostathis SG, Rozzi A, Sanders WTM, Siegrist H, Vavilin VA. 2002. *Anaerobic Digestion Model No 1*. IWA STR No. 13. London, UK: IWA Publishing.
- Bridle T, Shaw A, Cooper S, Yap KC, Third K, Domurad M. 2008. Estimation of greenhouse gas emissions from wastewater treatment plants. In: *Proceedings of IWA World Water Congress, Vienna, Austria, September 7–12, 2008*.
- Cakir FY, Stenstrom MK. 2005. Greenhouse gas production: A comparison between aerobic and anaerobic treatment technology. *Water Res* 39(17):4197–4203.
- Corominas LL, Rieger L, Takács I, Ekama G, Hauduc H, Vanrolleghem PA, Oehmen A, Gernaey KV, van Loosdrecht MCM, Comeau Y. 2010. New framework for standardized notation in wastewater treatment modelling. *Water Sci Technol* 61(4):841–857.
- Dong Y, Steinberg M. 1997. Hynol—An economical process for methanol production from biomass and natural gas with reduced CO₂ emission. *Int J Hydrogen Energy* 22(10–11):971–977.
- Flores-Alsina X, Corominas LL, Snip L, Vanrolleghem PA. 2011. Including greenhouse gases emissions during benchmarking of wastewater treatment plant control strategies. *Water Res* 45:4700–4710.
- Foley J, de Haas D, Yuan Z, Lant P. 2010. Nitrous oxide generation in full-scale biological nutrient removal wastewater treatment plants. *Water Res* 44:831–844.
- Gernaey KV, Jeppsson U, Vanrolleghem PA, Copp JB, Steyer J-P, editors. 2012. *Benchmarking of control strategies for wastewater treatment plants*. IWA Scientific and Technical Report. London, UK: IWA Publishing.
- Gori R, Jiang L-M, Sobhani R, Rosso D. 2011. Effects of soluble and particulate substrate on the carbon and energy footprint of wastewater treatment processes. *Water Res* 45:5858–5872.
- Grau P, de Gracia M, Vanrolleghem PA, Ayesa E. 2007. A new plant-wide modelling methodology for WWTPs. *Water Res* 41(19):4357–4372.
- GWRC. 2011. N₂O and CH₄ emission from wastewater collection and treatment systems - State of the Science Report. Global Water Research Coalition. ISBN 978.90.77622.23.0
- Hanaki K, Hong Z, Matsuo T. 1992. Production of nitrous oxide gas during denitrification of wastewater. *Water Sci Technol* 26(5–6):1027–1036.
- Hauduc H, Rieger L, Takacs I, Heduit A, Vanrolleghem PA, Gillot S. 2009. A systematic approach for model verification: Application on seven published activated sludge models. *Water Sci Technol* 61(4):825–839.
- Hellinga C, Vanrolleghem P, van Loosdrecht M, Heijnen J. 1996. The potentials of off-gas analysis for monitoring and control of waste water treatment plants. *Water Sci Technol* 33(1):13–23.
- Hiatt WC, Grady CPL, Jr. 2008. An updated process model for carbon oxidation, nitrification, and denitrification. *Water Environ Res* 80: 2145–2156.
- Hu S, Zeng RJ, Burow LC, Keller J, Yuan Z. 2009. Enrichment of denitrifying anaerobic methane oxidizing microorganisms. *Environ Microbiol Rep* 1(5):377–384.
- Huijie L, Chandran K. 2010. Factors promoting emissions of nitrous oxide and nitric oxide from denitrifying sequencing batch reactors operated with methanol and ethanol as electron donors. *Biotechnol Bioeng* 106(3):390–398.
- Inubushi K, Goyal S, Sakamoto K, Wada Y, Yamakawa K, Arai T. 2000. Influences of application of sewage sludge compost on N₂O production in soils. *Chemosphere Global Change Sci* 2:329–334.
- IPCC. 2006. 2006 IPCC Guidelines for National Greenhouse Gas Inventories. Intergovernmental Panel on Climate Change. Available at: <http://www.ipccnggip.iges.or.jp/public/2006gl/index.html>
- IPCC. 2007. 2007 IPCC Fourth Assessment Report (AR4),” Chapter 2, “Changes in Atmospheric Constituents and in Radiative Forcing,” Intergovernmental Panel on Climate Change. Available at: http://ipcc-wg1.ucar.edu/wg1/Report/AR4WG1_Print_Ch02.pdf
- Jeppsson U, Pons MN, Nopens I, Alex J, Copp JB, Gernaey KV, Rosen C, Steyer JP, Vanrolleghem PA. 2007. Benchmark Simulation Model No 2—General protocol and exploratory case studies. *Water Sci Technol* 56(8):287–295.
- Kampschreur MJ, van der Star WRL, Wielders HA, Mulder JW, Jetten MSM, van Loosdrecht MCM. 2008. Dynamics of nitric oxide and nitrous oxide emission during full-scale reject water treatment. *Water Res* 42:812–826.
