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Greenhouse gases from wastewater treatment — A review of modelling tools

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HIGHLIGHTS

- The state of the art in GHG production/emission/modelling from WWTPs was outlined.
- Detailed mechanisms of N_2O production by AOB are still not completely known.
- N_2O modelling could be improved considering both AOB pathways contribution.
- To improve protocols the regulatory framework among countries has to be equalized.
- Plant-wide modelling can help modeller/engineer/operator to reduce GHG emissions.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Nitrous oxide, carbon dioxide and methane are greenhouse gases (GHG) emitted from wastewater treatment that contribute to its carbon footprint. As a result of the increasing awareness of GHG emissions from wastewater treatment plants (WWTPs), new modelling, design, and operational tools have been developed to address and reduce GHG emissions at the plant-wide scale and beyond. This paper reviews the state-of-the-art and the recently developed tools used to understand and manage GHG emissions from WWTPs, and discusses open problems and research gaps.

The literature review reveals that knowledge on the processes related to N_2O formation, especially due to autotrophic biomass, is still incomplete. The literature review shows also that a plant-wide modelling approach that includes GHG is the best option for the understanding how to reduce the carbon footprint of WWTPs. Indeed, several studies have confirmed that a wide vision of the WWPTs has to be considered in order to make them more sustainable as possible. Mechanistic dynamic models were demonstrated as the most comprehensive and reliable tools for GHG assessment. Very few plant-wide GHG modelling studies have been applied to real WWTPs due to

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Methane
Nitrification
Denitrification
Wastewater

the huge difficulties related to data availability and the model complexity. For further improvement in GHG plant-wide modelling and to favour its use at large real scale, knowledge of the mechanisms involved in GHG formation and release, and data acquisition must be enhanced.

Contents

1. Introduction

Water resource recovery facilities, also referred to as wastewater treatment plants (WWTPs), can emit gases that are harmful to the climate, such as nitrous oxide (N_2O), carbon dioxide (CO_2), and methane (CH_4) (Kampschreur et al., 2009; Global Water Research Coalition — GWRC, 2011; Law et al., 2012a). In general, greenhouse gases (GHG) are emitted from a WWTP through three main mechanisms, i.e., direct, indirect internal, and indirect external (GRP, 2008), and these sources are also referred to as Scope I, II, and III emissions, respectively (LGOP, 2008). Direct emissions from WWTPs are primarily related to biological processes (emissions of CO_2 from microbial respiration, N_2O from nitrification and denitrification, and CH_4 from anaerobic digestion). Indirect internal emissions are associated with the consumption of imported electrical or thermal energy. Finally, indirect external emissions are related to sources not directly controlled within the WWTP (e.g., third-party biosolids hauling, production of chemicals and their transportation to the plant, etc.).

The traditional main goal of a WWTP, i.e., to meet effluent standards to protect the receiving water body, requires a broadening in scope if a reduction of GHG emissions is desired. The United States Environmental Protection Agency (USEPA, 2006) estimated that N_2O from WWTPs accounts for approximately 3% of N_2O from all national sources and ranks as the sixth largest contributor to GHG emissions (Law et al., 2012b). Regardless of the origin of the carbon in wastewater (i.e., fossil or non-fossil), quantification of GHG is necessary for a better understanding of how to reduce GHG emissions from WWTPs, and ultimately to maximize the accuracy in the emission reporting process.

The reduction of the carbon and energy footprint is of worldwide concern for global warming mitigation and adaptation strategies. Over the years, several approaches have been described to understand GHG production processes (e.g., Foley et al., 2010; Daelman et al., 2012), quantify and measure GHG emissions (GWRC, 2011; Pan et al., 2012, 2013; Peng et al., 2014) and predict and control their production (Flores-Alsina et al., 2011b; Corominas et al., 2012; Ni et al., 2013a, 2013b; Kim et al., 2015a). Although GHG emissions from WWTPs are currently an area of concern, the source and magnitude (mainly for N_2O) are relatively unknown, and the body of knowledge is still incomplete (Kampschreur et al., 2009, Law et al., 2012a; Peng et al., 2014), although attention must be placed on long-lived carbon (e.g., due to any oxidation of fossil carbon in WWTPs) and the other GHG.

In recent years, new GHG quantification and measuring techniques have increased the available data and literature on GHG emissions (GWRC, 2011; Daelman et al., 2012; Daelman et al., 2015). The Intergovernmental Panel on Climate Change (IPCC) has established emission factors to provide quantification guidelines for estimated GHG emissions in WWTPs. However, many of these measurements are site-specific. For example, the IPCC emission factor for N_2O is currently based on a single study in which the WWTP was not designed for removal of nitrogen (GWRC, 2011). Furthermore, GHG measurements contain a large amount of uncertainty (especially in terms of N_2O), which contrasts with the use of fixed emission factors (Daelman et al., 2015). Measurement uncertainties and lack of transposable data still hinder a correct and required GHG emission quantification process (Sweetapple et al., 2013; Guo and Vanrolleghem, 2014; Caniani et al., 2015; Kim et al., 2015b).

To fill this gap, mathematical models offer useful tools for assessing GHG and evaluating different mitigation alternatives before putting them into practice. GHG modelling can enhance the correct quantification of GHG emissions for different WWTP configurations and evaluate the effects of various operating conditions. A large portfolio of mathematical modelling studies has been developed to include GHG emissions during design, operation, and optimization of WWTPs (Ni et al., 2011, 2013a, 2013b, 2014; Flores-Alsina et al., 2011b; Snip et al., 2014). The incorporation of the carbon footprint and GHG emission quantification as an additional feature in WWTP modelling was suggested by several authors (e.g., Flores-Alsina et al., 2011b, 2014; Corominas et al., 2012; Guo et al., 2012).

Recent studies have demonstrated the paramount importance of applying a plant-wide approach that includes GHG (Flores-Alsina et al., 2014; Kim et al., 2015a). A plant-wide modelling approach includes liquid, solid, and gaseous emissions (Flores-Alsina et al., 2014). At this scale, models can assist users in identifying the synergies and interactions among the different treatment unit processes, thus facilitating quantitative prioritization of the most cost-efficient solutions (Grau et al., 2007). The increasing interest in climate change due to GHG emissions has emphasized the need to establish innovative/comprehensive approaches to better design/control/optimize WWTPs at the plant-wide scale. The traditional approaches that do not include GHG will likely lead to an undesirable increase of GHG emission when other process variables are optimized (Flores-Alsina et al., 2014; Kim et al., 2015b).

However, despite early efforts towards the integration of established activated sludge models (Henze et al., 2000) with GHG models (Batstone et al., 2002; Hiatt and Grady, 2008; Ni et al., 2013a, 2013b;

Mampaey et al., 2013; Guo and Vanrolleghem, 2014), few studies have discussed the benefits (in terms of reducing the GHG emissions coupled with the limitation of other pollutants from WWTPs) of applying GHG model at the plant-wide scale (Gori et al., 2011; Sweetapple et al., 2013; Flores-Alsina et al., 2014; Kim et al., 2015a).

The main goal of this paper is to critically review the state-of-the-art approaches in the modelling of GHG production/emission from WWTPs, with an emphasis on plant-wide modelling. Case studies of model applications are discussed here, and the research gaps and needs are highlighted.

The core of the paper is organized into four sections (Sections 2–5). The first section contains the historical overview of the plant-wide modelling in order to provide the "frames" which conduce to the current knowledge. In Section 3 the state of the art on the GHG modelling at the plant-wide scale is presented and discussed. In Section 4 the key elements/gaps of knowledge of the GHG–N$_2$O modelling at the process or treatment unit scale are summarized in order to deepen insight the key assumptions that can affect the results at plant-wide scale. Finally, Section 5 summarizes the key elements/gaps/findings deduced from the work.

2. Brief historical overview of plant-wide modelling

Plant-wide modelling can be considered one of the main results of the efforts during the last 40 years by the scientific community operating in the field of wastewater treatment. These efforts were aimed at increasing the amount of knowledge on WWTP processes, design, control and management. The interest of two scientific complementary areas was mainly focused on the plant-wide: 1) instrumentation, control and automation (ICA); and 2) modelling.

In the 1970s, ICA became more present in WWTPs, contributing to an increase in process knowledge at full-scale. The first ICA applications were used for simple activated sludge processes aimed at organic matter removal (Olsson, 2012a, Fig. 1). Over the years, the technological improvement of on-line instrumentation (sensors) and computers (storage capacity, speed etc.) has facilitated an understanding of the biological and physical processes that occur inside the WWTPs. In 1982, the International Association on Water Pollution Research and Control (IAWPRC) established a Task Group on Mathematical Modelling for Design and Operation of Activated Sludge Processes (Fig. 1).

From 1982 until the present, mathematical modelling has widely evolved and has been combined with control systems development (Olsson, 2012a,b). Knowledge acquired over the years has contributed to the evolution from simple growth-based kinetics, such as the Activated Sludge Models No. 1 (ASM1), to complex models, such as ASM2d

(Henze et al., 2000) (Fig. 1). Furthermore, mathematical models were developed to reproduce the physical separation processes that occur in settlers or are performed by membranes and processes in the sludge line of a WWTP (Takács et al., 1991).

For the sludge line, the IWA Task Group for Mathematical Modelling of Anaerobic Digestion Processes developed the generic Anaerobic Digestion Model No. 1 (ADM1; Batstone et al., 2002) to reach a common basis for further model development. Indeed, the first version of ADM1 neglects certain processes involved, such as sulphate reduction, acetate oxidation, homoacetogenesis, solid precipitation and inhibition due to sulphides, nitrates, long-chain fatty acids (LCFAs), and weak acids and bases (Fuentes et al., 2008).

Benchmarking tools were developed by combining process models (e.g., ASMs and ADM) and ICA. In 2002 the efforts of the International Water Association Task Group on Benchmarking of Control Strategies for Wastewater Treatment Plants produced the publication of Benchmark Simulation Model No. 1 (BSM1; Copp, 2002) (Fig. 1). The BSM1 represents a virtual plant and integrates an activated sludge system that operates according to ASM1 with a secondary clarifier (Takács et al.,1991). In 2007, the Benchmark Simulation Model No. 2 (BSM2) (Jeppsson et al., 2007; Nopens et al., 2010) was proposed by integrating the BSM1 with wastewater pre-treatment and a sludge train (Fig. 1). BSMs have been widely applied to test or verify different control strategies or to optimize the plant design. The use of BSM modellers optimized processes by addressing several driving forces, such as the reduction of electric energy demand or of pollutant discharge. Further, the use of BSMs has substantially contributed to increased knowledge in terms of innovative technologies or new pollutants of interest (e.g., GHG; Fig. 1). Maere et al. (2011) have presented a modified version of the BSM1 for membrane bioreactor systems (BSM-MBR).

