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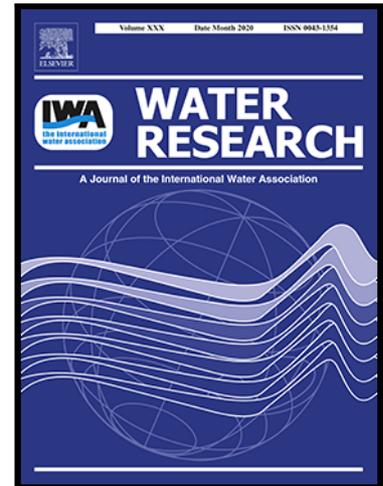
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A plant-wide model describing GHG emissions and nutrient recovery options for water resource recovery facilities

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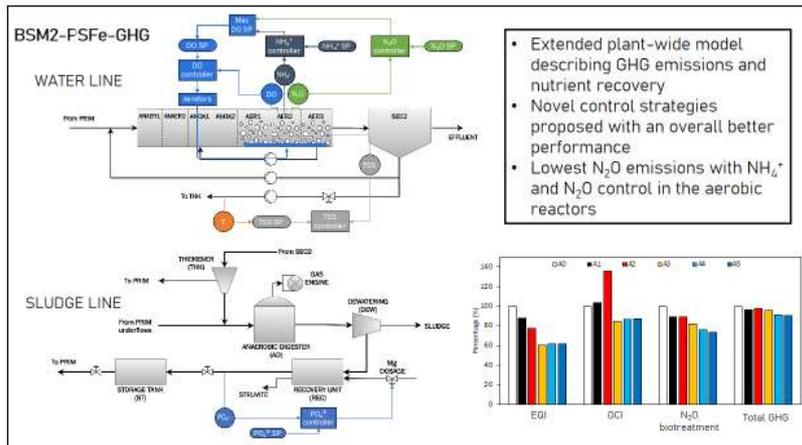
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Graphical abstract

HIGHLIGHTS

- The IWA-BSM2 was extended to account for chemical precipitation and N_2O emissions
- Detailed indirect and direct CO_2 (biogenic/non-biogenic) emissions were also included
- Control strategies balance plant performance, nutrient recovery and GHG mitigation
- Lowest emissions: control of NH_4^+ + N_2O in aerobic reactors and struvite recovery

Abstract

In this study, a plant-wide model describing the fate of C, N and P compounds, upgraded to account for (on-site/off-site) greenhouse gas (GHG) emissions, was implemented within the International Water Association (IWA) Benchmarking

Simulation Model No. 2 (BSM2) framework. The proposed approach includes the main biological N_2O production pathways and mechanistically describes CO_2 (biogenic/non-biogenic) emissions in the activated sludge reactors as well as the biogas production (CO_2/CH_4) from the anaerobic digester. Indirect GHG emissions for power generation, chemical usage, effluent disposal and sludge storage and reuse are also included using static factors for CO_2 , CH_4 and N_2O . Global and individual mass balances were quantified to investigate the fluxes of the different components. Novel strategies, such as the combination of different cascade controllers in the biological reactors and struvite precipitation in the sludge line, were proposed in order to obtain high plant performance as well as nutrient recovery and mitigation of the GHG emissions in a plant-wide context. The implemented control strategies led to an overall more sustainable and efficient plant performance in terms of better effluent quality, reduced operational cost and lower GHG emissions. The lowest N_2O and overall GHG emissions were achieved when ammonium and soluble nitrous oxide in the aerobic reactors were controlled and struvite was recovered in the reject water stream, achieving a reduction of 27% for N_2O and 9% for total GHG, compared to the open loop configuration.

Keywords Benchmarking; control strategies; EBPR; GHG emissions; BSM2.

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Nomenclature

| | |
|--|--|
| A ² /O | Anaerobic-Anoxic-Aerobic |
| ABAC | Aeration-based ammonium controller |
| AD | Anaerobic digester |
| ADM1 | Anaerobic Digestion Model No. 1 |
| AER | Aerobic section |
| ANAER | Anaerobic section |
| ANOX | Anoxic section |
| AOB | Ammonia Oxidizing Bacteria |
| AS | Activated Sludge |
| ASM | Activated Sludge Model |
| ASM2d | Activated Sludge Model No. 2d |
| BOD | Biological Oxygen Demand |
| BSM2 | Benchmark Simulation Model No. 2 |
| BSM2-PSFe | BSM2 for Phosphorus, Sulfur and Iron |
| BSM2G | BSM2 Greenhouse gas |
| C | Carbon |
| Ca ₃ (PO ₄) ₂ | Amorphous calcium phosphate |
| Ca ₅ (PO ₄) ₃ OH | Hydroxyapatite |
| CaCO ₃ | Calcite |
| CBIM | Continuity-based interfacing method |
| CH ₄ | Methane |
| CO ₂ | Carbon dioxide |
| CO _{2e} | Carbon dioxide equivalents |
| COD | Chemical Oxygen Demand |
| CONV _{AS-AD} | Conversion ASM-ADM interface |
| DEN pathway | Denitrification pathway |
| DEW | Dewatering unit |
| D _i | Diffusivity of component i in liquid phase (m ² d ⁻¹) |
| DO | Dissolved Oxygen |
| D _{O2} | Diffusivity of oxygen in liquid phase (m ² d ⁻¹) |
| EBPR | Enhanced Biological Phosphorus Removal |
| N ₂ O-EF | Nitrous Oxide Emission Factor (%) |
| E _{production} | Electricity production |
| EQI | Effluent Quality Index |
| FA | Free Ammonia |
| Fe | Iron |
| FeCl ₃ | Ferric Chloride |
| FeS | Iron Sulphide |
| FNA | Free Nitrous Acid |
| GHG | Greenhouse gas |
| GWP | Global Warming Potential |
| H ₂ | Hydrogen gas |
| H ₂ O | Water |

| | |
|-----------------------------------|--|
| H ₂ S | Hydrogen sulphide |
| HCO ₃ ⁻ | Bicarbonate |
| HFO | Hydrous Ferric Oxides |
| IC | Inorganic Carbon |
| K _{H,i} | Henry's constant for the specie i |
| k _{La} _i | Mass transfer coefficient for component i (d ⁻¹) |
| k _{LaO2} | Mass transfer coefficient for oxygen (d ⁻¹) |
| KNH ₄ PO ₄ | k-Struvite |
| Mg(OH) ₂ | Magnesium Hydroxide |
| MgCO ₃ | Magnesite |
| MgHPO ₄ | Newberyite |
| MgNH ₄ PO ₄ | Struvite |
| MLSS | Mixed Liquor Suspended Solids |
| MMP | Multiple Mineral Precipitation |
| N | Nitrogen |
| N ₂ | Nitrogen gas |
| N ₂ O | Nitrous oxide |
| NaOH | Sodium hydroxide |
| ND pathway | Nitrifier Denitrification pathway |
| NH ₂ OH | Hydroxylamine |
| NN pathway | Nitrifier Nitrification pathway |
| NO | Nitric Oxide |
| NO ₂ ⁻ | Nitrite |
| NO ₃ ⁻ | Nitrate |
| NO _x | Oxidized forms of nitrogen |
| O ₂ | Oxygen gas |
| OCI | Operational Cost Index |
| OHO | Ordinary Heterotrophic Organism |
| P | Phosphorus |
| PAO | Phosphorus Accumulating Organism |
| PCM | Physico-Chemical Models |
| P _i | Partial pressure of the gas specie i |
| PI | Proportional Integral controller |
| P _{inorg} | Inorganic phosphorus |
| P _{org} | Organic phosphorus |
| PRIM | Primary clarifier |
| PROCESS _{AS-AD} | Process ASM-ADM interface |
| Q _w | Purge flow rate |
| S | Sulphur |
| S _A | Acetate (ASM) (g m ⁻³) |
| S _{aa} | Amino acids (ADM) (kg m ⁻³) |
| S _{ac} | Acetate (ADM) (kg m ⁻³) |
| SEC | Secondary settler |
| S _F | Soluble fermentable (ASM) (g m ⁻³) |
| S _{fa} | Fatty acids (ADM) (kg m ⁻³) |
| SI | Saturation index for mineral precipitation |
| S _I | Unbiodegradable soluble organics (ASM) (g m ⁻³) |
| S _{IC} | Inorganic Carbon (ASM, ADM) (g m ⁻³) (kmol m ⁻³) |

| | |
|-------------|---|
| S_{N2O} | Nitrous oxide (ASM) ($g\ m^{-3}$) |
| S_{NH2OH} | Hydroxylamine (ASM) ($g\ m^{-3}$) |
| S_{NH4} | Ammonium plus ammonia nitrogen (ASM) ($g\ m^{-3}$) |
| S_{NO} | Nitric oxide (ASM) ($g\ m^{-3}$) |
| S_{NO2} | Nitrite (ASM) ($g\ m^{-3}$) |
| S_{O2} | Dissolved oxygen (ASM) ($g\ m^{-3}$) |
| S_{PO4} | Phosphate (ASM) ($g\ m^{-3}$) |
| SRT | Sludge Retention Time |
| S_{su} | Sugars (ADM) ($kg\ m^{-3}$) |
| ST | Storage tank |
| T | Temperature |
| THK | Thickener |
| TIV | Time In Violation |
| TKN | Total Kjeldahl Nitrogen |
| TN | Total Nitrogen |
| TP | Total Phosphorus |
| TSS | Total Suspended Solids |
| VS | Volatile Solids |
| WRRF | Water Resource Recovery Facility |
| WWTP | Waste Water Treatment Plant |
| X_{AOB} | Ammonia Oxidizing Bacteria (ASM) ($g\ m^{-3}$) |
| X_{ch} | Carbohydrates (ADM) ($kg\ m^{-3}$) |
| X_i | Mineral concentration in solid phase (PCM) ($kmol\ m^{-3}$) |
| X_I | Inert particulates organics (ASM, ADM) ($g\ m^{-3}$) ($kg\ m^{-3}$) |
| X_{li} | Lipids (ADM) ($kg\ m^{-3}$) |
| X_{NOB} | Nitrite Oxidizing Bacteria (ASM) ($g\ m^{-3}$) |
| X_{PP} | Polyphosphates (ASM, ADM) ($g\ m^{-3}$) ($kmol\ m^{-3}$) |
| X_{pr} | Proteins (ADM) ($kg\ m^{-3}$) |
| X_S | Biodegradable particulate organics (ASM) ($g\ m^{-3}$) |
| X_{TSS} | Total Suspended Solids (ASM) ($g\ m^{-3}$) |
| REC | Recovery unit |

1. Introduction

In recent years, the scarcity of natural resources and the concern about climate change have shifted the water sector paradigm. Therefore, wastewater treatment plants (WWTPs) are becoming water resource recovery facilities (WRRFs). This fact has promoted both the chemical and environmental engineering community and the water industry to widen the scope of these utilities. To better understand and to design these new facilities, plant-wide modelling tools have become essential (Jeppsson et al., 2013). Wastewater treatment modelling researchers have integrated the main unit operations of a WRRF (primary clarifier, biological reactor, secondary settler, thickeners, anaerobic digester, dewatering unit, etc.) to account for all the interactions among processes (Barat et al., 2013; Gernaey et al., 2014; Grau et al., 2007; Hauduc et al., 2019; Solon et al., 2017; Vaneeckhaute et al., 2018) in view of simulating WRRF under different scenarios and of designing novel control strategies for a better performance.