- LGO. 2008. Local Government Operations Protocol For the quantification and reporting of greenhouse gas emissions inventories. Version 1.0, September 2008. Available at: www.theclimaterestory.org/resources/protocols/local-government-operations-protocol/
- Mampae KE, Beuckels B, Kampschreur MJ, Kleerebezem R, van Loosdrecht MCM, Volcke EIP. 2011. Modelling nitrous and nitric oxide emissions by autotrophic ammonium oxidizing bacteria. In: *Proceedings IWA/WEF Nutrient Recovery and Management 2011 Conference*. Miami, FL (USA), 9–12 January 2011.
- Monteith HD, Sahely HR, MacLean HL, Bagley DM. 2005. A rational procedure for estimation of greenhouse-gas emissions from municipal wastewater treatment plants. *Water Environ Res* 77:390–403.
- NGER. 2008. National Greenhouse and Energy Reporting (Measurement) Technical Guidelines 2008 v1.1. July 2008. Australian Government Department of Climate Change. Available at: <http://www.climatechange.gov.au/reporting/>
- Ni BJ, Rusalleda M, Pellicer i Nàcher C, Smets BF. 2011. Modelling nitrous oxide production during biological nitrogen removal via nitrification and denitrification: Extensions to the general ASM models. *Environ Sci Technol* 45:7768–7776.
- Ni B-J, Yuan Z, Chandran K, Vanrolleghem PA, Murthy S. 2012. Evaluating mathematical models for N₂O production by ammonia-oxidizing bacteria: Towards a unified model. In: *Proceedings of 3rd IWA/WEF Wastewater Treatment Modelling Seminar, Mont-Sainte-Anne, Québec, Canada, February 26–28, 2012*.

- Nopens I, Batstone DJ, Copp JB, Jeppsson U, Volcke E, Alex J, Vanrolleghem PA. 2009. An ASM/ADM model interface for dynamic plant-wide simulation. *Water Res* 43(7):1913–1923.
- Nopens I, Benedetti L, Jeppsson U, Pons M-N, Alex J, Copp JB, Gernaey KV, Rosen C, Steyer J-P, Vanrolleghem PA. 2010. Benchmark Simulation Model No 2: Finalisation of plant layout and default control strategy. *Water Sci Technol* 62(9):1967–1974.
- Pagilla K, Shaw A, Kuntz T, Schiltz M. 2009. A systematic approach to establishing carbon footprints for wastewater treatment plants. In: *Proceedings of WEFTEC 2009, Orlando, Florida, USA, October 10–14, 2009*.
- Parker D, Stone RW, Stenquist RJ. 1975. *Process design manual for process control*. Cincinnati, Ohio (US): Environmental protection agency. 476 p.
- Rassamee V, Sattayatewa C, Pagilla K, Chandran K. 2011. Effect of oxic and anoxic conditions on nitrous oxide emissions from nitrification and denitrification processes. *Biotechnol Bioeng* 108(9):2036–2045.
- Ratkowsky DA, Olley J, McMeekin TA, Ball A. 1983. Model for bacterial culture growth rate throughout the entire biokinetic temperature range. *J Bacteriol* 154:1222–1226.
- Rieger L, Gillot S, Langergraber G, Ohtsuki T, Shaw A, Takacs I, Winkler S. 2012. Guidelines for using activated sludge models—IWA Task Group on Good Modelling Practice. IWA Scientific and Technical Report. ISBN: 9781843391746.
- Schulthess RV, Kuehni M, Gujer W. 1995. Release of nitric and nitrous oxides from denitrifying activated sludge. *Water Res* 29(1):215–226.
- Spanjers H, Vanrolleghem P, Nguyen K, Vanhooren H, Patry GG. 1998. Towards a simulation-benchmark for evaluating respirometry-based control strategies. *Water Sci Technol* 37(12):219–226.
- Tchobanoglous G, Burton FL, Stensel HD. 2003. *Wastewater engineering: treatment, disposal and reuse*. New York: McGraw-Hill Higher Education.
- Vanhooren H, Meirlaen J, Amerlinck Y, Claeys F, Vangheluwe H, Vanrolleghem PA. 2003. WEST: Modelling biological wastewater treatment. *J Hydroinf* 5:27–50.
- von Schulthess R, Gujer W. 1996. Release of nitrous oxide (N₂O) from denitrifying activated sludge: Verification and application of a mathematical model. *Water Res* 30(3):521–530.
- Wunderlin P, Mohn J, Joss A, Emmenegger L, Siegrist H. 2012. Mechanisms of N₂O production in biological wastewater treatment under nitrifying and denitrifying conditions. *Water Res* 46(4):1027–1037.
- Yu R, Kampschreur MJ, van Loosdrecht MCM, Chandran K. 2010. Mechanisms and specific directionality of autotrophic nitrous oxide and nitric oxide generation during transient anoxia. *Environ Sci Technol* 44(4):1313–1319.