Recently, Puchongkawarin et al. (2015) adopted a plant-wide modelling approach to optimize an existing industrial WWTP in Australia. The authors confirmed the importance of using plant-wide modelling and stressed the need for setting up dedicated databases for reliable and feasible WWTP analysis at the plant-wide scale. During the last years, the interest in moving towards a wastewater treatment plant-wide control (including GHG) with the use of BSM was emphasized in literature (Guo et al., 2012; Guo and Vanrolleghem, 2014; Kim et al., 2015b) (Fig. 1). Thus, a plant-wide approach that includes GHG has become a common goal among researchers.

The overview presented herein shows that the historical need to converge between best plant management and environmental protection has been fulfilled by strengthening the use of the plant-wide approach. Undoubtedly, the "strengthened process" has been aided by technological progress and the process of knowledge advancement.
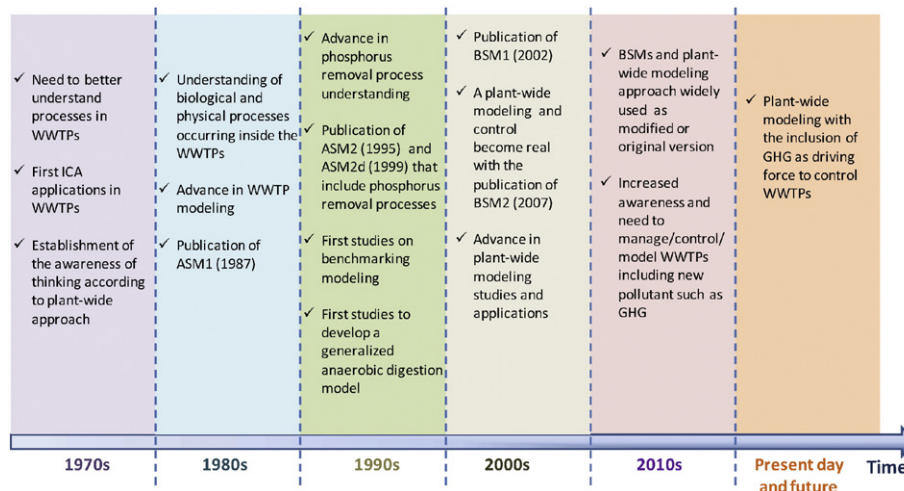

Fig. 1. Milestones in the historical evolution of plant-wide modelling approach.

Thus, the use of plant wide techniques has become a powerful approach to guide designers and operators. However, despite the numerous advantages of the plant-wide approach, modellers cannot exclude the difficulties related to the use/management of complex models, e.g., amount of data required for model calibration, computational intensity, reliability of field use of complex tools for operators, etc. Such difficulties are amplified at the plant-wide scale. As discussed below, the knowledge of the mechanisms of GHG formation is not complete and requires further studies (Castro-Barros et al., 2015). Therefore, extensive and robust databases on GHGs for plant-wide applications are recommended.

3. Previous studies of GHG modelling at the plant-wide scale

The approaches for GHG modelling can be grouped (Corominas et al., 2012): i) empirical models based on the emission factors at the treatment unit scale (e.g., IPCC, 2006; LGOP, 2008); ii) simple comprehensive process-based models at the treatment unit scale (e.g., Monteith et al., 2005; Gori et al., 2011); iii) dynamic mechanistic models at the treatment unit (e.g., Mannina and Cosenza, 2015) or plant-wide scale (e.g., Guo and Vanrolleghem, 2014).

In this study, the attention is primarily focused on the third approach with an emphasis on the plant-wide approach, which is recognized as the most comprehensive and reliable method for effective reduction of overall WWTP emissions (i.e., from liquids, solids, and gases). Attention has been mainly focused on the GHG modelling in water line on which an immature and controversial knowledge still exists.

Mathematical modelling of GHG formation and emission at a plant-wide scale is recent. Previous models presented in the last decade were relatively simple due to limited process knowledge (Corominas et al., 2012). These models were primarily based on linear relationships between GHG emission factors and factors related to the water system (sewer, wastewater, and river), such as operating conditions, treated volume, or discharged effluent volume. Acquisition of experimental data, system analysis and increased computing capacity have led to the development and integration of more reliable models.

Mathematical models of GHG at the plant-wide scale can be divided into two main classes based on the approach adopted to describe the biological processes involved in the GHG and formation/transformation/degradation of other compounds: i) simple steady-state comprehensive process models and ii) dynamic mechanistic models. Details on plant-wide GHG models found in literature for each class and the findings obtained from their applications are reported in Table 1. To each model reported in Table 1 a subjective complexity degree (low, medium, high), established on the basis to the authors experience, has been assigned. Table 2 summarizes the most important relationships between GHG emissions and the corresponding emission factors. In the following sections, a description and the main features of the two groups are provided.

3.1. Simple steady-state process models

The first plant-wide model for GHG was developed by Monteith et al. (2005). Their rational procedure for calculation of greenhouse gas emissions from wastewater treatment facilities contained a streamlined set of equilibrium operations that became the backbone for several subsequent works (e.g., Gori et al., 2011). One of the early plant-wide models was presented and applied by Préndez and Lara-González (2008), who combined several models proposed by the IPCC (1997) and other authors (USEPA, 2007) with the aim of evaluating GHG emissions (in terms of CH_4, CO_2, and N_2O; Table 1). Préndez and Lara-González (2008) analysed different management scenarios and stressed the importance of N_2O, although its emission was lower than that of CO_2 and CH_4 due to its high GWP. Thus, Préndez and Lara-González (2008) began to note the need to investigate the processes related to the formation of N_2O, even at the plant-scale. Despite this need, N_2O modelling at

the plant scale was not a common practice during the first decade of this century. In fact, only the role of CO_2 or CH_4 was often considered (e.g., Rosso and Stenstrom, 2008). For example, Bani Shahabadi et al. (2009) elaborated a complex mathematical model able to quantify the on-site (direct emission) and off-site (due to the used materials, energy demand, and solid disposal) CO_2 and CH_4 emissions from WWTPs (Table 1) without taking into account N_2O. The mathematical model proposed by Bani Shahabadi et al. (2009), based on established kinetic relationships and mass balances, had a more detailed structure than the previous models and showed that off-site emissions of anaerobic and hybrid treatment systems contributed significantly to the overall GHG emissions compared with the on-site emissions due to material usage for on-site consumption. The authors showed that nutrient removal processes play a relevant role in terms of total GHG emissions in aerobic and hybrid processes. Indeed, compared with other studies (Cakir and Stenstrom, 2005; Greenfield and Batstone, 2005; Monteith et al., 2005), higher total GHG production was observed. In terms of energy production/recovery, the authors suggested the implementation of an aerobic reactor combined with anaerobic solid digestion for energy recovery. In 2010, Bani Shahabadi et al. applied the same model to evaluate the GHG emissions (on-site and off-site) of a hybrid treatment system for food wastewater with highly variable influent BOD and nitrogen concentrations (Table 1). The results showed that to reduce GHG emissions, it was necessary to recover and reuse biogas to generate the required energy for the heating needs of the plant. Indeed, the total energy needs of the WWTP for aeration, heating and electricity could be completely satisfied by adopting biogas as fuel. Therefore, the internal GHG emissions associated with the consumption of imported electrical or thermal energy are severely reduced.

Even Gori et al. (2011) presented a simplified model based on a plant-wide COD balance by expanding on the rational procedures by Monteith et al. (2005) and Rosso and Stenstrom (2008) and neglecting the role of N_2O. The model was able to quantify the carbon and energy footprint of a conventional activated sludge WWTP based on a modified Ludzack–Ettinger process for denitrification with primary sedimentation, anaerobic stabilization and energy recovery (Table 1). The authors observed that by increasing the ratio between soluble and total COD, an increase of the carbon and energy footprint took place due to aeration. Conversely, an increase in particulate (e.g., pCOD/COD) removal in primary sedimentation reduced the energy demand in the aerated tank and the CO_2 emissions, both due to aerobic respiration and power demand for aeration blowers. Indeed, the amount of organic carbon that has to be degraded inside the aerobic tank decreases. The model presented in Gori et al. (2011) was further developed by coupling the biological activated sludge and digestion processes using the ASM3 (Henze et al., 2000) and the ADM1 (Batstone et al., 2002). Integration of these models allowed a discussion of the role of primary sedimentation in plant-wide energy recovery and carbon footprint (Gori et al. 2013) (Table 1). The authors found that the presence of a primary settler allowed reduction of the overall CO_2 equivalent emissions and energy requirements. Indeed, primary sludge has a higher methane yield because secondary sludge is primarily composed of bacteria and highly reduced colloids. However, the model of Gori et al. (2013) does not consider the N_2O emissions, thus, neglecting the potential negative effect of the primary settler in terms of N_2O emission. Indeed several experimental studies have investigated the role of the carbon amount fed into the aerobic biological treatment section (Kampschreur et al., 2009). With the increase of the ratio between carbon and nitrogen that could be obtained without the primary settler, the N_2O formation during the denitrification decreases the available biodegradable organic carbon is not limiting (Kampschreur et al., 2009). However, as authors are aware, no modelling study has yet investigated the effect of removing the primary settling at plant-wide scale in terms of total GHG emission including N_2O.

Also, the role of upstream operations considered innocuous for energy and carbon footprint, such as grit removal, was highlighted: a neglect

Table 1
Summary of the main relevant models based on the plant-wide approach found in literature.