Plant-wide WRRF modelling comprises chemical and physico-chemical models to assess the new challenges of the wastewater treatment. Particularly, precipitation models of common chemical compounds in wastewater (Hauduc et al., 2015; Kazadi Mbamba et al., 2016, 2015b), aqueous phase chemistry models (Flores-Alsina et al., 2015; Solon et al., 2015) and mass transfer models (Amaral et al., 2019; Lizarralde et al., 2015) have been proposed and calibrated to study different subprocesses of a WRRF in addition to the traditional activated sludge models (ASM) based on biological processes (Batstone et al., 2002; Henze et al., 2015). Recently, Solon and co-workers (Solon et al., 2017) proposed a novel plant-wide model capable of predicting the fate of phosphorus (P) in both water and sludge lines as well as the interactions with sulphur (S) and iron (Fe) thanks to the implementation of comprehensive physico-

chemical process models. This work combined a modified Activated Sludge Model No. 2d (ASM2d) model with a speciation model routine to predict pH at each time step (Flores-Alsina et al., 2015). This model evaluated and compared several energy and nutrient recovery strategies, but without accounting for GHG emissions.

Indeed, GHG emissions should be included when evaluating the overall sustainability of control/operational strategies for water resource recovery to add another important criterion in the multivariable space of performance assessment; otherwise, a good a priori control structure providing excellent effluent quality and lower costs could obtain this at the expense of high GHG emissions that are not being considered. Previous modelling studies have already included GHG emissions as a potential performance criterion when evaluating the sustainability of WWTPs. Among the GHGs, N₂O emissions, which have a 300-fold stronger global warming effect than carbon dioxide CO₂ (IPCC, 2013), have recently received a lot of attention. Several extensions based on ASM models have been proposed in the literature to better describe N₂O emissions during biological nitrogen removal (Domingo-Félez et al., 2017; Mannina et al., 2016; Massara et al., 2018; Ni and Yuan, 2015; Pocquet et al., 2016). However, although some parameters of the models are pH-dependent, the evolution of pH in the different reactors is not predicted since the effect on pH of the processes taking place are not considered. Specifically the growth rate of nitrifiers depends on pH, and consequently the N₂O emissions produced by nitrifiers cannot be described accurately for several operational conditions (Su et al., 2019). In addition, CO₂ emissions are typically not accounted for, since the evolution of inorganic carbon (IC) is not modelled. However, nitrifiers growth depends on IC availability (Guisasola et al., 2007; Torà et al., 2010; Wett and Rauch, 2003; Zhang et al., 2018) and its limitation could be significant in some scenarios.

One of the most used plant-wide model that takes into account the GHG emissions is the BSM2G (Flores-Alsina et al., 2011). Several works in the literature have applied this model to study the effect on GHG emissions when implementing different control/operational strategies (Barbu et al., 2017; Flores-Alsina et al., 2014, 2011; Santín et al., 2018, 2017; Sweetapple et al., 2015). However, BSM2G cannot describe the transformations and fate of P in the plant and, moreover, not all the known N₂O production pathways are included in this model. Indeed, N₂O could be produced during the denitrifying phosphorus removal process (Liu et al., 2015). Hence, a new model extension is needed to enable the evaluation of all the potential GHG emission sources when integrating the potential resource recovery mechanisms in WRRFs.

The current limitations of the previous approaches create the need to define a new extended benchmarking scenario (BSM2-PSFe-GHG) including biological COD/N/P removal, GHG emissions, and chemical and physico-chemical models to evaluate resource recovery in WRRFs. The main objective of the present work is to develop and evaluate this BSM2-PSFe-GHG plant-wide benchmarking scenario by integrating: i) the biological model ASM2d-N₂O proposed by Massara et al. (2018) accounting for both enhanced biological phosphorus removal (EBPR) and the most recently reported N₂O production pathways, ii) potential sources of GHG emissions through the WRRF (updated from Flores-Alsina et al. (2011)), iii) plant-wide modelling of detailed P chemical processes (Solon et al., 2017) and iv) development of novel control strategies based on nitrite and nitrous oxide sensors to mitigate N₂O emissions. Once the development of the BSM2-PSFe-GHG sub-models and their interfaces is detailed, simulations will help to understand how novel nutrient recovery/control strategies can affect GHG emissions in a plant-wide context. In this sense, this work aims at i) studying the effect on GHG emissions when implementing nutrient recovery/control

strategies and ii) designing and implementing novel control/operational strategies to optimise plant performance while reducing the GHG emissions.

2. Material and Methods

2.1. BSM2-PSFe-GHG description

2.1.1. Biological models

The ASM2d-PSFe-N₂O model defined in this work merges the BSM2-PSFe approach of Solon et al. (2017) and the ASM2d-N₂O model of Massara et al. (2018) that has been successfully applied to describe N₂O emissions in full-scale WWTPs (Solís et al., 2022). Hence, ASM2d-PSFe-N₂O describes simultaneous biological C, N and P removal, as well as the chemical and biological processes related to S and Fe and N₂O production and emission. Therefore, ASM2d-PSFe-N₂O presents five new state variables compared to the BSM2-PSFe model (i.e., S_{NO₂}, S_{NO}, S_{N₂O}, S_{NH₂OH} and X_{NOB}). The N₂O biological pathways adapted from Massara et al. (2018) are:

- 1) NH₂OH oxidation pathway (NN pathway): N₂O is produced from the reduction of NO by the enzyme “Nor” of AOB coupled with the oxidation of NH₂OH to NO₂⁻ (Pocquet et al., 2016);
- 2) AOB nitrifier denitrification pathway (ND pathway): N₂O is produced from NO₂⁻ reduction to NO and subsequently to N₂O by AOB. These two processes are lumped in one single reaction as in Pocquet et al. (2016);
- 3) heterotrophic denitrification pathway (DEN pathway): N₂O is produced as an intermediate of the denitrification processes either by OHO or PAO (Hiatt and Grady, 2008).

The three biological N₂O production pathways were included in the ASM2d-PSFe-N₂O model to account for all the known biological N₂O production pathways and to fairly assess the contribution of each pathway under dynamic conditions and under the different control/operational strategies implemented. The stoichiometric matrix and the continuity verification of the modified ASM2d-PSFe-N₂O model were calculated as in Hauduc et al. (2010) and are provided in the Supplementary Information Section.

The anaerobic digestion model (ADM) implemented is an extension of the ADM1 model (Batstone et al., 2002), reproducing the biological and chemical interactions between P, S and Fe as reported in previous works (Flores-Alsina et al., 2016; Solon et al., 2017). The kinetic parameters of both models can be obtained from the software implementation or from the original sub-models (Flores-Alsina et al., 2016; Massara et al., 2018; Solon et al., 2017).

2.1.2. Physico-Chemical Models (PCMs)

BSM2-PSFe-GHG embraces three different PCMs as proposed in the BSM2-PSFe approach (Solon et al., 2017): the pH and ion speciation/pairing model (aqueous phase chemistry model), the multiple mineral precipitation (MMP) model and the gas-liquid mass transfer model.

2.1.2.1. pH and ion speciation/pairing

A general aqueous phase chemistry model is used in both ASM and ADM, describing the pH variation and ion pairing at each time step (Flores-Alsina et al., 2015; Solon et al., 2015). The aqueous phase chemistry model corrects for ionic strength via the Davies' approach for chemical activity (Solon et al., 2017). The acid-base parameters and the activity coefficients are temperature-dependent and all calculations are performed under non-ideal conditions. The acid-base equilibria are described as a set of

implicit algebraic equations and solved at each integration step of the ordinary differential equation solver. The species concentrations take part in the biological and physico-chemical processes. A more detailed description of the aqueous phase chemistry model can be found in Flores-Alsina et al. (2015) and Solon et al. (2015).

The integration of the pH and ion speciation allows to account for weak acid-base conditions within the N_2O production processes, since the growth rates of nitrifiers (X_{AOB} and X_{NOB}) are functions of their substrates, i.e. free ammonia (FA, NH_3) and free nitrous acid (FNA, HNO_2), respectively.