Reference	Type of WWTP	Type of model	Model complexity	Evaluation criteria	Variables	Remarks
Plant-wide approach						
Flores-Alsina et al. (2014)	Primary clarifier, modified Ludzack–Ettinger configuration of the activated sludge unit (2 anoxic and 3 aerobic tanks), sludge thickener, anaerobic digester, storage tank and dewatering unit	BSM2G (dynamic)	H	Effluent quality index; Operational Costs Index; GHG emissions due to: direct secondary treatment, sludge processing, net power, chemicals, sludge disposal and reuse.	Dissolved oxygen, primary clarifier efficiency by varying the TSS removal, temperature in the anaerobic digester, by controlling the return flowrate of the anaerobic digester supernatants	High (66%) TSS removal efficiency in the primary settler entails: reduction of the off-site CO_2 emission due to the aeration, increase of the energy recovery due to the anaerobic digestion (higher CO_2 credit), increase of N_2O emission due to the inadequate C/N ratio. Low DO concentration (1 mg O_2 L^{-1}) leads: energy saving, decrease in effluent quality, increase of the total plant N_2O emission.
Flores-Alsina et al. (2011a)	Primary clarifier, modified Ludzack–Ettinger configuration of the activated sludge unit (2 anoxic and 3 aerobic tanks), sludge thickener, anaerobic digester, storage tank and dewatering unit	BSM2G (dynamic)	H	Effluent quality index; Operational Costs Index; GHG emissions due to: direct secondary treatment, sludge processing, net power, chemicals, sludge disposal and reuse.	3 scenarios where the role of the dissolved oxygen concentration in the aerated section (scenario 1), the sludge retention time (scenario 2) and COD/N ratios in the biological reactor (scenario 3) as promoters of GHG emissions is examined	Low concentration of oxygen ($=1$ mg L^{-1}) leads to a reduction of CO_2 thanks to the lower energy consumption and the increase of N_2O emissions due to nitrite accumulation. At low SRT (around 14 days) GHG emissions due to the sludge treatment and disposal increase. At high SRT (around 18 days) non-N_2O GHG emissions and off-site emissions due to electrical use increase. High COD/N ratio increase the GHG emissions in the secondary treatment. At low COD/N the total GHG emissions are very low.
Flores-Alsina et al. (2011b)	Primary clarifier, modified Ludzack–Ettinger configuration of the activated sludge unit (2 anoxic and 3 aerobic tanks), sludge thickener, anaerobic digester, storage tank and dewatering unit	BSM2G (dynamic)	H	Effluent quality index; Operational Costs Index; GHG emissions due to: direct secondary treatment, sludge processing, net power, chemicals, sludge disposal and reuse.	Primary clarifier efficiency by varying the TSS removal (33%, 50%, 66%)	High (66%) TSS removal efficiency in the primary settler entails: reduction of the off-site CO_2 emission due to the aeration, increase of the energy recovery due to the anaerobic digestion (higher CO_2 credit), increase of N_2O emission due to the inadequate C/N ratio.
Corominas et al. (2012)	Primary clarifier, modified Ludzack–Ettinger configuration of the activated sludge unit (2 anoxic and 3 aerobic tanks), sludge thickener, anaerobic digester, storage tank and dewatering unit	BSM2G (dynamic and Steady-state) and plant wide-model based on Bridle et al., 2008 (steady-state)	L/M/H	Total direct secondary treatment emissions; Total sludge processing GHG emissions; Total net power GHG emissions; Total GHG emissions (GHG total).	Anaerobic digester volume (large or small). Steady-state (flow-based average data) and dynamic (flow-based dynamic data) simulations are performed by using both models.	The generation of GHGs is not a linear process and daily–weekly–seasonal variations and operating conditions affect their production and emission. Estimating GHGs using a single factor would not capture variability in the emissions related to changes in process configuration, operating conditions and temperature. The use of dynamic process-based models helps to better evaluate GHG emissions.
Guo et al. (2012)	Primary clarifier, modified Ludzack–Ettinger configuration of the activated sludge unit (2 anoxic and 3 aerobic tanks), sludge thickener, anaerobic digester, storage tank and dewatering unit	ASMG + ADM1 (Batstone et al., 2002) (steady state and dynamic) + integrated model of Sharma et al. (2008) and Guisasola et al. (2009) for evaluating CH_4 and H_2S produced inside the sewer system	H	Effluent quality index; Operational Costs Index; GHG emissions	Four scenarios where the role of influent COD/N ratio (default scenario), dissolved oxygen in the aerobic tanks, ammonia and dissolved concentration in the last aerobic tank is assessed.	The default scenario shows that more carbon dosing emits more total net WWTP GHGs, the carbon dosing can affect the N_2O production. DO shows an important effect on N_2O emissions and its spatial distribution should be considered in the strategy design. Controlling both DO and ammonia concentration in the

last aerobic tank OCI and EQI increase.

Gori et al. (2011)	Real plant: headworks, primary clarifier, pre-denitrification (modified Ludzack–Ettinger configuration with 1 anoxic and 1 aerobic tanks), secondary clarifier, disinfection, sludge thickener, anaerobic digester, dewatering unit, sludge deposal	Carbon and energy footprint models as function of COD fractions (Monteith et al., 2005; Rosso and Stenstrom, 2008)	L	CO_2 from activated sludge respiration, CO_{2eq} from combustion of CH_4 in biogas, CO_2 from combustion of CH_4 in biogas, CO_{2eq} from biogas fugitive emission, CO_{2eq} from biosolids dewatering. Energy footprint variables: energy recovery, energy demand.	COD fractions	The increase of the ratio between soluble COD (sCOD) and total COD (COD) increases the energy demand on the aeration reactors, the associated CO_2 direct emission from respiration, and the indirect emission for power generation. In case of excessive bCOD removal in the primary settler care must be used since the nutrient removal process downstream may suffer.
Gori et al. (2013)	Two real plants: plant 1 (located in a warm region in USA) — headworks, primary clarifier, predenitrification (modified Ludzack–Ettinger configuration with 1 anoxic and 1 aerobic tanks), secondary clarifier, disinfection, sludge thickener, anaerobic digester, dewatering unit, sludge deposal; plant 2 (located in Italy) — headworks, predenitrification (modified Ludzack–Ettinger configuration with 1 anoxic and 1 aerobic tanks), secondary clarifier, disinfection, sludge thickener, anaerobic digester, dewatering unit, sludge deposal	ASM3 (Henze et al., 2000) + ADM1 (Batstone et al., 2002)	M	CO_2 from activated sludge respiration, CO_{2eq} from combustion of CH_4 in biogas, CO_2 from combustion of CH_4 in biogas, CO_{2eq} from biogas fugitive emission, CO_{2eq} from biosolids dewatering. Energy footprint variables: energy recovery, energy demand.	Primary settler COD removal efficiency	Primary settling increases the solid fraction of COD that is processed in anaerobic digestion, with an associated increase in biogas production and energy recovery, and a reduction in overall emissions of CO_2 and CO_{2eq} from power importation.
Bani Shahabadi et al. (2009)	Three plant schemes for treating industrial wastewater (average BOD = 2000 kg BOD/d): plant 1 — primary clarifier, anoxic and aerobic biological treatment, secondary clarifier, anaerobic digester; plant 2 — primary clarifier, anaerobic biological treatment, secondary clarifier, anaerobic digester; plant 3 — primary clarifier, anaerobic, anoxic and aerobic biological treatment (hybrid), secondary clarifier, anaerobic digester.	Model based on established kinetics relationships and mass balances	M	Total GHG emissions: on-site biological processes, off-site biological processes, due to materials used, due to energy demands, due to solid disposal, extra saving of GHG emissions due to biogas recovery.	Two scenarios for each plant scheme: 1) flaring of biogas without energy recovery and reuse; 2) energy recovery and combustion of biogas	The on-site biological processes made the highest contribution to GHG emissions in the aerobic treatment system while the highest emissions in anaerobic and hybrid treatment systems were obtained by off-site GHG emissions, mainly due to on-site material usage. Biogas recovery and reuse as fuel cover the total energy needs of the treatment plants for aeration, heating and electricity for all three types of operations, and considerably reduce GHG emissions by 512, 673, and 988 kg CO_{2eq}/d from a total of 3265, 6625, and 7640 kg CO_{2eq}/d for aerobic, anaerobic, and hybrid treatment systems, respectively.
Bani Shahabadi et al. (2010)	Primary clarifier, anaerobic, anoxic and aerobic biological treatment (hybrid), secondary clarifier, anaerobic digester where food processing wastewaters are treated.	Model based on established kinetics relationships and mass balances	M	Total GHG emissions (as sum of CO_2 and CH_4): by on-site biological processes, by off-site biological processes, due to materials used, due to energy demands, due to solid disposal, extra saving of GHG emissions due to biogas recovery.	Two scenarios for each plant scheme: 1) flaring of biogas without energy recovery and reuse; 2) energy recovery and combustion of biogas	The recovery of biogas and its reuse as fuel have a remarkable impact on GHG emissions and reduce the overall emissions by 1023 kg CO_{2eq}/d from a total of 7640 kg CO_{2eq}/d when treating a wastewater at 2000 kg BOD/d. Furthermore, the recovery of biogas and its combustion may be used to cover the entire energy needs of the treatment plant for aeration, heating and electricity generation while creating emissions credit equal to 34 kg CO_{2eq}/d.
Sweetapple et al.	Primary clarifier, modified	BSM2-e (BSM2 model adjusted in	H	Effluent quality index;	Local and global sensitivity	Uncertainty in modelled nitrous oxide

Table 1 (*continued*)

Reference	Type of WWTP	Type of model	Model complexity	Evaluation criteria	Variables	Remarks
(2013)	Ludzack–Ettinger configuration of the activated sludge unit (2 anoxic and 3 aerobic tanks), sludge thickener, anaerobic digester, storage tank and dewatering unit	order to model N_2O emission from a four-step denitrification as detailed by Samie et al. (2011). Stripping of N_2O from solution is then modelled using Henry's law (dynamic modelling)		Operational Costs Index; GHG emissions due to: Aerobic substrate utilization (CO_2), biomass decay (CO_2) and denitrification (CO_2 and N_2O) in activated sludge reactors; biogas leakage (CO_2 and CH_4) and combustion (CO_2); Stripping of dissolved gases (CH_4) in dewatering unit; Generation of energy imported; Manufacture of chemicals; Offsite degradation of effluent; transport and offsite degradation of sludge.	analysis performed considering 39 model parameters that vary within a defined range established on the basis of an uncertainty class.	emissions is the primary contributor to uncertainty in total GHG emissions, due largely to the interaction effects of three nitrogen conversion modelling parameters.
Sweetapple et al. (2014a)	Primary clarifier, modified Ludzack–Ettinger configuration of the activated sludge unit (2 anoxic and 3 aerobic tanks), sludge thickener, anaerobic digester, storage tank and dewatering unit	BSM2-e (Sweetapple et al., 2013)	H	Effluent quality index; Operational Costs Index; GHG emissions due to: Aerobic substrate utilization (CO_2), biomass decay (CO_2) and denitrification (CO_2 and N_2O) in activated sludge reactors; Biogas leakage (CO_2 and CH_4) and combustion (CO_2); Stripping of dissolved gases (CH_4) in dewatering unit; Generation of energy imported; Manufacture of chemicals; Offsite degradation of effluent; Transport and offsite degradation of sludge;	Three optimization problems are implemented with the aim to: minimize OCI and total GHG emission (set x); minimize OCI, EQI and total GHG emission (set y); minimize OCI, total GHG emission, effluent BOD_5, effluent ammonia, effluent nitrogen (set z). The variables are: Internal recycle flow rate, carbon source addition rate in the first, second and fifth activated sludge reactors, KLa in tanks 1, 2, 3 and 5; DO.	Multi-objective optimization can facilitate a significant reduction in GHG emissions. The reduction of GHG emissions is likely to incur an increase in effluent ammonia and total nitrogen concentrations
Porro et al. (2011)	Collection system; Wastewater treatment plant: Primary and secondary clarifier, predenitrification activated sludge unit (2 anoxic and 3 aerobic tanks), sludge thickener, anaerobic digester, storage tank and dewatering unit; river.	ASMG + ADM1 (Batstone et al., 2002) (steady state and dynamic) + integrated model of Sharma et al. (2008) and Guisasola et al. (2009) for evaluating CH_4 and H_2S produced inside the sewer system	H	Effluent quality index; Operational Costs Index; GHG emissions.	3 scenarios where the role of the COD/N ratios in the biological reactor (scenario 1, default), dissolved oxygen concentration fixed at 2 mg/L (scenario 2) and 1.3 mg/L (scenario 3) in the aerated section as promoters of GHG emissions is examined	Sewer methane emissions accounted for approximately eight percent of the total system GHG emissions, while WWTP N_2O emissions accounted for approximately 25%. lowering the DO and aeration electric CO_2 emissions actually increased the overall GHG emissions due to an increase in N_2O emissions. Steady state models and/or emission factors may not adequately capture the full N_2O emission potential, as it is largely dependent on system dynamics.
Préndez and Lara-González (2008)	Real plant	linear equations relating sanitation activity information to design parameters, emission factors and the biochemical process for organic matter decomposition in wastewater and sludge (steady state)	L	Total GHG emissions as: CH_4, CO_2, N_2O	Six scenario analysis where the % of wastewater treated with aerobic and anaerobic processes is varied. Further the biogas reused or not was considered.	For the end of the modelled period (2027), results show emissions of about 65 Tg CO_{2e}/year (as global warming potential), which represent around 50% of national emissions. These values could be reduced if certain sanitation management strategies were introduced in the environmental management by the sanitation company in charge of wastewater treatment.
Rodriguez-Garcia et al. (2012)	Real plant with modified Ludzack–Ettinger configuration (steady	Direct emissions estimation model	M	Total GHG emissions due to: biological processes (nitrification,	Results were compared with ASM1 (Henze et al., 2000)	Direct N_2O emissions are far more relevant than those associated with

electricity use, so far considered the main source of GWP impact, and thus should be taken into account for Life Cycle Assessment (LCA). CO_2 emissions, although traditionally not taken into account, can be of similar importance to electricity associated ones if 20% are supposed not to be of biogenic origin.

denitrification), nitrogen stripping, methane combustion, energy requirement.

state)

of such operations may have detrimental or catastrophic effects on the downstream operations which carry significant weight on the energy and carbon balance at the plant-wide scale (e.g., excessive grit accumulation in digesters, resulting in poor or no biogas production and excessive biosolids mass outflow; Nolasco and Rosso, 2014).

Plant-wide models that include GHG in terms of N_2O have been published since 2012. Rodriguez-Garcia et al. (2012) presented a critical review of the on-site GHG emissions of WWTPs and suggested a methodology for systematically quantifying these emissions in the life-cycle inventory (Table 1), including the role of N_2O. Specifically, they applied the diffusive emissions estimation model (DEEM), a modified version of the ASM1 (Henze et al., 2000), which allows CO_2 and N_2O emissions quantification. The DEEM model was implemented by including both CO_2 and N_2O formation during the nitrification pathway, as proposed by Mampaey et al. (2011). The DEEM A considers ammonia as the electron source, and DEEM B considers biomass as the electron source. Rodriguez-Garcia et al. (2012) applied DEEM to an existing Spanish WWTPs with a modified Ludzack–Ettinger configuration and compared the results with the results obtained by applying the ASM1 and Activated Sludge/Anaerobic Digestion models (this was later implemented within the BioWin® modelling simulator, Envirosim, ON). The results showed that the DEEM model provided results similar to those of other models but with the advantage of easy application for Life Cycle Assessment applications. Garrido-Baserba et al. (2012) adapted and extended this approach for the assessment of WWTP configurations and treatment technologies. Recently Kyung et al. (2015) by combining a simple and comprehensive model established a method to estimate on-site and off-site GHG emissions during full-scale operation of a WWTP. Since the model of Kyung et al. (2015) was applied excluding the sludge line treatment contribution has not be detailed in this study as a plant-wide model. With the aim of evaluating the effectiveness of simple steady-state comprehensive process models, Corominas et al. (2012) compared the model proposed by Bridle et al. (2008) with a process-based model (Benchmark Simulation Model No. 2 for greenhouse gas — BSM2G) in terms of effluent quality index (EQI), operational cost index (OCI) and total GHG emissions. The authors demonstrated that simplified models compared with process-based models underestimate GHG emissions, mainly in terms of N_2O. Thus, detailed process-based models are required to better understand and describe the processes involved in GHG emissions and their relationship to the other processes (Corominas et al., 2012; Guo and Vanrolleghem, 2014). Corominas et al. (2012) also investigated the role of dynamic and steady-state simulations in predicting GHG emissions (Table 1). The authors found that the steady-state and dynamic results did not differ significantly in terms of GHG emissions. However, significant variability was observed in the dynamic results due to the changes in influent COD/N ratio and temperature. Steady-state models are not able to capture the N_2O variability.

From the literature review, we conclude that simple steady-state comprehensive process models have undoubtedly provided an important contribution to the understanding and to the identification of the major factors of GHG formation in WWTPs. Furthermore, such models provided proof of the high level of interconnection and interaction among the treatment units and advocated the importance of a plant-wide approach. The use of simple models has pinpointed the need to understand the mechanisms related to N_2O formation (often neglected in earlier models). These mechanisms have been since investigated with the use of dynamic mechanistic models. However, our review shows that the results of this group of models are strongly affected by the assumptions used to simplify the models, thus overestimating or underestimating the evaluated GHG emissions (Corominas et al., 2012). Therefore, the use of this group of models is appropriate for use as a screening tool because it provides only a rough approximation of the emitted GHG. Therefore, the use of mechanistic process-based models (such as ASM based modes) is suggested. However, it is important to specify that plant-wide models based on ASM concept that

Table 2
Most relevant emission factors derived from literature.

Reference	Equation	Factors	Remarks
Off-site emissions			
Power generation (kg CO_2/d)			
Bani Shahabadi et al. (2009)	$P_{CO_2} = E_{required} \cdot \sum (Fi \cdot EFi)$	$E_{required}$ (kWh/d) is the electricity demands of the plant obtained by multiplying the electricity consumption rate of 0.2 kWh/mc_{ww} with the daily influent flow (mc/d) Fi (dimensionless) is the percentage contribution of fuel i to satisfy electricity generation needs EFi (g CO_{2e}/kWh) is the GHG emission factor of fuel i in producing electricity.	Electricity consumption rate of 0.2 kWh/mc_{ww} for aerobic and anaerobic treatment systems
Gori et al. (2011, 2013)	$P_{CO_2} = k_{PG} \cdot (e_D - e_R)$	e_D (kWh/d) is the total energy demand calculated as the sum of five component: energy demand for primary sedimentation, energy demand for secondary sedimentation, energy demand for anaerobic digestion, energy demand for other equipment. k_{PG} (kg CO_{2e}/kWh) = 0.245 is the site-specific CO_2 emission factor per unit of energy generated e_R (kWh/d) is the energy recovery; it is proportional to the biogas produced which is in turn proportional to the removal of bCOD (biodegradable COD) in the digester	The authors assume a site-specific CO_2 emission factor (k_{PG}) per unit of energy generated, instead of energy mix. A portion of biogas produced from anaerobic digester is considered to be recovered to cover a portion of plant energy requirements.
Listowski et al. (2011)	$P_{CO_2} = k_{PG} \cdot e_D$	e_D (kWh/d) is the total energy demand calculated as the sum of five component: energy demand for primary sedimentation, energy demand for secondary sedimentation, energy demand for anaerobic digestion, energy demand for other equipment. k_{PG} (kg CO_{2e}/kWh) = 0.967 is the site-specific CO_2 emission factor per unit of energy generated	The authors assume a site-specific CO_2 emission factor (k_{PG}) per unit of energy generated, instead of energy mix
Degradation of remaining biosolids in the digester effluent (gCO_{2e}/d)			
Bani Shahabadi et al. (2009)	$P_{CO_2} = (0.58 \text{ g } CO_2/\text{g VSS} \cdot M_{remaining\,biosolid}) + (23 \cdot 0.35 \text{ gCH}_4/\text{gVSS} \cdot M_{remaining\,biosolid})$	The coefficient 0.58 is the conversion factors to transform the remaining biosolids in CO_2 $M_{remaining\,biosolid}$ (gVSS/d) is the remaining biodegradable solids in the digester effluent The coefficient 23 is the GWP (Global Warming Potential) of CH_4 The coefficient 0.35 g is the conversion factors to transform the remaining biosolids in CH_4	The off-site GHG emissions also incorporate those due to the degradation of remaining biodegradable solids in the digester effluent. The emissions are calculated by assuming that the residual organic matter is degraded under anaerobic condition with the resulting generation of CH_4 and CO_2. The GHG emissions from off-site carbon biodegradation can be calculated by using the stoichiometric equation for biomass decay in anaerobic environment provided by Monteith et al.(2005): $0.05C_5H_7O_2N + 0.2H_2O = 0.075CO_2 + 0.125CH_4 + 0.05NH_4^+ + 0.05HHCO_3$
Biological degradation in the wastewater treatment effluent (kg N_2O/y)			
Préndez and Lara-González (2008)	$P_{N_2O} = N_{effluent} \cdot EF_{effluent}$	$N_{effluent}$ (kg N/y) is the nitrogen load in the effluent discharged into aquatic environments $EF_{effluent} = 0.005 * 44/28$ kg N_2O/kg N is the emission factor for N_2O emissions from discharged wastewater The coefficient 0.35 g is the conversion factors to transform the remaining biosolids in CH_4	The default IPCC emission factor for N_2O emissions from domestic wastewater effluent is 0.005 kg N_2O-N/kg N, with a values range of 0.0005 to 0.25 kg N_2O–N/kg N (IPCC Guidelines 2006, Volume 5, Chapter 6, Table 6.11) are based on limited field data and on specific assumptions regarding the occurrence of nitrification and denitrification in rivers and in estuaries.
On-site emissions			
Water–Line. Aerobic biological processes			
Gori et al., 2011	$P_{CO_{2e},ASP} = Q \cdot 0.99 \cdot (1-Y_H) \cdot \eta_{ASP} \cdot bCOD + Q \times 1.03 \cdot Y_H \cdot \eta_{ASP} \cdot bCOD \cdot \frac{k_{d,H} \cdot MCRT}{1+k_{d,H} \cdot MCRT}$	Q (mc/d) is the plant influent flow rate The coefficient 0.99 is the emission factor (kg CO_{2e}/kg COD) related to organic compound Y_H (massVSS/massCOD) is the heterotrophic biomass yield The coefficient 1.03 is the emission factor (kg CO_{2e}/kg COD) related to activated sludge biomass η_{ASP} (%) is the bCOD removal in the activated sludge process $k_{d,H}$ (1/d) is the decay rate of heterotrophic biomass MCRT (d) is the mean cell retention time.	In this study, the authors hypothesise that wastewater organic compounds and activated sludge biomass could be represented through the formula $C_{10}H_{19}O_3N$ and $C_5H_7O_2N$, respectively, which is widely used for the case of domestic wastewater.
Préndez and Lara-González (2008)	$P_{N_2O,PLANT} = P \cdot T_{PLANT} \cdot F_{IND-COM} \cdot EF_{PLANT}$	P is the served population T_{PLANT} (%) is the degree of utilization of modern centralized WWT plants $F_{IND-COM}$ (dimensionless) is the fraction of industrial and commercial co-discharged protein (the IPCC default value is 1.25, based on data in Metcalf & Eddy, Inc. (2003) and expert judgement, but it has a values range of 1 to 1.5, IPCC Guidelines 2006, Volume 5, Chapter 6, Table 6.11) $EF_{PLANT} = 3.2$ gN_2O/person···y is the emission factor.	The overall default emission factor to estimate N_2O emissions (EF_{PLANT}) from WWTP is 3.2 gN_2O/person···y, with a values range of 2 to 8 gN_2O/person···y (IPCC Guidelines 2006, Volume 5, Chapter 6, Table 6.11). This emission factor was determined during field testing at a plant that received only domestic wastewater treatment plant in the Northern United States; no other country-specific emission factors are available. This wastewater already included non-consumption protein, but did not include any co-discharged industrial and commercial wastewater.
Sludge-line. Anaerobic digestion and biogas combustion (kg CO_2/d)			