2.1.2.2. Multiple Mineral Precipitation (MMP)

The precipitation equations are integrated as temperature dependent reversible processes with the saturation index (SI) as the chemical driving force (Stumm and Morgan, 1996). The SI was calculated by comparing the multiplication of the chemical activities of the dissolved ions of each mineral with its solubility product. For a given aqueous phase, three conditions can occur (Kazadi Mbamba et al., 2015a): i) $SI < 0$, the aqueous phase is undersaturated and the mineral is dissolved; ii) $SI = 0$, the aqueous phase is at equilibrium; or iii) $SI > 0$, the aqueous phase is oversaturated and chemical precipitation may occur. The precipitation rate depends on the kinetic rate coefficient, the species concentration, the mineral solid phase and the order of the reaction (Kazadi Mbamba et al., 2015a, 2015b; Solon et al., 2017). The MMP model includes the most likely minerals to precipitate during wastewater treatment: calcite ($CaCO_3$), hydroxyapatite ($Ca_5(PO_4)_3(OH)$), amorphous calcium phosphate ($Ca_3(PO_4)_2$), struvite ($MgNH_4PO_4 \cdot 6H_2O$), K-struvite ($MgKPO_4 \cdot 6H_2O$), newberyite ($MgHPO_4 \cdot 3H_2O$), magnesite ($MgCO_3$) and iron sulphide (FeS). The simplified approach of Hauduc et al. (2015) is implemented to describe the precipitation of hydrous ferric oxides (HFOs), the

phosphate adsorption and phosphate co-precipitation to better estimate the phosphorus chemical precipitation.

2.1.2.3. Gas-liquid transfer

In the ASM2d-PSFe-N₂O model, the gas-liquid transfer processes are described for the gas components: CO₂, O₂, NO, N₂O, N₂ and H₂S. The gas-liquid transfer is based on Fick's first law (Equation 1), which states that the transfer rate (ρ_i) is proportional to the global mass transfer coefficient ($k_L a_i$) and the driving force is the difference between the saturation concentration and the concentration of the gas in the liquid phase. The saturation concentration is calculated through Henry's law, which states that there is a proportionality ($K_{H,i}$) between the saturation concentration of the gas dissolved in the liquid and the partial pressure of the gas (P_i):

$$\rho_i = k_L a_i \cdot (K_{H,i} \cdot P_i - C_i) \quad (\text{Eq. 1})$$

The mass transfer coefficient for each gas ($i = \text{CO}_2, \text{O}_2, \text{NO}, \text{N}_2\text{O}, \text{N}_2$ and H_2S) is calculated from Equation 2 as the square root of the ratio of the diffusivities of the gaseous component in the liquid (D_i) to that of oxygen (D_{O_2}) and proportional to the mass transfer coefficient of the reference compound oxygen (Lizarralde et al., 2015):

$$k_L a_i = k_L a_{\text{O}_2} \cdot \left(\frac{D_i}{D_{\text{O}_2}} \right)^{1/2} \quad (\text{Eq. 2})$$

The gas-liquid transfer processes in ADM are included for the following gas components: H₂O, CO₂, H₂, CH₄ and H₂S, and are implemented as described by Batstone et al. (2002).

2.2. Model integration

The different sub-models (ASM2d-PSFe-N₂O, ADM and PCMs) in BSM2-PSFe-GHG were integrated using model interfaces. The ASM→ADM and ADM→ASM interfaces are based on the continuity-based interfacing method (Nopens et al., 2009) to ensure elemental mass and charge conservation. The interfaces consider instantaneous processes (i.e. PROCESS_{AS-AD}) and state variable conversions (i.e. CONV_{AS-AD}). The ASM→ADM interface PROCESS_{AS-AD} involves: (1) the removal of COD demanding compounds (NH₂OH, O₂, NO₃⁻, NO₂⁻, NO and N₂O) with the associated growth of biomass, and (2) the decay of biomass (OHO, PAO, AOB and NOB) to produce proteins (X_{pr}), lipids (X_{li}), carbohydrates (X_{ch}) and inert particulate organics (X_I). The CONV_{AS-AD} involve (1) the conversion of soluble fermentable organics (S_F) to amino acids (S_{aa}), sugars (S_{su}) and fatty acids (S_{fa}); (2) the conversion of biodegradable particulate organics (X_S) to X_{pr}, X_{li} and X_{ch}; and (3) the direct mapping of acetate (S_A to S_{ac}) and inert soluble and particulate organics (S_I and X_I) (Solon et al., 2017). Regarding the ADM→ASM interface, a comprehensive description of the involved processes and conversion can be found in Flores-Alsina et al. (2016). Finally, the PCMs integration into ASM and ADM models was made following the procedures detailed in the original works (Flores-Alsina et al., 2015; Solon et al., 2017, 2015).

2.3. Plant layout and ancillary processes

BSM2-PSFe-GHG was implemented in the same plant layout as the BSM2-PSFe (Solon et al., 2017). The WRRF consists of a primary clarifier (PRIM), an activated sludge section (AS), a secondary clarifier (SEC), a sludge thickener (THK), an anaerobic digester (AD), a dewatering unit (DEW) and finally a storage tank (ST) (Figure 1). Additional models were considered to simulate the ancillary processes PRIM, SEC, THK, DEW and ST. The PRIM (900 m³) was modelled according to Otterpohl and Freund (1992) with different settling velocities for biodegradable and non-

biodegradable compounds (Wentzel et al., 2006). The AS had an A²/O configuration consisting of 7 tanks in series: Tanks 1 and 2 were anaerobic (ANAER1 and ANAER2) with a total volume of 2000 m³; tanks 3 and 4 were anoxic (ANOX1 and ANOX2) with a total volume of 3000 m³ while tanks 5, 6 and 7 were aerobic (AER1, AER2 and AER3) with a total volume of 9000 m³. The SEC (surface of 1500 m² and height of 4 m) was modelled according to the double exponential settling velocity function of Takács et al. (1991) in a ten-layer one-dimensional settler. The THK and DEW units were modelled as ideal units, with no biological activity and a constant percentage of TSS in the concentrated sludge flows. The AD had a working volume of 3400 m³ and a headspace volume of 300 m³. The ST was modelled as a non-reactive, ideally mixed tank of 160 m³. Additional information about the plant design and default operational conditions can be found in Gernaey et al. (2014) and Solon et al. (2017).

The influent was generated following the principles proposed by Gernaey et al. (2011). Finally, the sensors and actuators were modelled with response time, delay and white noise to avoid creating unrealistic control applications (Rieger et al., 2003).

2.4. Estimation of GHG emissions

Different GHG compounds (CO₂, CH₄ and N₂O) type of emissions (biogenic and non-biogenic) and sources of emissions (direct or indirect) were accounted for in BSM2-PSFe-GHG. Estimates not explicitly calculated by the sub-models were estimated following the comprehensive methodology suggested by Flores-Alsina et al. (2014, 2011). The different sources of GHG emissions considered throughout the WRRF are:

- *Direct secondary treatment GHG emissions:* CO₂ generated from biomass respiration, CO₂ generated from BOD₅ oxidation, CO₂ credit from nitrification

and N₂O generated during biological N-removal. CO₂ emissions are explicitly accounted for by ASM2d-PSFe-N₂O and PCMs (i.e. pH and ion speciation/pairing and gas-liquid transfer models), by including IC instead of alkalinity as a state variable (Flores-Alsina et al., 2015). N₂O was emitted via the NN and ND pathways of AOB and DEN pathway of heterotrophic organisms (Massara et al., 2018).

- *Sludge processing GHG emissions:* GHG emissions during sludge processing are generated in the anaerobic digester. CO₂ and CH₄ emissions are explicitly calculated by the modified ADM1 model (Flores-Alsina et al., 2016; Solon et al., 2017). Fugitive emissions from AD and co-generation units are included as a total of 2.7% of the produced biogas that was slipped and un-combusted (Magnus Arnell, 2016). The remaining biogas is combusted in the gas-engine turbine and all the CH₄ is converted to CO₂, generating electricity and heat. The CO₂ produced in the AD and the CO₂ produced in the combustion are released into the atmosphere. Finally, dissolved CH₄ (and H₂) in the digester effluent is assumed to be fully stripped in the following process units and emitted to the atmosphere. These emissions are accounted for in the AD (important to maintain mass balances). Potential N₂O emissions due to denitrification downstream of the AD unit (Oshita et al., 2014) were not considered since the DEW unit was modelled as a non-reactive unit. Moreover, it should be noted that neither NO₃⁻ nor NO₂⁻ were present in the AD.
- *Net power-related GHG emissions:* Net power is the difference between energy consumption and production. Energy production is the electricity produced by the AD turbine and it is calculated using a factor for the energy content of CH₄ (50 014 MJ (kg CH₄)⁻¹) and assuming an efficiency of 43% for electricity

generation (Flores-Alsina et al., 2011). Energy consumption involves pumping, mixing, aeration and heating and is calculated using the OCI, see section 2.5. A value of $0.359 \text{ kg CO}_2 \text{ kWh}^{-1}$ is selected for the CO_2 emission from net power production (European production mix) (IEA, 2011).

- *Embedded GHG emissions from chemicals use:* The possible addition of chemicals in the WRRF produces embedded indirect GHG emissions. The specific chemicals considered are: i) methanol dosage as external carbon source with a static factor of $1.54 \text{ kg CO}_2 (\text{kg methanol})^{-1}$ (Flores-Alsina et al., 2011), ii) FeCl_3 for P precipitation, $0.16 \text{ kg CO}_2 (\text{kg FeCl}_3)^{-1}$, iii) NaOH to raise the pH, $1.24 \text{ kg CO}_2 (\text{kg NaOH})^{-1}$ and iv) $\text{Mg}(\text{OH})_2$ to favour the struvite precipitation, $1.17 \text{ kg CO}_2 (\text{kg Mg}(\text{OH})_2)^{-1}$ (Gustavsson and Tumlin, 2013).
- *GHG emissions from effluent disposal:* N_2O is produced in the effluent recipient due to the partial conversion of the remaining TN. An emission factor of 5 g per kg TN discharged to recipient is obtained from the N_2O emissions corresponding to disposal in lakes and rivers (Arnell, 2016).
- *Sludge storage, disposal and reuse:* Direct emissions from sludge storage are estimated by assuming uncovered storage for 12 months as 8.68 kg CH_4 per ton of VS and 1.1% of TN in sludge is emitted as N_2O (Arnell, 2016). After the sludge storage, it is transported for disposal and reuse, causing indirect emissions of CO_2 , CH_4 and N_2O . The CO_2 emissions associated with the transport of biosolids are quantified by multiplying the truck movements by the distance of reuse. CO_2 emissions from mineralization are calculated based on the sludge mass multiplied by the carbon concentration and the conversion factor from C to CO_2 . N_2O emissions are calculated based on a static factor of $0.01 \text{ kg N-N}_2\text{O}$ per kg of TN. In total, three different sludge disposal alternatives are

included: Agriculture (38% sludge disposal, 150 km from the WRRF), Compost (45% sludge, 20 km) and Forestry (17% sludge, 144 km) (Arnell, 2016; Bridle et al., 2008; Flores-Alsina et al., 2011).

Finally, all GHG emissions are converted into units of CO₂ equivalents (CO_{2e}) by the Global Warming Potentials (GWP). The GWP for a 100-year time horizon for N₂O and CH₄ are 298 kg CO_{2e} per kg N₂O and 34 kg CO_{2e} per kg CH₄, respectively (IPCC, 2013). Additional details on the implementation of GHG emissions can be found in section 6.

2.5. Evaluation criteria

Three performance indices were used to assess the plant performance for the different control/operational strategies. Besides the classical evaluation criteria based on the effluent quality index (EQI) and the OCI (Gernaey et al., 2014; Nopens et al., 2010), total GHG emissions (in CO_{2e}) were added as an additional criterion, as first proposed by Flores-Alsina et al. (2014). This value enables the understanding of the synergies and trade-offs that different nutrient recovery control strategies can have on overall GHG emissions. On the other hand, EQI (kg pollution units d⁻¹) represents the overall pollution leaving the plant and is calculated with Equation 3 as a weighted sum of effluent TSS, COD, BOD, TKN, NO_x (oxidized forms of nitrogen, including NO₃⁻, NO₂⁻, NO, N₂O and NH₂OH) and organic and inorganic P (P_{org} and P_{inorg}, respectively) (Solon et al., 2017).

$$EQI = \frac{1}{t_{obs} \cdot 1000} \int_{t_{start}}^{t_{stop}} \left(\beta_{TSS} \cdot TSS(t) + \beta_{COD} \cdot COD(t) + \beta_{BOD} \cdot BOD(t) + \beta_{TKN} \cdot TKN(t) + \beta_{NO_x} \cdot NO_x(t) + \beta_{P_{org}} \cdot P_{org}(t) + \beta_{P_{inorg}} \cdot P_{inorg}(t) \right) \cdot Q_e(t) \cdot dt$$

(Eq. 3)

where t_{obs} is the total evaluation period, the β_i are weighting factors for the different pollutants to convert them into general pollution units (Solon et al., 2017) and Q_e is the effluent flow rate in $m^3 d^{-1}$.

The OCI is calculated with Equation 4 as a weighted sum of the costs related to aeration, pumping, mixing and heating energy, external carbon source, sludge production disposal, chemicals as well as the potential benefits of methane production and nutrients recovered (e.g. struvite).

$$OCI = AE + PE + f_{SP} \cdot SP + f_{EC} \cdot EC + ME - f_{MP} \cdot MP + \max(0, HE - 7MP) + f_{MA} \cdot MA + f_{Mg} \cdot Mg - f_{S_{recovered}} \cdot S_{recovered}$$

(Eq. 4)

where AE is aeration energy, PE is pumping energy, SP is sludge production, EC is external carbon addition, ME is mixing energy, MP is methane production, HE is required heating energy for the AD, MA is metal addition, Mg is magnesium addition and $S_{recovered}$ is struvite recovered. The f_i are weighting factors and are selected as in Gernaey et al. (2014) and Solon et al. (2017).

Finally, other legal criteria, such as the percentage of time the plant is in violation (TIV), i.e. when effluent concentrations are above discharge limits for selected nutrients in the effluent, were also used to evaluate the plant performance.

2.6. Control strategies

Table 1 summarises the individual controllers and control strategies combining different controllers that were applied in this work. Figures S1-S5 (Supplementary Information Section) show the schematics of the control loops implemented in each control strategy. The default scenario (A_0) is the open-loop configuration (Gernaey et al., 2014), thus the air flow rate supplied to the aerobic reactors (value of the mass transfer coefficient k_{La})

and the purge flow rate were kept constant. The performance of each implemented control strategy is evaluated by comparison with A_0 by means of the evaluation criteria indices. The control strategies A_1 to A_3 are based on the improvement of the water quality (reduction of EQI and TIV for N and P species) by optimizing the aeration strategy, the sludge age in winter or by including nutrient recovery. Finally, the control strategies A_4 and A_5 are mainly focused on reducing the GHG emissions while maintaining good effluent quality and low operating costs.

All dynamic simulations (609 days) are preceded by a steady state simulation (300 days) but only data generated during the last 364 days of dynamic simulations are used to evaluate the implemented control strategies. The sensors characteristics applied in the implemented control strategies are summarized in section S2.

3. Results

3.1. Steady State Simulations

Figure 1 shows the total GHG emissions, combined with the fractionation of GHG emissions (on-plant and off-plant), and the overall and individual mass balances for C, N and P as well as the pH under steady-state conditions for the A_0 scenario. Among the total GHG emissions, 65% consisted of CO_2 (of which 63% of the total CO_2 emissions was biogenic CO_2 emitted in the biotreatment), 29% of N_2O (21% of the total N_2O emitted was produced in the biotreatment section through N-removal) and 6% of CH_4 . The low CH_4 emissions were due to all the produced CH_4 in the AD was burnt in the gas engine unit and, therefore, transformed to CO_2 and energy. Most of the GHG emissions were direct emissions (80%), i.e. produced in the WRRF. The predicted indirect GHG emissions were mainly produced due to sludge disposal and reuse, since the CO_2 emissions produced due to electricity production were mitigated from the

electricity generated in the cogeneration unit of CH_4 and no imbedded GHG emissions from chemicals use were produced.

Regarding the fate of C, the inlet C ends up in three different forms: i) 51.3% is emitted as CO_2 : 32.8% in the AS section as biogenic CO_2 , due to the organic matter oxidation and biomass respiration and 18.5% as combustion and leakages of biogas in the AD (this represents 38.7% of the inlet C to the digester), ii) 23.1% is dissolved in the effluent mainly in the form of S_{IC} (80%) and S_{I} (13.4%) and iii) 25.5% is disposed of in the sludge as particulate organics and biomass.

In the case of N, the inlet N ends up in three different phases: i) 49% is discharged in the effluent mainly as S_{NO_3} (31.4%) and dissolved S_{N_2} (56.5%), ii) 21.4% ends up in the gas phase of the biological reactors, mainly as N_2 , but with 1.0% of the inlet N as $\text{N-N}_2\text{O}$, which is within the ranges reported by Massara et al. (2017) and Ahn et al. (2010) who obtained values of 0–3.3% of N_2O emission in 12 different WWTPs, and iii) the remaining 29.6% of the inlet N is disposed in the sludge, mainly as biomass and entrapped in particulate organics. One important outcome of this A_0 operation is its feasibility to accomplish N-removal despite its lack of active control, since the values of TKN (2.8 g N m^{-3}) and TN (11.0 g N m^{-3}) in the effluent for A_0 are below the BSM discharge limits ($\text{TKN}_{\text{limit}} = 4 \text{ g N m}^{-3}$, $\text{TN}_{\text{limit}} = 18 \text{ g N m}^{-3}$). The analysis of this scenario also shows the important effects of some recycled streams, such as the overflows of the thickener and the dewatering unit, which increase the N influent load to the plant by 21.5%.

Regarding the P results, only 22.3% of the influent P leaves the plant through the water line, mainly as soluble orthophosphate S_{PO_4} (43.6%) and X_{PP} (39.7%) that overflows in the secondary settler. The obtained effluent TP concentration is 2.37 g P m^{-3} , above the

BSM discharge limit of $TP_{\text{limit}} = 2.0 \text{ g P m}^{-3}$. The remaining 77.7% of inlet P remain in the waste sludge, pointing out the possibility of recovering P from the anaerobic digestate. Moreover, the recycles of the thickener overflows and the reject water, 7.7 and $229.9 \text{ kg P d}^{-1}$, respectively, increase the influent P load by 95%.

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3.2. Dynamic Simulations

The dynamic simulation results of the default A_0 scenario and the runs with implemented control strategies A_1 - A_5 are summarized in Table 2. In the case of A_0 , 22.5% of the total GHG emissions come from N_2O during biological N-removal, which represents a N_2O emission factor (N_2O -EF) of 2.10%. This emission factor could be reduced by analysing which biological pathways are producing most of the N_2O and, then, designing adequate mitigation strategies. Table 2 also shows that the effluent obtained is acceptable in terms of effluent average concentrations during the evaluated period. However, the percentages of TIV for ammonium and P are high (35.3% and 40.5%, respectively) and thus, there is a niche for a performance improvement using control strategies. In the following sections, the results for each implemented control strategy (Table 1) are presented and discussed. The GHG emissions and the overall and individual mass balances (Q, C, N and P) and pH for the main streams of the WRRF for each control strategy are reported in sections S3 and S4 (Supplementary Information Section).

3.2.1. Control strategy A_1 : Ammonium cascade & waste controller

The A_1 control strategy involves three controllers. The first two control loops include two controllers following a cascade configuration, currently known as aeration-based ammonium controller (ABAC). In this configuration, the DO controller of the secondary feedback control loop is in charge of maintaining the DO concentration in AER2 by manipulating the aeration flow (k_{La} value), while the primary feedback control loop manipulates the DO set-point in AER2 using the ammonium concentration in AER2 as the controlled variable. The ammonium set-point in AER2 reactor is fixed at 2 g N m^{-3} . An additional control loop acts on the purge flow (Q_w) to maintain the desired X_{TSS} concentration in AER3.

The X_{TSS} set-point depends on the temperature (Table 1). The X_{TSS} concentration is increased from 3 000 to 4 000 g TSS m⁻³ during winter conditions (i.e. $T < 15$ °C) to establish a longer sludge retention time (SRT) and to maintain the nitrification capacity (Solon et al., 2017; Vanrolleghem et al., 2010).