Table 2 (*continued*)

Reference	Equation	Factors	Remarks
Gori et al. (2011, 2013)	$P_{CO_2,AD} = \frac{m_{BG}}{\rho_{BG}} \cdot \rho_{CO_2} \cdot 0.35$ $P_{CO_2,comb} = m_{BG} \cdot (1-\eta_{FE}) \cdot \frac{44}{16}$	$m_{BG}(\frac{kg_{biogas}}{d})$ is the mass flow of biogas $\rho_{BG}(\frac{kg_{biogas}}{Nmc})$ is the biogas density $\rho_{CO_2}(\frac{kg\_CO_2}{Nmc})$ is the CO_2 density The coefficient 0.35 g is the biogas emission factor η_{FE} is the percentage of total methane produced The coefficient 44/16 is the ratio between the gramme molecular weights of CO_2 and CH_4	In the anaerobic environment, the direct emissions from anaerobic digester and from biogas combustion are calculated

***Sludge-Line. Fugitive emission during sludge dewatering*(kg CO$_2$/d)**

Gori et al. (2011, 2013)	$P_{CO_{2e},fugitive} = 25 \cdot (m_{CH_4,fugitive} \cdot \mu_{FE} + m_{CH_4,dewatering})$	the coefficient 25 is the GWP of CH_4 μ_{FE} is the methane fugitive emission (% of total methane produced) mCH_4 is the mass flow of methan	In the anaerobic environment the methane emissions as CO_2 equivalent are calculated

***Sludge– Line. Methane emissions during wastewater processes*(kg CO$_4$/d)**

Préndez and Lara-González (2008)	$P_{CH_4} = (Total\,Organic\,Waste \cdot EF) - Methane\,Recovery$	total organic waste (kg BOD/d) is generated by domestic units EF is the emission factor (kg CH_4/kg BOD) that represents the mass of methane generated per mass of organic matter degraded	Good practice is to use country/site-specific emission factor, expressed in terms of kg CH_4/kg BOD to be consistent with the activity data; if country/site-specific data are not available a default value can be used. The emission factor is a function of the maximum methane producing potential of each waste type (Bo) and the weighted average of the methane conversion factors (MCFs) for the different wastewater treatment systems used in the country, as shown in the following equation: $EF = Bo \cdots MCFs$ The IPCC Guidelines (2000, Chapter 5) suggest a Bo default value of 0.25 kg CH_4/kg COD or 0.6 kg CH_4/kg BOD, based on a theoretical calculation. Note that degradable carbon in organic waste can be measured in terms of either BOD (Biological Oxygen Demand) or COD (Chemical Oxygen Demand); for typical domestic raw sewage COD is from 2 to 2.5 times higher than BOD. The MCF is an estimate of the fraction of BOD or COD that will ultimately degrade anaerobically; it is a country/site-specific parameter and depends on the type of the treatment: in the case of anaerobic digester for sludge without methane recovery the default value is 0.8, with a values range of 0.8 to 1 (IPCC Guidelines 2006, Volume 5, Chapter 6, Table 6.3).

include the N$_2$O modelling are often very complex compared to the simple steady-state comprehensive models. Indeed, state variables (N$_2$O, NO etc.) and model factors have to be added in the Gujer matrix. The model complexity amplifies in case the contribution of autotrophic biomass in the N$_2$O formation is also taken into account.

3.2. Dynamic mechanistic models

The IWA Task Group "on the use of water quality and process models for minimizing wastewater utility greenhouse gas footprints" has strongly contributed to development of a benchmarking model based on the existing BSMs to test control and monitoring strategies for reduction of GHG emissions in urban water systems. The evolution of plant-wide dynamic models over the years has provided robust and detailed tools to minimize GHG emissions while maintaining high liquid effluent quality.

Porro et al. (2011) and Guo et al. (2012) presented the first results of the IWA Task Group (Table 1). Specifically, Porro et al. (2011) presented a modified version of BSM2 in which GHG modelling is taken into account. In the modified version of BSM2, the ASM1 was replaced with the Activated Sludge Models for Nitrogen (ASMN) model proposed by Hiatt and Grady (2008) and corrected by Corominas et al. (2012). The

ASMN model is based on the ASM1 (Henze et al., 2000) and describes the nitrification process using two steps and the denitrification using four steps (details about the ASMN model will be provided in the Section 5). Thus, in an attempt to better describe the N$_2$O formation process, the two steps of nitrification and the four steps of the denitrification processes were added. Further, to predict the N$_2$O emissions due to nitrification, the BSM2 was extended with the model proposed by Mampaey et al. (2011). Moreover, the model proposed by Guisasola et al. (2009) was included to predict CH$_4$ production and emission in the sewer system. Porro et al. (2011) applied the extended BSM2 to a sewer network and to a WWTP with the same scheme used in the BSM platform. Porro and co-authors found that CH$_4$ emissions due to the sewer system accounted for approximately 8% of the total system GHG emissions, whereas N$_2$O emissions from WWTP accounted for approximately 25% of the total amount of GHG (Table 1). Furthermore, the authors showed that by operating the aerobic tanks at a low dissolved oxygen (DO) concentration, the CO$_2$ emissions related to the aeration decreased, but the overall GHG emissions increased due to the increase in N$_2$O emission. These results emphasized the importance of using plant-wide and arguably system-wide tools to evaluate control strategies aimed at reducing not only the N$_2$O and CO$_2$ emissions but also the overall GHG footprint.

Using the BSM2G, Flores-Alsina et al. (2011a) investigated the effect of Total Suspended Solids (TSS) removal efficiency in the primary clarifier on the EQI, OCI and total GHG emissions value (Table 1). Their results were in agreement with those of Gori et al. (2011) and von Schulthess and Gujer (1996) in terms of COD/N ratio and N_2O production. Specifically, these researchers showed that the higher TSS efficiency removal in the primary clarifier decreased the CO_2 on-site emissions (due to the lower CO_2 production during endogenous and respiration biomass growth) and the CO_2 off-site emission (due to the lower aeration requirement) (Table 1). High TSS removal efficiency in the primary clarifier increases energy recovery in the anaerobic digestion but leads to an increase of N_2O emissions due to the low COD/N ratio (Table 1). However, Flores-Alsina et al. (2011a) showed that in terms of N_2O production, the results are in contrast with those of Kampschreur et al. (2009), who showed that N_2O production increases during winter. Using the BSM2G model, Flores-Alsina et al. (2011b) evaluated different control strategies using the EQI, OCI and time in violation (TIV) and included the total GHG emissions (Table 1). The results confirmed the findings derived from other studies in terms of dependence among DO, COD/N ratio and GHG emissions (Table 1). For example, it was demonstrated that the lowest GHG emissions were found at a low sludge retention time (SRT, of approximately 12 days). Furthermore, Flores-Alsina et al. (2011b) demonstrated that no unique best strategy exists to simultaneously optimize EQI, OCI, TIV and GHG emissions. For example, the strategies that minimize GHG emissions cause poor performance in EQI due to the high nitrogen concentration discharged. Thus, the authors underlined the need to balance the criteria adopted to select the best strategy. Again, this demonstrates the need for a plant-wide approach.

More recently, Flores-Alsina et al. (2014) demonstrated the potential of adding GHG emissions using a plant-wide approach to elaborate the best strategies for control of WWTPs (Table 1). The authors used the BSM2G model to investigate the influence of process variables (e.g., DO in the aerobic tanks, removal efficiency of TSS in the primary clarifier, etc.) on such performance indicators as EQI, OCI, and GHG emissions.

Sweetapple et al. (2013) presented the BSM-e, a modified version of BSM2 (Jeppsson et al., 2007) that is able to quantify on-site and off-site GHG emissions from a WWTP with the same configuration as the BSM2 (as detailed by Jeppsson et al., 2007 and Nopens et al., 2010; Table 1). The BSM-e model differs from the BSM2G because it includes four-steps for denitrification, as detailed by Samie et al. (2011), including stripping of N_2O and CO_2 emissions, as suggested by Monteith et al. (2005) (Table 1). Sweetapple et al. (2013) used the BSM-e model to identify the key sources of uncertainty in GHG modelling and found that uncertainty in the modelled N_2O emissions is the primary contributor to uncertainty in GHG emissions due to the large interaction effects of the three modelling parameters for nitrogen conversion. This emphasizes the need for detailed knowledge of the N_2O mechanism and a reliable database.

The BSM-e model has been adopted by Sweetapple during the recent years to evaluate strategies and criteria aimed at reducing GHG emissions at the plant-wide scale (Table 1). Sweetapple et al. (2014b) presented multi-objective optimization criteria corroborating the importance of using a plant-wide view for optimal plant control. Sweetapple et al. (2014a) investigated the effects of adjusting control handle values on GHG from WWTP using the BSM-e model (Sweetapple et al., 2013) and the BSM2 model (Jeppsson et al., 2007). The authors found that the variance in total GHG emissions is primarily related to the changes in direct N_2O emissions, selection of values for waste flow rates, and aeration intensity in the final activated sludge reactor. The results emphasize the need for better investigation of the N_2O dynamics. Indeed, detailed dynamic mechanistic models are recommended to better account for the strong non-linearity and interconnections among the different WWTP treatment units (Flores-Alsina et al., 2014).

Bisinella de Faria et al. (2015) have recently attempt to combine dynamic WWTP modelling (BSM2 and the BioWin Activated Sludge/Anaerobic Digestion models) with Life Cycle Assessment to compare five wastewater treatment plant (WWTP) scenarios. However, the model of Bisinella de Faria et al. (2015) has the limit of quantifying GHG by adopting emission factors which have the limit of neglecting the variability of GHG. The literature review presented above shows that despite the huge efforts to include GHG at a plant-wide scale, the studies performed thus far have taken place only at the research level and are often applied to hypothetic case studies (with exception of Ni et al. (2013b), Guo (2014) and Lim and Kim (2014)), yet not currently within the realm of practitioners or WWTP operators. This situation is mostly likely due to certain critical aspects that are in need of future studies/work for widespread GHG modelling: i) incomplete process knowledge, especially in terms of N_2O production; ii) difficulty in understanding the interactions among the plant sections needed to properly balance GHG emissions; iii) lack of data for model calibration; and iv) model complexity that leads to excessive computational intensity.

4. Previous studies of GHG–N_2O modelling at the process or treatment unit scale

The literature includes a wide variety of physical, biological or integrated models. The acquired knowledge on CO_2 and CH_4 formation is mature. Therefore, we here focus our attention on N_2O modelling.

Several efforts are provided in the literature to better understand the N_2O production processes (Table 3). The N_2O models can be grouped based on the biomass involved during its production (heterotrophic or autotrophic). Table 4 summarizes the key algorithms for each model related to N_2O production.

The ASMN represents one of the most important models that are able to predict N_2O production using heterotrophic denitrifier bacteria (Hiatt and Grady, 2008). The ASMN model is based on the ASM1 (Henze et al., 2000) and incorporates several processes of the ASM1. The main difference between ASM1 and ASMN is related to the nitrification and denitrification processes. The ASMN describes the nitrification process using two steps (Eqs. (3)–(4) in Table 4) and the denitrification using four steps (Eqs. (6)–(9) in Table 4). Moreover, the ASMN model includes the mixotrophic growth of NOB in the case in which nitrite is present (Eq. (5) in Table 4). A particular key element of the ASMN model is represented by the denitrification steps, which are described independently. Furthermore, the model hypothesises that the total electron demand during denitrification is satisfied in each denitrification step. This key feature of the structure of ASMN, which simplifies the denitrification process, could influence the reliability of its results.

The denitrification process was modelled more simply by Kaelin et al. (2009). Indeed, Kaelin et al. (2009) proposed a two-step nitrification process (Eqs. (10), (11) in Table 4) and a two-step denitrification process (Eqs. (12), (13) in Table 4) in their model as an extension of the ASM3 (Henze et al., 2000). The application of the models has revealed the satisfactory ability of the two-step denitrification model to describe correctly the N_2O formation, despite its simplicity. Indeed, the mechanism of N_2O formation from the heterotrophic denitrification process is well known and knowledge is robust.

Regarding the role of autotrophic bacteria, based on the current knowledge on the N_2O formation processes, several of the mathematical models proposed consider their contribution (AOB — nitrifier denitrification and NH_2OH pathways; Table 4). Specifically, models that consider N_2O production by AOB describe this complex process according to two major pathways: i) N_2O formation as a product of the incomplete NH_2OH oxidation to nitrite (e.g., Law et al., 2012a), and ii) N_2O formation as a product of AOB denitrification in which NO_2^- is adopted as an electron acceptor (e.g., Ni et al., 2013a; Mampaey et al., 2011). Therefore, N_2O model by AOB can be grouped into single-pathway (only one pathway is considered) models and two-pathway (both pathways are considered) models (Ni and Yuan, 2015). The majority of these

Table 3
Summary of the main relevant GHG mathematical models based on the process–approach found in literature.

Reference	Type of WWTP	Type of model	Evaluation criteria	Variables	Remarks
Hiatt and Grady (2008)	Three plant schemes are compared: 1) single continuous stirred tank reactor (CSTR) with clarifier; 2) two CSRTs in series with clarifier; 3) two CSRTs in series with clarifier and internal recirculation in the modified Ludzack–Ettinger configuration	ASMN (dynamic), incorporates two nitrifying populations — AOB and NOB and four steps denitrification. Model uses the Ratkowsky equation (Ratkowsky et al., 1983) to describe the effect of temperature on microbial growth.	Dissolved NO and N_2O	Plant scheme	ASMN model provides the important capability to address the effects of elevated temperature, salt conditions and priority pollutants.
Kaelin et al. (2009)	Pilot plant: mechanical pretreatment (screen, grid chamber), primary settler, secondary settler, 1 anoxic tank (BIO 1), 2 continuously or intermittently aerated tanks (BIO 2 and BIO 3).	Extension of ASM3 (Henze et al., 2000) for two-step nitrification and denitrification	NH_4, NO_2, NO_3, DO concentration	–	Controlling ammonium effluent concentration could lead to a partial washout of NOB and increased nitrite peaks, especially during temperature shocks in fall.
Ni et al. (2011)	Sequential Batch Reactor	Pseudomechanistic model able to describe N_2O dynamics during N removal via mixed-culture nitrification and denitrification	N_2O production	Dissolved oxygen, influent ammonium shock loads; Low COD/N Ratio; NH_2OH as Substrate	N_2O production can account for 0.1–25% of the consumed N in the different nitrification and denitrification systems. The DO concentration is considered a very important parameter governing N_2O emissions during nitrification; with lower DO concentrations leading to higher emissions.
Law et al. (2012a)	Sequential Batch Reactor	Mechanistic model that assumes that N_2O production is due to the chemical decomposition of unstable NOH, an intermediate of NH_2OH oxidation. The chemical decomposition of NOH occurs with first order kinetics.	N_2O production	–	–
Ni et al. (2013a)	Sequential Batch Reactor	Mechanistic model that assumes reduction of NO, produced from the oxidation of NH_2OH, into N_2O. DO has no inhibitory effect on NO reduction	NH_4, NO_2, NO_2 concentration; cumulative N_2O emissions	Comparison of the proposed model with the models of Mampaey et al. (2013), Law et al. (2012a) and Ni et al. (2011) by evaluating the role of dissolved oxygen; NH_2OH as substrate, NH_4^+ as substrate. SRT, aeration stripping rate	The four models can describe the NH_4^+, NO_2^- and NO_3^- data. None of the model is able to reproduce all N_2O measured data. Both AOB denitrification and NH_2OH pathways could be involved in N_2O production. No ambiguous decision of the true NO and N_2O formation mechanism can be made.
Mampaey et al. (2013)	Two plant schemes are compared: 1) SHARON process operated in continuous stirred tank reactor without biomass retention, with ammonia oxidation and without further oxidation to nitrate; 2) SHARON process with 1.5 days of sludge retention time (SRT) in case of continuously aerated reactor and intermittently aerated reactor.	Dynamic model that includes NO and N_2O formation through denitrification by AOBs. Ammonia oxidation is modelled as one-step process.	NO and N_2O production rate, NO and N_2O concentration as gas phase, dissolved NO and N_2O concentration		
Ni et al. (2014)	Sequential Batch Reactor	Dynamic model that incorporates both the nitrifier denitrification and the NH_2OH pathways for N_2O production.	N_2O production	Model validation has been performed by means of batch tests where different NO_2^- dosing were done. Moreover, tests with NO_2^- accumulation and stepwise DO increase with stepwise NO_2^- were performed.	The unified two-pathway model proposed is able to describe N_2O dynamics from two different nitrifying cultures

models is based on the nitrifier denitrification pathway (one pathway model). Specifically, Mampaey et al. (2011) proposed a model in which the nitrifier denitrification pathway (Eqs. (15) and (16) in Table 4) is considered during N_2O formation (Table 3). Furthermore, Mampaey et al. (2013) presented a model to simulate the NO and N_2O emissions by means of nitrifier denitrification (i.e., using AOB activity; Table 3) with consideration of two different production mechanisms. The results obtained did not provide any unambiguous suggestions for the true mechanism of NO and N_2O formation. Thus, the need for further investigation was recommended by the authors, suggesting that knowledge of the role of AOB in NO and N_2O formation is still incomplete.

Ni et al. (2011) proposed a model that is able to simulate N_2O production during both the nitrification and the denitrification processes (Table 3). The model includes two-step nitrification (Eqs. (17) and

(18) in Table 4) and four-step denitrification processes. In contrast to that of Mampaey et al. (2013), the model proposed by Ni et al. (2011) considers the inhibition effect of DO on nitrite and NO reduction by AOB. Furthermore, a difference between the model proposed by Ni et al. (2011) and Mampaey et al. (2013) is related to the ammonia oxidation. The model of Ni et al. (2011) considers the ammonia oxidation as a two-step (ammonia to hydroxylamine and then to nitrite) process, conversely in Mampaey et al. (2013) a one step oxidation process (ammonia to nitrite) is considered. The model of Ni et al. (2011) has been modified subsequently modified by Pocquet et al. (2013) by removing the DO inhibition effect on AOB denitrification pathway and inserting the pH effect on N_2O formation. Indeed, Pocquet et al. (2013) have added two new state variables (free ammonia and free nitrous acid) as AOB substrate during the denitrification. Law et al. (2012a) proposed

Table 4
Summary of the key algorithms of the literature N_2O models.