Table 2 shows that there is a reduction in N₂O emissions due to the increase of the DO-setpoint, which decreases the nitrite concentration compared to A₀ and leads to a reduction of N₂O emissions through the ND pathway. Figure 2a shows that there are two different trends in N₂O emission rates depending on the season. On the one hand, the aeration demand is low during summer (day 254 to 357 and day 549 to 609), the DO ranges between 1 and 2 g O₂ m⁻³ and nitrite is accumulating in the reactors (Figure 2g). This causes N₂O emissions via the ND pathway of AOBs to increase (Figure 2d). On the other hand, during winter conditions, aeration increases and nitrite levels decrease, which deactivates the ND pathway. However, the production of N₂O by the NN and DEN pathways increases because the cascade NH₄⁺ control has difficulty in maintaining the desired NH₄⁺ concentration during winter (see Figures 2d and 2g) considering the applied constraints in the DO set-point to avoid unrealistic control applications (minimum of 0 g O₂ m⁻³ and maximum of 6 g O₂ m⁻³). The GHG emissions from the biotreatment (CO₂ biogenic plus N₂O from N-removal) and the total GHG emissions decreased (4.0% and 3.6%, respectively), due to the decrease in N₂O emissions. The variation of the waste flow rates during summer and winter led to an improvement in the AD performance, since more methane was produced ($E_{production}$ increased), which however led to an increase in AD emissions due to increased combustion of biogas.

EQI improved in A_1 due to lower effluent N concentrations: TKN decreased from 5.8 to 3.6 g N m⁻³ (A_0 vs A_1) and the TIV of ammonium decreased from 35.3 to 0.2%. The average P concentration remained the same and the total P concentration in the effluent decreased by only 0.1 g P m⁻³ compared to A_0 . The OCI increased compared to A_0 mainly due to increased aeration costs during the winter period (i.e. when the temperature is below 15°C, between days 357 and 549 of the simulation), since a higher DO set-point is required to maintain the desired ammonium concentration (Figure 2g).

3.2.2. Control strategy A_2 : Fe chemical precipitation of PO₄³⁻

Control strategy A_2 aims at reducing the effluent P concentration via its chemical precipitation with Fe by adsorption and co-precipitation of phosphate species onto HFOs. A_2 includes A_1 and a PI controller that regulates the FeCl₃ addition in AER3 reactor to maintain the P concentration in AER3 reactor at the desired set-point of 1 g P m⁻³ (Table 1). The average S_{PO_4} concentration in scenario A_0 already was 1 g P·m⁻³, but high P peaks were observed in the effluent. The objective of A_2 is mitigating these P peaks avoiding the high TIV = 40.5% observed.

Regarding GHG emissions, total emissions in A_2 increased slightly due to i) more biogenic CO₂ was emitted: PAO activity decreased because there was less phosphate in the anaerobic reactor, resulting in a higher fraction of COD removed by heterotrophic biomass; this biomass produces more inorganic carbon than PAO when removing COD, ii) higher production of biogas and therefore higher emissions from the AD: the iron species enhance primary clarification and more COD is redirected to the AD system and iii) indirect CO₂ emitted by the use of FeCl₃. The observed N₂O emissions were the same as in control strategy A_1 because the N fluxes were not affected by the addition of iron (see Table 2).

A₂ led to a lower concentration of P in the effluent and, consequently, the TIV of total P decreased from 40.5% with A₀ to 20.0% with A₂ and the EQI was reduced by about 23% (Table 2). The phosphate controller was able to reduce the S_{PO4} peaks in the AER3 reactor with the addition of Fe, compared to control strategy A₀ (Table 2). However, the controller was not able to maintain the S_{PO4} at the desired set-point. The average FeCl₃ flow rate throughout the evaluation period was 88 kg Fe/d, which led to a considerable increase of the operational cost, mainly due to the iron dosage (2400 \$ (Ton Fe)⁻¹, (Solon et al., 2017)).

3.2.3. Control strategy A₃: Struvite recovery

Control strategy A₃ complements A₁ by including P- (and N-) recovery as struvite in the digester supernatant. The layout of the WRRF was modified by including a recovery unit (REC) based on struvite precipitation (see Figure S3 in Supplementary Information Section). The REC unit includes a crystallizer to support struvite precipitation, a storage tank for magnesium hydroxide (Mg(OH)₂) and a dewatering unit (Kazadi Mbamba et al., 2016; Solon et al., 2017). A PI controller was added to control the effluent P from the recovery unit at a set-point of 50 g P m⁻³ by manipulating the Mg(OH)₂ flow rate (Q_{Mg(OH)2}).

GHG emissions from the whole WRRF decreased (Table 2). N₂O emissions decreased slightly because the influent N load to the AS unit decreased due to struvite crystallization in the reject water stream and, thus, P- and N-recovery as struvite also had a potential benefit on GHG emissions due to more diluted streams. The struvite recovered was 442 kg d⁻¹, which resulted in 99.8 kg P d⁻¹ (48.5% of the total P influent load)

and 45.0 kg N d⁻¹ recovered (4.2% of the total N influent load), respectively. The reject water P load was reduced from 232.3 kg P d⁻¹ (A₁) to 11.2 kg P d⁻¹ (A₃), which resulted in a 95% reduction in the influent P load to the biological reactors.

Table 2 shows that the average effluent P concentrations in A₃ were lower than those in strategies A₀ to A₂: the WRRF was able to discharge P below the legal limits most of the time (TIV of 0.3%) and EQI decreased by a significant 31% with respect to A₁. Table 2 also shows that OCI decreased 18% compared to A₁, i.e. struvite recovery is techno-economically feasible considering only the operational costs associated with the addition of Mg and struvite revenues in a current market scenario. More struvite could be recovered by lowering the phosphate set-point of the controller, since there was still a surplus of 11.2 kg d⁻¹ of inorganic P available to be precipitated as struvite (Figure 3a). However, this would imply a higher cost of Mg(OH)₂ and with the selected setpoint it was enough to meet P discharge limits. Struvite can be precipitated in a wide range of pH (between 7 and 11) with an optimum pH range between 8.0 and 9.5. The addition of Mg(OH)₂ was enough to increase pH from 7.1 to 8.3 (Figure 3b) favouring struvite precipitation without requiring an additional aeration unit for CO₂ stripping nor the addition of more alkalinity such as NaOH (Kazadi Mbamba et al., 2016; Solon et al., 2017). Further studies are required to assess the capital costs associated with struvite recovery and additional transport costs (these costs were not considered in the evaluation criteria).

3.2.4. Control strategy A4: Ammonium & nitrite cascade controllers and struvite recovery

Control strategy A₄ aims at reducing GHG emissions with a particular emphasis on N₂O emissions derived from biological N-removal. A₄ extends A₃ with a cascade PI nitrite controller in AER2 reactor. Nitrite concentration was maintained at the desired set-point by manipulating the

set-point of the DO controller in conjunction with the ammonium cascade PI controller. Both controllers calculated an adequate DO set-point and the maximum value was chosen (see Table 1 for the characteristics of the controllers). The set-point signal of both controllers was smoothed using a first-order exponential filter with a time constant of 15 min to avoid numerical instabilities during solver integration.

A₄ led to the minimum GHG emissions with respect to the previously implemented strategies (A₀ to A₃): the N₂O emissions were reduced by 7.5% compared to A₃. The implementation of the nitrite PI cascade controller reduced the N₂O emissions during the summer conditions compared to A₁ (Figures 2a and 2b), since one of the substrates of the ND pathway, i.e. nitrite, was minimized (Figures 2d and 2e). The N₂O emissions during winter conditions remained the same as in A₁ because the ammonium PI cascade was preferentially fixing the DO set-point. The nitrification capacity should be increased in order to further reduce the N₂O emissions during winter by, for example, increasing the DO levels or the MLSS concentration, with the trade-off of further increasing the operational costs.

A₄ slightly increased the effluent N concentration in comparison to A₃ (2.8% increase in total N compared to A₃) due to more ammonium being nitrified in A₄ compared to A₃ (effluent TKN decreased by 5%) and the effluent nitrate concentration increased. In this sense, the implementation of ammonium and nitrite cascade controllers also slightly increased OCI by 1.8%, compared to A₃, since the applied DO set-point was always the maximum of the ammonium and nitrite controllers and the aeration costs incremented by 2.3% compared to A₃. The same amount of struvite was obtained as in A₃ because the fluxes of P in the sludge line remained unaffected. Figure 2h shows that during summer conditions (i.e. T above 15 °C) the DO set-point is mostly defined by the nitrite controller (NH₄⁺ is below the set-point of 2 g N m⁻³ and NO₂⁻ concentration is around the set-

point of 0.5 g N m^{-3}). The NH_4^+ controller is only activated during the daily peaks when the influent N load is high (in summer the DO set-point is defined by the NH_4^+ controller only 23% of the time). On the other hand, during winter conditions the DO set-point is defined most of the time (62%) by the NH_4^+ controller to ensure complete nitrification.

3.2.5. Control strategy A₅: Ammonium & nitrous oxide cascade controllers and struvite recovery

A₅ is a modification of A₄ that also aimed at reducing N₂O emissions. New sensors have appeared in the market that enable the monitoring of soluble N₂O concentration in the reactors with high accuracy and, thus, allow designing novel mitigation strategies. For this reason, A₅ included a cascade PI controller based on the measurement and control of N₂O concentration in AER2. In a similar way to A₄, N₂O and NH_4^+ controllers calculated S_{O₂} set-points for the DO controller and the chosen value was the maximum (Table 1).

The GHG emissions obtained were the lowest among all the control strategies implemented (Table 2), with a 13% reduction in N₂O emissions compared to A₁, and a 1% reduction compared to A₄. Figure 4 shows the concentration of soluble N₂O in AER2 predicted in A₄ and A₅. N₂O concentration in A₅ was much more constant due to the N₂O PI cascade controller, which actively imposed the DO set-point when the N₂O concentration in AER2 was too high. Only in the transition period from summer to winter (T around 15°C), the cascade PI controllers of A₄ achieved lower N₂O concentrations (and lower N₂O emissions) than in A₅. This was due to the N₂O PI of A₅ being deactivated and the DO

setpoint was being fixed by the NH_4^+ controller. On the other hand, during summer and winter, i.e. T above $\sim 16^\circ\text{C}$ and T below $\sim 14^\circ\text{C}$, the cascade controllers of A_5 achieved lower N_2O soluble concentration in AER2 (Figure 4) and lower global N_2O emissions (Figures 2b and 2c). These results also point to a simpler alternative strategy that could lead to reduction in N_2O and GHG emissions. Reducing the NH_4^+ set-point in strategy A_1 or implementing a properly selected temperature-dependent NH_4^+ set-point (similar to the TSS controller) would probably provide some further improvements, although the automated set-point selection of the closed-loop control would be lost in this case.

The effluent concentrations and the TIV obtained for A_5 were the same as for A_4 , therefore, a high effluent quality was obtained. However, the OCI was 1.3% higher than A_4 , since slightly more oxygen was required to maintain the N_2O set-point: the DO set-point was set by the N_2O cascade PI in A_5 58% of the time whereas the DO set-point was fixed by the nitrite controller in A_4 56% of the time.

3.2.6. Comparison of the evaluation criteria for the control strategies implemented

Figure 5 compares EQI, OCI, biogenic N_2O emissions and total GHG emissions for each control strategy implemented. The data are normalised considering 100% for the values obtained with the reference operation A_0 . All control strategies led to a more sustainable overall plant performance, since all of them obtained a better effluent quality (i.e. lower EQI) and lower GHG emissions compared to the default scenario. Regarding operational costs, the ammonium cascade controller (A_1) increased the OCI by 4% compared to A_0 due to the more intense aeration demands. The chemical P precipitation strategy (A_2) increased the OCI by 36% compared to A_0 due to the high cost of FeCl_3 dosage. On the other hand, struvite precipitation in the reject water (control strategy A_3) was the most successful strategy in terms of EQI and OCI, leading to a

reduction in EQI of 40% compared to A₀ and 31% compared to A₁, and a reduction in OCI of 11% and 14% compared to A₀ and A₁, respectively, due to: 1) the potential benefits of struvite sales and 2) the reduction in influent load of P and N, which led to lower aeration demand. Control strategies A₄ and A₅ obtained higher reduction in N₂O emission from N-removal compared to A₀. Control strategies A₄ and A₅ merged the ammonium cascade controller of A₁ with another nitrite or soluble N₂O cascade controller and the struvite precipitation of A₃. Both control strategies led to higher operational costs than A₃, 1.8 and 2.8%, respectively, due to the increased aeration demand imposed by the cascade controllers. A₅ seems to have a better performance since it led to a reduction of the emitted N₂O in the biotreatment of 27% but at the expense of higher costs (i.e. 1.3% higher in A₅ compared to A₄). There is therefore a compromise between operational costs and GHG emissions, since operational costs increased slightly in both strategies compared to A₃, where the main difference between the objectives of A₃ compared to A₄ and A₅ was the reduction of GHG emissions, and moreover, A₄ and A₅ achieved the same EQI.

Finally, Figure 5 shows that the largest reduction in total GHG emissions was 9% compared to A₀, despite the fact that the main aim of the novel control strategies is N₂O reduction. Other sources of GHG emissions were not reduced, such as indirect emissions (electricity, chemical usage, sludge storage and reuse) which represented about 20% of the total GHG emissions, and other direct GHG sources that were not controllable, such as biogenic CO₂ and methane combustion, which together represented around 50% of the total GHG emissions (see Table S1 of Supplementary Information Section).

4. Comparison with other works and limitations of the proposed methodology

The proposed BSM2-PSFe-GHG plant-wide model and the implemented control strategies results represent an improvement to the current BSM modelling framework BSM2-PSFe (Solon et al., 2017) by adding the GHG production and emission during nutrient removal and recovery operational/control strategies. In this sense, the BSM2-PSFe-GHG provides a new tool that shows, in a plant-wide context, the trade-offs that different novel control strategies had on the sustainability of the WRRF. On the other hand, the BSM2-PSFe-GHG updates previous works addressed to characterize GHG emissions, with a particular emphasis on N₂O emissions, which were designed for different plant-wide models (Flores-Alsina et al., 2014, 2011; Sweetapple et al., 2014) by: i) adding the GHG emissions to the most recent BSM modelling framework capable of simulating nutrient recovery strategies (Solon et al., 2017), ii) adding all the known biological N₂O pathways reported in the ASM2d-N₂O model (Massara et al., 2018), iii) improving the calculation of CO₂ emissions by including the general aqueous phase model (Flores-Alsina et al., 2015; Solon et al., 2017) and iv) updating the sources of direct and indirect GHG emissions (Flores-Alsina et al., 2011; Arnell, 2016).

The results reported for each control strategy were unified into three main groups (EQI, OCI and GHG) as proposed by Flores-Alsina et al. (2014). This enabled a fairer evaluation of the different strategies, since none of the criteria depended on the others. Other works have proposed to unify the multicriteria into a single cost function by transforming effluent quality into monetary units by defining tariffs or taxes when the concentrations in the effluent are above a certain limit (Guerrero et al., 2012; Stare et al., 2007), or applying a defined weighted average of the different evaluation criteria (Machado et al., 2020). The benefits of the latter approach are that control strategies are compared with a single index. In this work, a unified cost function could be defined if GHG emissions were also translated into monetary units, by imposing tariffs due

to high emissions. Special attention should be paid to defining the different weights of the cost function, since an optimisation of the cost function could lead to high GHG emissions or to poor effluent quality with low operational costs.

P recovery as struvite (strategies A₃ onwards) showed an improvement in the operational costs due to the potential revenues from struvite; however, these results should be taken with caution as the assumed price of struvite (200 \$ ton⁻¹ as in Solon et al. (2017)) is very uncertain. In addition, struvite recovery improved effluent quality due to reduced P and N loading in the sludge line recycles and that also decreases operational costs. In fact, the OCI would also improve by 17.6%, compared to A₁, assuming no benefit from struvite sales. Finally, P recovery as struvite also showed a reduction in GHG emissions from the AS unit, mainly due to the decrease in the N influent load. Other important assumptions were made in the crystallizer unit model, such as ideal solids separation and simplified precipitate dissolution (Solon et al., 2017). In addition, potential pipe clogging in the REC unit due to struvite precipitation was not considered and is known to be a major issue during P recovery as struvite. These limitations in the crystallizer model should be addressed in future work to obtain a better estimation of struvite recovery.

One limitation of BSM2-PSFe-GHG is that capital expenditure was not included in the evaluation criteria and the comparison between control strategies was only subject to operational costs. Adding the capital costs of equipment, sensors, civil, electrical and piping will provide a more complete assessment (Machado et al., 2020; Ostace et al., 2013; Solon et al., 2017). For example, integrating P-recovery as struvite recovery implies a modification of the plant layout or adding a REC unit and all related equipment. That would result in a higher capital investment when

retrofitting or upgrading the WRRF. On the other hand, P precipitation by Fe addition (control strategy A₂), showed higher operational costs than A₃ but this strategy “only” implies adding an extra dosing tank to the existing plant layout.

The proposed control strategies showed the logical steps that a WRRF manager should take to improve effluent quality (A₁ to A₃) and, afterwards, to reduce GHG emissions (A₄ and A₅). However, each of the control strategies could be optimized:

i) the location of the Fe addition in A₂ can be optimised to reduce operational costs as already reported (Kazadi Mbamba et al., 2019);

ii) each of the set-point values can be optimized as in Guerrero et al. (2011) in order to decrease the EQI and OCI, and to minimise GHG emissions. For instance, the reduction of the NH₄⁺ set-point value from 2.0 to 1.0 g N m⁻³ in A₁ (Table 1) led to a 45% reduction in N₂O emissions, while the OCI increased by 4% and the EQI by 14%.

iii) N₂O emissions in the AS unit could be reduced by adding DO, NH₄⁺, NO₂⁻ or N₂O sensors and controllers in each aerobic reactor to better control the WRRF as in Santín et al. (2017), who also aimed at reducing GHG emissions during wastewater treatment by using the BSM2G modelling framework (Flores-Alsina et al., 2011). This strategy enabled a more robust DO control and, therefore, a more robust control of N₂O emissions. However, the addition of multiple controllers in each aerobic reactor results in a more complex control structure for the biological reactors and would increase the capital and maintenance costs of the associated sensors, instruments and controllers.

5. Conclusions

In this paper, a novel plant-wide model that integrates the latest advances in energy and nutrient recovery modelling for an accurate description of N₂O- and EBPR-related processes is proposed. Five control strategies are evaluated in view of optimising plant performance, minimizing GHG emissions and implementing nutrient recovery. The main findings of the work are:

- Direct and indirect GHG emissions for CO₂, N₂O and CH₄ were quantified in the whole WRRF;
- Overall and individual mass balances quantify the distribution of C, N and P in the whole WRRF;
- All five control strategies led to an overall more efficient and sustainable plant performance;
- P-recovery as struvite led to more diluted streams in the biological reactors which reduced the N₂O emissions in the biotreatment by 17%, compared to the open loop configuration;
- The lowest N₂O and overall GHG emissions were achieved when ammonium and soluble nitrous oxide in the aerobic reactors were controlled, achieving a reduction of 24% and 27% for N₂O, respectively, and 9% for total GHG, compared to the open loop configuration.

6. Software availability

The MATLAB/SIMULINK code of the models presented in this work is available upon request. Using this code, readers will be able to reproduce the results included in this paper. To express interest, please contact with Dr. Juan Antonio Baeza (JuanAntonio.Baeza@uab.cat) or Dr. Albert Guisasola (Albert.Guisasola@uab.cat).