Process		Process rate equation	Reference	No. equation
Ammonia oxidation	–	$\mu_{AOB} \cdot X_{AOB} \cdot \left(\frac{S_{FA}}{K_{FA}+S_{FA}+S^2_{FA}/K_{FA,AOB}}\right) \cdot \left(\frac{S_O}{K_{O,AOB}+S_O}\right) \cdot \left(\frac{K_{FNA,AOB}}{K_{FNA,AOB}+S_{FNA}}\right)$	Hiatt and Grady (2008)	3
Nitrite oxidation	Autotrophic growth of NOB	$\mu_{NOB} \cdot X_{NOB} \cdot \left(\frac{S_{FNA}}{K_{FNA}+S_{FNA}+S^2_{FNA}/K_{FNA,nob}}\right) \cdot \left(\frac{S_O}{K_{O,NOB}+S_O}\right) \cdot \left(\frac{K_{FA,NOB}}{K_{FA,NOB}+S_{FA}}\right)$		4
	Mixotrophic growth of NOB	$\beta_g \cdot \left(\frac{S_S}{K_S+S_S}\right) \cdot \mu_{NOB} \cdot X_{NOB} \cdot \left(\frac{S_{FNA}}{K_{FNA}+S_{FNA}+S^2_{FNA}/K_{FNA,nob}}\right) \cdot \left(\frac{S_O}{K_{O,NOB}+S_O}\right) \cdot \left(\frac{K_{FA,NOB}}{K_{FA,NOB}+S_{FA}}\right)$		5
Denitrification	Heterotrophic growth using nitrate	$\beta_g \cdot \mu_H \cdot \eta_g \cdot \left(\frac{S_S}{K_S+S_S}\right) \cdot \left(\frac{S_{NO_3}}{K_{NO_3}+S_{NO_3}}\right) \cdot \left(\frac{K_{OH}}{K_{OH}+S_O}\right)$		6
	Heterotrophic growth using nitrite	$\beta_g \cdot \mu_H \cdot X_H \cdot \left(\frac{S_S}{K_S+S_S}\right) \cdot \left(\frac{S_{NO_2}}{K_{NO_2}+S_{NO_2}}\right) \cdot \left(\frac{K_{OH}}{K_{OH}+S_O}\right) \cdot \left(\frac{K_{INO}}{K_{INO}+S_{NO}}NO\right)$		7
	Heterotrophic growth using nitric oxide	$\eta_g \cdot \mu_H \cdot X_H \cdot \left(\frac{S_S}{K_S+S_S}\right) \cdot \left(\frac{S_{NO}}{K_{NO}+S_{NO}+S^2_{NO}/K_{INO}}\right) \cdot \left(\frac{K_{OH}}{K_{OH}+S_O}\right)$		8
	Heterotrophic growth using nitrous oxide	$\eta_g \cdot \mu_H \cdot X_H \cdot \left(\frac{S_S}{K_S+S_S}\right) \cdot \left(\frac{S_{N_2O}}{K_{N_2O}+S_{N_2O}}\right) \cdot \left(\frac{K_{OH}}{K_{OH}+S_O}\right) \cdot \left(\frac{K_{INO}}{K_{INO}+S_{NO}}\right)$		9
Ammonia oxidation	Autotrophic growth of AOB	$\mu_{AOB} \cdot X_{AOB} \cdot \left(\frac{S_O}{K_{O,AOB}+S_O}\right) \cdot \left(\frac{S_{NH}}{K_{H,NH_4}+^{H,NH_4}S_{NH})\cdot\left(\frac{S_{ALK}}{k_{N,ALK}+^{N,ALK}S_{ALK}}\right)}\right)$	Kaelin et al. (2009)	10
Nitrite oxidation	Autotrophic growth of NOB	$\mu_{NOB} \cdot X_{NOB} \cdot \left(\frac{S_O}{K_{O,NOB}+S_O}\right) \cdot \left(\frac{S_{NO2}}{K_{N,NO_2}+^{N,NO_2}S_{NO_2})\cdot\left(\frac{S_{ALK}}{k_{N,ALK}+^{N,ALK}S_{ALK}}\right)\cdot\left(\frac{S_{NH}}{K_{H,NH4}+^{H,NH4}S_{NH}}\right)}\right)$		11
Denitrification	Heterotrophic growth using nitrate	$\mu_H \cdot \eta_{H,NO_3} \cdot \left(\frac{K_{HO}}{K_{HO}+S_O}\right) \cdot \left(\frac{S_{NH}}{K_{H,NH_4}+^{H,NH_4}S_{NH})\cdot\left(\frac{S_{ALK}}{k_{H,ALK}+^{H,ALK}S_{ALK}}\right)\cdot\left(\frac{x_{STO}/x_H}{k_{H,STO}+x_{STO}/x_H}\right)\cdot\left(\frac{S_{NO_3}}{K_{H,NO_3}+S_{NO_3}}\right)}\cdot X_H\right)$		12
	Heterotrophic growth using nitrite	$\mu_H \cdot \eta_{H,NO_2} \cdot \left(\frac{K_{HO}}{K_{HO}+S_O}\right) \cdot \left(\frac{S_{NH}}{K_{H,NH_4}+^{H,NH_4}S_{NH})\cdot\left(\frac{S_{ALK}}{k_{H,ALK}S_{ALK}}\right)\cdot\left(\frac{x_{STO}/x_H}{k_{H,STO}+x_{STO}/x_H}\right)\cdot\left(\frac{S_{NO_2}}{K_{H,NO_2}+S_{NO_2}}\right)}\cdot X_H\right)$		13
Ammonia oxidation	–	$\mu_{AOB} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NH_4}}{K_{NH_4,AOB}+S_{NH_4}}\right) \cdot X_{AOB}$	Mampaey et al. (2011)[a]	14
AOB denitrification contribution	NO_2 reduction	$\mu_{AOB,HAO} \cdot \eta_{\mu AOB} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NO_2}}{K_{NO_2,AOB}+S_{NO_2}}\right) \cdot \left(\frac{S_{NH_4}}{K_{NH_4,AOB}+S_{NH_4}}\right) \cdot X_{AOB}$		15
	NO reduction	$\mu_{AOB,HAO} \cdot \eta_{\mu AOB} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NO}}{K_{NO,AOB}+S_{NO}}\right) \cdot \left(\frac{S_{NH_4}}{K_{NH_4,AOB}+S_{NH_4}}\right) \cdot X_{AOB}$		16
Ammonia oxidation	–	$\mu_{AOB,AMO} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NH_4}}{K_{NH_4,AOB}+S_{NH_4}}\right) \cdot X_{AOB}$	Ni et al. (2011)[a]	17
NH_2OH oxidation	–	$\mu_{AOB,HAO} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NH_2OH}}{K_{NH_2OH,AOB}+S_{NH_2OH}}\right) \cdot X_{AOB}$		18
AOB denitrification contribution	NO_2 reduction	$\mu_{AOB,HAO} \cdot \eta_{\mu AOB} \cdot \left(\frac{K_{O_2,AOB}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NO_2}}{K_{NO_2,AOB}+S_{NO_2}}\right) \cdot \left(\frac{S_{NH_2OH}}{K_{NH_2OH,AOB}+S_{NH_2OH}}\right) \cdot X_{AOB}$		19
	NO reduction	$\mu_{AOB,HAO} \cdot \eta_{\mu AOB} \cdot \left(\frac{K_{O_2,AOB}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NO}}{K_{NO,AOB}+S_{NO}}\right) \cdot \left(\frac{S_{NH_2OH}}{K_{NH_2OH,AOB}+S_{NH_2OH}}\right) \cdot X_{AOB}$		20
Ammonia oxidation	–	$\mu_{AOB} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NH_4}}{K_{NH_4,AOB}+S_{NH_4}}\right) \cdot X_{AOB}$	Law et al. (2012b)[a]	21
AOB denitrification contribution (NH_2OH/NOH pathway)	–	$q_{AOB,,max} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NH_2OH}}{K_{NH_2OH,AOB}+S_{NH_2OH}}\right) \cdot X_{AOB}$		22
	–	$q_{AOB,,max} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NOH}}{K_{NOH,AOB}+S_{NOH}}\right) \cdot X_{AOB}$		23
	–	$q_{AOB,max} \cdot S_{NOH}$		24
	–	$\mu_{AOB} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NH_4}}{K_{NH_4,AOB}+S_{NH_4}}\right) \cdot X_{AOB} + q_{AOB,,max} \cdot \frac{1}{2}\left(\left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NH_2OH}}{K_{NH_2OH,AOB}+S_{NH_2OH}}\right) \cdot X_{AOB} - \mu_{AOB} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right)\cdot\right)\left(\frac{S_{NH_4}}{K_{NH_4,AOB}+S_{NH_4}}\right) \cdot X_{AOB}$		25
Ammonia oxidation	–	$\mu_{AOB} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NH_4}}{K_{NH_4,AOB}+S_{NH_4}}\right) \cdot X_{AOB}$	Ni et al. (2013b)[a]	26
AOB denitrification contribution (NH_2OH/NO pathway)	–	$\mu_{AOB,HAO} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NH_2OH}}{K_{NH_2OH,AOB}+S_{NH_2OH}}\right) \cdot X_{AOB}$		27
	–	$\mu_{AOB,HAO} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NO}}{K_{NO,AOB}+S_{NO}}\right) \cdot X_{AOB}$		28
	–	$\mu_{AOB,HAO} \cdot \eta_{\mu AOB} \cdot \left(\frac{S_{NO}}{K_{NO,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NH_2OH}}{K_{NH_2OH,AOB}+S_{NH_2OH}}\right) \cdot X_{AOB}$		29
Ammonia oxidation	–	$\mu_{AOB} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NH_3}}{K_{NH_3,AOB}+S_{NH_3}}\right) \cdot X_{AOB}$	Mampaey et al. (2013)	30
Nitric acid oxidation	Scenario A	$f_{DNT,A} \cdot \mu_{AOB} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NH_3}}{K_{NH_3,AOB}+S_{NH_3}}\right) \cdot \left(\frac{S_{HNO_2}}{K_{HNO_2,AOB}+S_{HNO_2}}\right) \cdot X_{AOB}$		31
	Scenario B	$f_B \cdot f_{DNT,A} \cdot \mu_{AOB} \cdot \left(\frac{S_{HNO_2}}{K_{HNO_2,AOB}+S_{HNO_2}}\right) \cdot X_{AOB}$		32
AOB denitrification contribution	Scenario A	$\mu_{AOB} \cdot \left(\frac{S_{O_2}}{K_{O_2,AOB}+S_{O_2}}\right) \cdot \left(\frac{S_{NH_3}}{K_{NH_3,AOB}+S_{NH_3}}\right) \cdot \left(\frac{S_{NO}}{K_{NO,AOB}+S_{NO}}\right) \cdot X_{AOB}$		33
	Scenario B	$f_B \cdot \mu_{AOB} \cdot \left(\frac{S_{NO}}{K_{NO,AOB}+S_{NO}}\right) \cdot X_{AOB}$		34
Ammonia oxidation	–	$r_{NH_3,ox} \cdot \left(\frac{S_{O_2}}{K_{O_2,NH_3}+S_{O_2}}\right) \cdot \left(\frac{S_{NH_3}}{K_{NH_3}+S_{NH_3}}\right) \cdot \left(\frac{S_{Mred}}{K_{Mred,1}+S_{NH_3}}\right) \cdot X_{AOB}$	Ni et al. (2014)[b]	35
NH_2OH oxidation	–	$r_{NH_2OH,ox} \cdot \left(\frac{S_{NH_2OH}}{K_{NH_2OH}+S_{NH_2OH}}\right) \cdot \left(\frac{S_{Mox}}{K_{Mox}+S_{Mox}}\right) \cdot X_{AOB}$		36
NO oxidation	–	$r_{NO,ox} \cdot \left(\frac{S_{NO}}{K_{NO,ox}+S_{NO}}\right) \cdot \left(\frac{S_{Mox}}{K_{Mox}+S_{Mox}}\right) \cdot X_{AOB}$		37
NO reduction to N_2O	–	$r_{NO,red} \cdot \left(\frac{S_{NO}}{K_{NO,red}+S_{NO}}\right) \cdot \left(\frac{S_{Mred}}{K_{Mred,2}+S_{Mred}}\right) \cdot X_{AOB}$		38
Oxygen reduction to H_2O	–	$r_{O_2,red} \cdot \left(\frac{S_{O_2}}{K_{O_2,red}+S_{O_2}}\right) \cdot \left(\frac{S_{Mred}}{K_{Mred,3}+S_{Mred}}\right) \cdot X_{AOB}$		39
NO_2 reduction to N_2O	–	$r_{NO_2^-,red} \cdot \left(\frac{S_{NO_2-}}{K_{NO_2^-}+S_{NO_2-}}\right) \cdot \left(\frac{S_{Mred}}{K_{Mred,4}+S_{Mred}}\right) \cdot X_{AOB}$		40
NH_3 oxidation to hydroxylamine with oxygen consumption		$q_{AOB,AMO} \frac{S_{O_2}}{S_{O_2}+K_{O_2,AOB.1}} \frac{S_{NH_3}}{S_{NH_3}+K_{NH_3,AOB}} X_{AOB}$	Pocquet et al. (2016)	41
NH_2OH oxidation to nitric oxide coupled with oxygen reduction		$\mu_{AOB,HAO} \frac{S_{O_2}}{S_{O_2}+K_{O_2,AOB.2}} \frac{S_{NH_2OH}}{S_{NH_2OH}+K_{NH_2,OH,AOB}} X_{AOB}$		42
NO oxidation to nitrite coupled with oxygen reduction		$q_{AOB,HAO} \frac{S_{O_2}}{S_{O_2}+K_{O_2,AOB.2}} \frac{S_{NO}}{S_{NO}+K_{NO,AOB.HAO}} X_{AOB}$		43
NO reduction to N_2O by the enzyme "Nor" coupled				44