Declaration of interests

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

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Table 1. Characteristics of the implemented controllers and control strategies.

| Controller→ | DO | NH ₄ ⁺ | MLSS | PO ₄ ³⁻ | Magnesium | Nitrite | N ₂ O |
|-------------------------|--------------------------------|-----------------------------------|---|-------------------------------|---------------------------------------|-----------------------------------|-----------------------------------|
| Characteristics↓ | | | | | | | |
| Measured variable(s) | S _{O2} in AER2 | S _{NH4} in AER2 | X _{TSS} and T in AER3 | S _{PO4} in AER3 | Effluent S _{PO4} in REC unit | S _{NO2} in AER2 | S _{N2O} in AER2 |
| Controlled variable | S _{O2} in AER2 | S _{NH4} in AER2 | X _{TSS} in AER3 | S _{PO4} in AER3 | X _{Mg(OH)2} in REC unit | S _{NO2} in AER2 | S _{N2O} in AER2 |
| Set-point | - | 2 g N m ⁻³ | 3000 g m ⁻³ (if T > 15 °C) 4000 g m ⁻³ (if T < 15 °C) | 1.0 g P m ⁻³ | 50 g P m ⁻³ | 0.5 g N m ⁻³ | 0.01 g N m ⁻³ |
| Manipulated variable | k _{LA} in AER1, 2 & 3 | S _{O2} set-point in AER2 | Q _w | Q _{FeCl3} | Q _{Mg(OH)2} | S _{O2} set-point in AER2 | S _{O2} set-point in AER2 |
| Control algorithm | PI | Cascaded PI | PI | PI | PI | Cascaded PI | Cascaded PI |
| Control strategy | | | | | | | |
| A ₀ | | | | | | | |
| A ₁ | X | X | X | | | | |
| A ₂ | X | X | X | X | | | |
| A ₃ | X | X | X | | X | | |
| A ₄ | X | X | X | | X | X | |
| A ₅ | X | X | X | | X | | X |

Table 2. Performance evaluation criteria for each control strategy.

| Control strategy → | A ₀ | A ₁ | A ₂ | A ₃ | A ₄ | A ₅ | units |
|--|----------------|----------------|----------------|----------------|----------------|----------------|--|
| Emitted CO ₂ biogenic | 7 467 | 7 510 | 7 616 | 7 470 | 7 569 | 7 527 | kg CO _{2e} d ⁻¹ |
| Emitted N ₂ O N-removal | 5 237 | 4 681 | 4 685 | 4 312 | 3 987 | 3 832 | kg CO _{2e} d ⁻¹ |
| N ₂ O-EF total | 2.10 | 1.33 | 1.35 | 1.27 | 1.17 | 1.11 | % |
| Total emissions biotreatment | 12 703 | 12 191 | 12 301 | 11 782 | 11 556 | 11 359 | kg CO _{2e} d ⁻¹ |
| AD emissions | 4 366 | 4 462 | 4 528 | 4 252 | 4 238 | 4 261 | kg CO _{2e} d ⁻¹ |
| Total GHG emissions | 23 339 | 22 494 | 22 844 | 22 363 | 21 333 | 21 164 | kg CO_{2e} d⁻¹ |
| Direct GHG emissions | 18 970 | 18 582 | 18 796 | 17 743 | 17 491 | 17 326 | kg CO _{2e} d ⁻¹ |
| Indirect GHG emissions | 4 369 | 3 912 | 4 049 | 4 620 | 3 842 | 3 837 | kg CO _{2e} d ⁻¹ |
| N _{sjeldahl} | 5.8 | 3.6 | 3.5 | 3.8 | 3.6 | 3.6 | g N m ⁻³ |
| N _{total} | 13.0 | 11.3 | 11.4 | 10.6 | 10.9 | 10.9 | g N m ⁻³ |
| P _{inorg} | 1.0 | 1.0 | 0.5 | 0.1 | 0.1 | 0.1 | g P m ⁻³ |
| P _{total} | 2.5 | 2.4 | 1.8 | 0.9 | 0.9 | 0.9 | g P m ⁻³ |
| TIV S _{NH4} (= 4 g N m ⁻³) | 35.3 | 0.2 | 0.6 | 0.2 | 0.1 | 0.1 | % |
| TIV N _{total} (= 18 g N m ⁻³) | 0.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | % |
| TIV P _{total} (= 2 g P m ⁻³) | 40.5 | 34.1 | 20.0 | 0.3 | 0.3 | 0.3 | % |
| EQI | 11 769 | 10 338 | 9 074 | 7 129 | 7 240 | 7 238 | kg p.u. d⁻¹ |

| Control strategy → | A ₀ | A ₁ | A ₂ | A ₃ | A ₄ | A ₅ | units |
|--|----------------|----------------|----------------|----------------|----------------|----------------|--------------------------|
| E _{aeration} | 4 000 | 4 445 | 4 838 | 4 031 | 4 126 | 4 237 | kWh d ⁻¹ |
| E _{production} ^a | 5 674 | 5 791 | 5 897 | 5 906 | 5 829 | 5 860 | kWh d ⁻¹ |
| SP _{disposal} | 4 033 | 4 068 | 4 532 | 3 643 | 3 632 | 3 641 | kg TSS d ⁻¹ |
| Q _{FeCl₃} ^b | 0 | 0 | 88 | 0 | 0 | 0 | kg Fe d ⁻¹ |
| Q _{Mg(OH)₂} ^b | 0 | 0 | 0 | 80 | 80 | 80 | kg Mg d ⁻¹ |
| S _{recovered} ^c | 0 | 0 | 0 | 442 | 442 | 442 | kg struv d ⁻¹ |
| OCI | 11 864 | 12 306 | 16 109 | 10 045 | 10 224 | 10 362 | - |

^a Energy production. The electricity generated by the turbine, calculated as the energy content of methane gas.

^b Relative costs for FeCl₃, Mg(OH)₂ and recovered struvite are the same as in Solon et al. (2017).

^c S_{recovered} refers to recovered struvite.

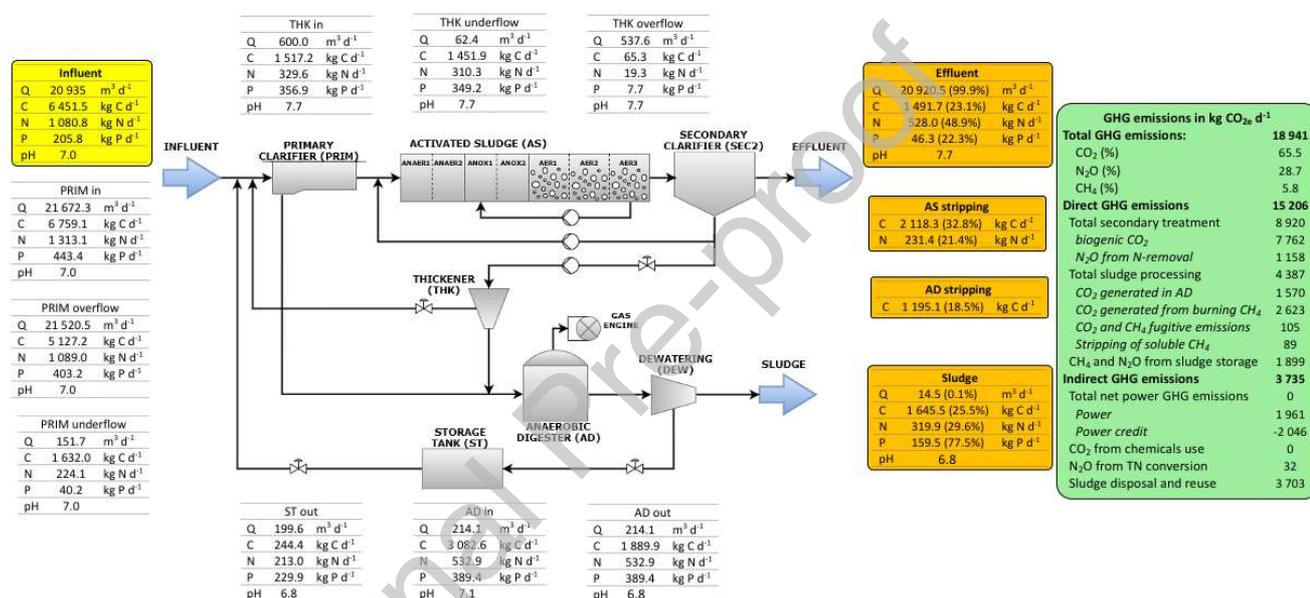


Figure 1. Layout of the WRRF from the BSM2-PSFe-GHG. GHG emissions (green box) and overall and individual mass balances (C, N and P) and pH for the main streams of the WRRF are indicated in the tables (steady state results for A₀ open loop configuration). Inlet and outlet streams of the mass balances are highlighted in yellow and orange, respectively.

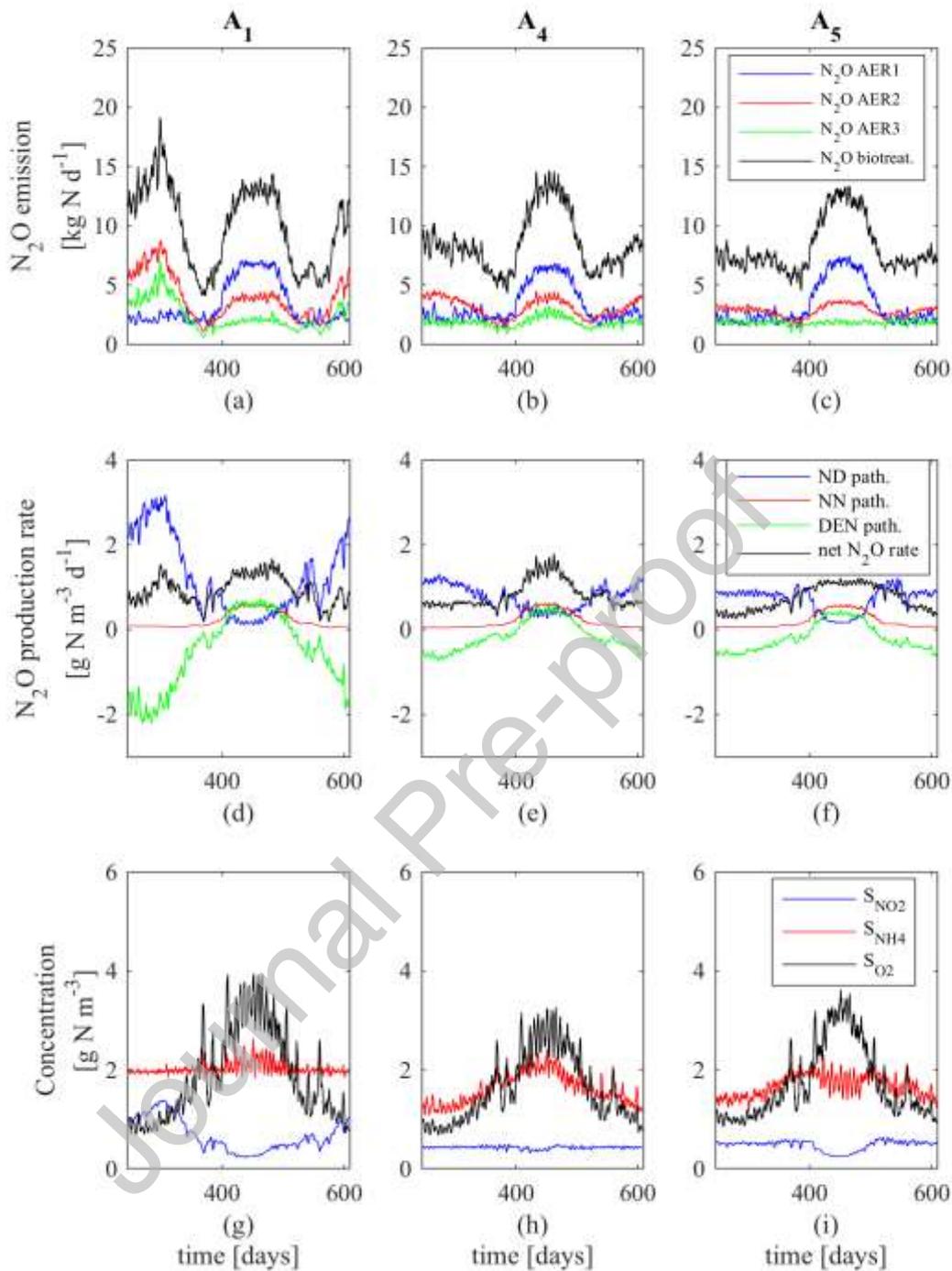


Figure 2. Dynamic profiles of control strategies A_1 (a, d, g), A_4 (b, e, h) and A_5 (c, f, i). (a, b, c): N_2O emissions in the AS unit; (d, e, f): N_2O production rates in AER2 reactor and (g, h, i): nitrite, ammonium and DO concentrations in AER2 reactor. A 3-day first-order exponential filter is used to improve visualization of the results. Negative values of the DEN pathway mean that, for the 4-step denitrification process, the rate of N_2O reduction to N_2 is higher than that of N_2O production from NO. Additional dynamic profiles for all the control strategies are shown in section S4 of SI.

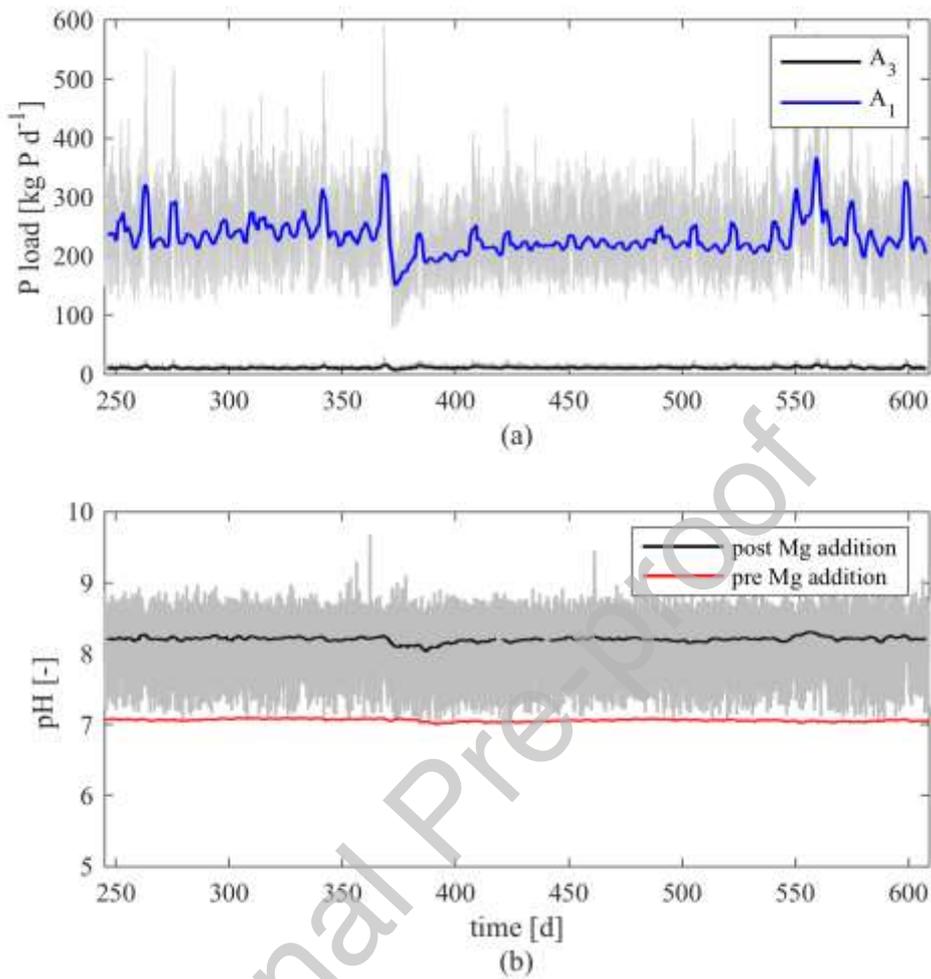


Figure 3. a) total P effluent load of the recovery unit (returns to water line) for control strategies A₁ and A₃. b) Simulated pH values of the recovery unit influent prior and post magnesium addition for control strategy A₃. A 3-day first-order exponential filter is used to improve the visualization of the results. Raw data is shown in grey.

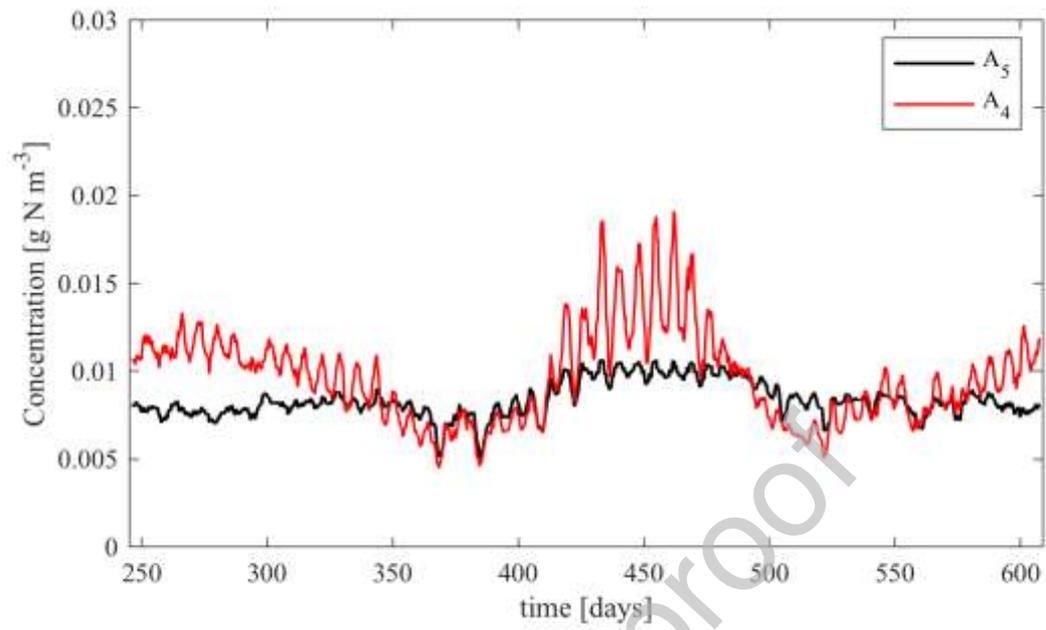


Figure 4. Simulated soluble N₂O concentration in AER2 for A₄ and A₅. A 3-day first-order exponential filter is used to improve the visualization of the results.

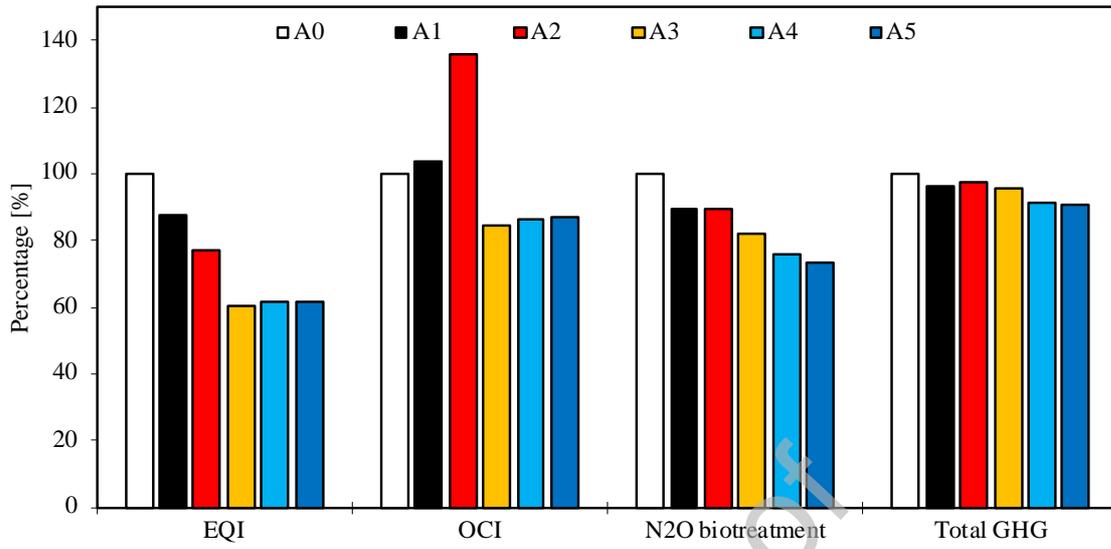


Figure 5. Comparison of the evaluation criteria for the control strategies implemented. Data is shown in relative percentage compared to control strategy A_0 .