Table 4 (continued)

Process	Process rate equation	Reference	No. equation
with the hydroxylamine oxidation to nitrite	$q_{AOB,N_2O,NN} \frac{S_{NH_2OH}}{S_{NH_2OH}+K_{NH_2OH,AOB}} \frac{S_{NO}}{S_{NO}+K_{NO,AOB,NN}} X_{AOB}$		
HNO$_2$ reduction to N$_2$O coupled with NH$_2$OH oxidation to nitrite	$q_{AOB,N_2O,ND} \frac{S_{NH_2OH}}{S_{NH_2OH}+K_{NH_2OH,AOB}} \frac{S_{HNO_2}}{S_{HNO_2}+K_{HNO_2,AOB}} f(S_{O_2}) X_{AOB}{}^c$		45

Scenario A = NO and N$_2$O formation take place using 2 out of 6 electrons from ammonium oxidation to nitrite.
Scenario B = NO and N$_2$O formation take place at the expense of AOB biomass (using intracellular electron donor).
[a] Endogenous decay and aerobic NO$_2$ oxidation by NOB is also included.
[b] Incorporates both the nitrifier denitrification and the NH$_2$OH pathways for N$_2$O production.
[c] $f(S_{O_2}) = \frac{S_{O_2}}{K_{O_2,AOB,ND}+(1-2\sqrt{K_{O_2,AOB,ND}/K_{I,O_2,AOB}})S_{O_2}+S_{O_2}^2/K_{I,O_2,AOB}}$.

a model based on the NH$_2$OH oxidation pathway which considers the N$_2$O formation as a product of the NOH decomposition NOH.

To deepen the insight into the model describing the N$_2$O formation, Ni et al. (2013a) recently applied four models (all one pathway models) that use different concepts in terms of the N$_2$O formation pathway: Model I proposed by Mampaey et al. (2011); Model II proposed by Ni et al. (2011); Model III based on NH$_2$OH/NOH pathway as suggested by Law et al. (2012a); and Model IV proposed by the authors. The results showed that all four models were able to reproduce the measured data in terms of NH$_4$, NO$_2$ and NO$_3$ but not in terms of N$_2$O. This result suggested to the authors that both AOB denitrification and the NH$_2$OH pathway are probably involved in N$_2$O formation. Therefore, despite the higher complexity than the one pathway model, two pathway N$_2$O formation models have to be investigated.

With this regard Law et al. (2012b) proposed a model that considers the NH$_2$OH/NOH pathway, as reported in Table 2 (Eqs. (22)–(25) in Table 4). Thus, different from the models proposed by Mampaey et al. (2013) and Ni et al. (2011), in this model, a double pathway formation is considered for N$_2$O. The model proposed by Law et al. (2012a) assumes first-order kinetics for the NOH decomposition.

Moreover, to better reproduce the dominant pathway involved during the AOB growth that leads to N$_2$O formation for different conditions (i.e., DO concentration), Ni et al. (2014) recently proposed a new model. This model represents the first model that incorporates both nitrifier denitrification and the NH$_2$OH pathway for N$_2$O production (Table 4). The model of Ni et al. (2014) has the particularity of basing the complex metabolism of AOB on three oxidation processes (Eqs. (35)–(37) in Table 4) and three reduction processes (Eqs. (38)–(40) in Table 4). The processes are connected by electron carriers which enable the electron transfer from oxidation to reduction. More recently, Peng et al. (2015) proposed a two-pathway model that represent an extension of the model proposed by Ni et al. (2014) that takes into account the dependency between N$_2$O produced by AOB and the content of inorganic carbon available for ammonia oxidation. In this way the effect of inorganic compound availability on the N$_2$O formation, never taken into account, has been considered. Very recently, a two-pathway N$_2$O model was proposed by Pocquet et al. (2016). The model of Pocquet et al. (2016) is based on five enzymatic reactions (Eqs. (41)–(45) in Table 4). Differently to the original one pathway models (of Ni et al. (2011) and Mampaey et al. (2013)) from which originated, the model of Pocquet et al. (2016) describes the reduction of nitrite into N$_2$O as a single process (process related to the Eq. (45) in Table 4) without considering the intermediate formation of NO. Therefore, differently to previous models, it was assumed that the amount of NO accumulated by the AOB denitrification pathway was negligible compared to that emitted by the incomplete NH$_2$OH oxidation to nitrite pathway. Differently to Peng et al. (2015) the model proposed by Pocquet et al. (2016) does not consider the NH$_3$ and HNO$_2$ inhibition effect on the AOB growth. The model of Pocquet et al. (2016) is able to describe the pattern of NO/N$_2$O ratio inside the modelled system (that cannot be described by means of a single-pathway model). The NO/N$_2$O ratio provides information about the dominant N$_2$O pathway (decrease of NO/N$_2$O ratio is due to the

predominance of AOB denitrification pathway; increase of NO/N$_2$O ratio is due to the predominance of hydroxylamine

pathway). The model of Pocquet et al. (2016) was successfully calibrated and validated on N$_2$O and NO measured data. However, the model contains intrinsic assumptions due to case study and merit to be further extended. Our conclusion is that, despite the two-pathway N$_2$O model has been identified as being more adequate than the single-pathway one, convergence towards the "best" model N$_2$O formation has not been yet achieved. However, further studies must be performed to improve modelling knowledge of the role of AOB in denitrification and consequently in producing N$_2$O. Although the existing models still contain limitations, the development of adequate measurement techniques and an increase in the available datasets should improve future applications. However, the interest in a better understanding of N$_2$O (especially in terms of AOB pathways) formation still represents the driving force to improve the existing models. A better understanding of AOB N$_2$O pathways could have a twofold advantage: i. a more accurate prediction of N$_2$O production from WWTP; ii. better identify the WWTP operation conditions influencing the N$_2$O formation.

5. Discussion and future outlooks

The scientific community has to examine the key elements of GHG modelling using a plant-wide approach. This has several advantages and potentials: i) it takes into account the role of each plant treatment unit process and the interactions among them and ii) it operates/controls each unit, not only at local level but as a component of a system, thus avoiding the risk of a sub-optimization (e.g., reduction of the effluent quality at higher operational costs; Jeppsson et al., 2006). Thus, by including GHG in a plant-wide modelling approach, it is possible to evaluate how control strategies used to minimize GHG emissions can impact the plant carbon footprint and *vice versa*. Indeed, as recently discussed by Sweetapple et al. (2015) WWTPs has to be managed by adopting a wide vision and including all the aspects related with the sustainability (e.g., GHG production, operational costs, net energy, etc....) during the identification of control strategies.

Despite the clear advantages in using plant-wide modelling approaches that include GHG, their use is currently confined to the research domain, mainly due to the intrinsic high complexity of the system and incomplete knowledge of the key processes involved in the GHG formation. Furthermore, including the GHG formation processes, plant-wide models become more complex and often overparameterized (a great number of model factor to be calibrated with respect to the available measured data). Therefore, to facilitate effective applications of plant-wide GHG models, efforts should be dedicated to tackling crucial aspects: lack of data, poor knowledge of key processes involved in the N$_2$O formation and lack of plant-wide tools. Furthermore, knowledge on the GHG production in case of using of advanced WWTP, such as moving bed biofilm reactors, granular sludge reactors or on the anaerobic treatment, has still to be matured.

Particular attention has been focused on the type of plant-wide mathematical models to be used, i.e., simple steady-state process models

or dynamic mechanistic (process-based) models. It was demonstrated that simplified models based on emission factors often provide local results and underestimate the GHG emissions (Corominas et al., 2012). Although simplified models (namely, steady-state models) can be used to estimate the order of magnitude of GHG emissions from the WWTP, several applications in the literature have demonstrated that the dynamics of GHG formation cannot be captured using steady-state modelling. Dynamic modelling is always recommended to provide more reliable GHG prediction. Particular attention must be focused on N_2O dynamics to achieve better control of the total GHG emissions from WWTPs.

The general trend in the literature is to adopt more detailed dynamic process-based models. However, these models are characterized by a multitude of factors and require a large amount of data for calibration. Furthermore, full-scale mathematical model experiments must be performed to establish clear kinetics and formation mechanisms of GHG (especially N_2O) for different biomass cultures. Moreover, the existing plant-wide GHG models are affected by incomplete process knowledge, especially in terms of N_2O. Knowledge of the involved N_2O production pathways must be expanded to improve the existing models and to establish a comprehensive model that is able to reproduce all of the processes involved in N_2O formation. Indeed, the immature knowledge on N_2O formation (especially in terms of AOB pathways) can strongly affect (underestimating or overestimating) the N_2O prediction of a plant-wide models.

The critical aspects related to GHG plant-wide modelling have limited the spread/use of the existing models, which are used only as research tools. Future efforts should be dedicated to setting up mathematical software and plant-wide tools/platforms for practical and feasible application during plant operation. Further, efforts on the plant-wide models calibrations should be performed in order to establish a specific procedure for calibrating such complex (and often overparameterized) models.

The environmental trade-off is now recognized, and further studies and modelling development will enable process optimization for GHG emissions. Thus, an increase in the quantity and quality of measured data for GHG emissions from WWTPs is critical. Although improved on-line instrumentation and extended sampling campaigns for GHG emission monitoring will be required, standardized analytical protocols must be set up, and operators and plant managers must be educated on how to monitor/control/reduce GHG emissions from WWTPs.

Currently, it must be stressed that despite the importance of including the GHG emissions due to the processes occurring inside the receiving water body, these topics are often neglected as a result of a lack of knowledge. This is mainly due to the current inability to establish an accurate method to measure GHG diffusive fluxes over water bodies (Tremblay et al., 2005). Further a great variability in GHG production from RWB occurs. Conversely, in order to obtain an adequate quantification of the GHG emitted from a natural water body a large amount of accurate measured data are required (Tremblay et al., 2005). This could aid to better interpret the key mechanism/processes that occur in the water body affecting the GHG production. Thus, further experiments are required to evaluate the role of the processes occurring inside the receiving water body that contribute to total GHG emissions.

6. Conclusions

The plant-wide modelling approach represents the best option to understand how to reduce the carbon footprint of WWTPs. Literature demonstrates that to manage WWTPs in a sustainable way indicators include operational costs, net energy and multiple environmental performance

measures including GHG has to be considered. In this context, GHG modelling should be applied using dynamic mechanistic (process-based) models. The use of emission factors or simple steady-state models can provide only the magnitude of the GHG emissions.

Improvement in on-line instrumentation for data acquisition (especially for N_2O) is required in the future for a feasible plant-wide approach that includes GHG as a common practice.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.01.163.

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