

Fugitive methane emissions from full-scale wastewater treatment plants: A plant-wide model

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Abstract

Greenhouse gases (GHGs) such as carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) naturally occur in the atmosphere; however, emissions from anthropogenic activities are driving the rapid increase in global temperatures, with wastewater treatment plants (WWTPs) contributing nearly 5% of global non-CO₂ GHG emissions. Plant-wide monitoring campaigns remain resource-intensive and limited in their inability to capture temporal variability, whereas plant-wide models offer an effective and representative means of characterising CH₄ emissions across treatment processes. Since previous plant-wide models have poorly evaluated fugitive CH₄ emissions, this study develops the first plant-wide modelling framework derived from a full-scale WWTP to quantify fugitive CH₄ emissions. Major contributors including anaerobic digesters, biosolids handling, and bioreactors were identified, while potential sources such as sewers, fermenters, and clarifiers were evaluated. Emission factors (EFs) were consistent with full-scale monitoring studies and were 70% higher than the current Canadian EF for biological nutrient removal (BNR) plants (0.0036 kg CH₄/kg BOD) and 33% lower than that of the Intergovernmental Panel on Climate Change (IPCC; 0.018 kg CH₄/kg BOD). Monte Carlo simulations revealed uncertainties ranging from 39.1% to 46.1% in fugitive emissions and EFs across multiple scenarios. The sensitivity analyses revealed that sewers and anaerobic digesters exerted the greatest influence on plant-wide emissions. Overall, the results demonstrate that plant-wide models provide an effective alternative to intensive monitoring campaigns while supporting targeted mitigation strategies.

Keywords

Greenhouse gas emissions; plant-wide model; uncertainty analysis; sensitivity analysis; diagnostics

1 Introduction

Historically, wastewater treatment plants (WWTPs) have been exclusively assessed by meeting their regulatory effluent standards and have often escaped scrutiny as a significant contributor to greenhouse gas (GHG) emissions, estimated to account for almost 5% of total non-CO₂ GHG emissions (Maktabifard et al., 2023). GHGs such as carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) are intentionally and unintentionally produced through biologically mediated carbon and nitrogen transformations across various process units within WWTPs. While GHGs naturally occur in the atmosphere and play a crucial role in maintaining and regulating the Earth's temperature, intensified emissions from anthropogenic activities are the primary driver of global warming (Venegas et al., 2023).

Unlike N₂O, which can be produced under diverse redox environments, CH₄ is strictly produced in anaerobic environments by methanogenic archaea, with approximately 70% derived from acetate as the primary precursor (G. Chen et al., 2023; Schreiber et al., 2012). Consequently, fugitive CH₄ emissions from WWTPs have often been attributed solely to anaerobic digesters despite full-scale evidence of CH₄ emissions from nearly all process units within the WWTP, as depicted in Figure 1. CH₄ is intentionally produced only during anaerobic digestion (AD) and is considered non-fugitive. However, CH₄ emissions from the liquid and solids trains, due to infrastructural integrity, turbulence, or gas-liquid exchange, are considered fugitive.

Wang et al. (2011) demonstrated that all process units emitted CH₄, with the highest emissions being from the anaerobic selectors, followed by aerobic selectors, aerated grit chambers, and biosolids storage tanks. Notably, uncovered process units, such as clarifiers and biological selectors, were identified as potential CH₄ hotspots, particularly when sufficient residence time is provided and under suboptimal operation. In a year-long study, Daelman et al. (2012) found

that 88% of the plant's CH₄ emissions were in the headspace of the carousel reactor receiving the off-gas of the digested sludge buffer tank, the centrifuge, and the dewatered sludge storage tank, while the remaining 12% were due to stripping in aerated units. Additionally, dissolved CH₄ accounted for 1% of the influent chemical oxygen demand (COD) load, and emissions from the headworks, primary clarifiers, selectors, and plug flow reactors accounted for 31 ± 16% of the total CH₄ emissions going to the ozone washer.

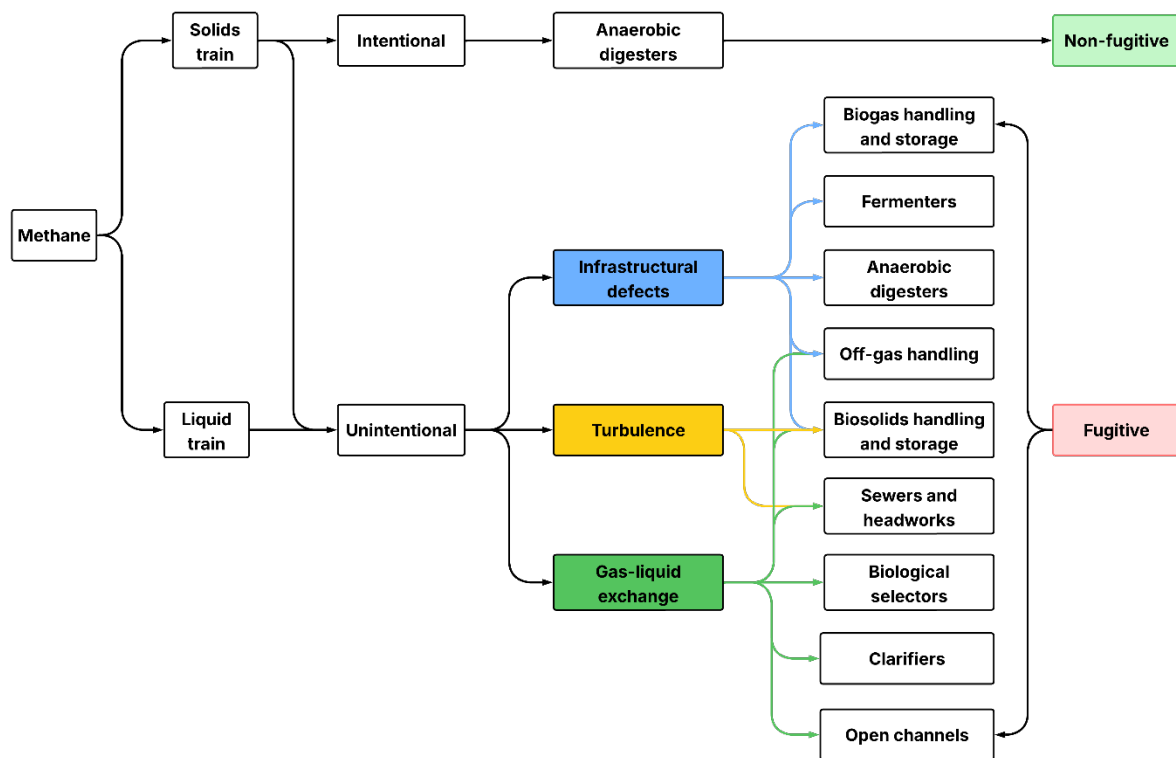


Figure 1. Classification of fugitive CH₄ emission sources and mechanisms in WWTPs.

Nevertheless, plant-wide monitoring campaigns are highly resource-intensive and logistically demanding, particularly when emissions must be characterised across multiple process units over extended periods to capture diurnal and seasonal variability. Their effectiveness is further constrained by equipment accuracy and detection limits, the need for stable weather and favourable wind conditions, the availability of skilled operators, and the limited windows during which measurements can be taken. These constraints not only hinder long-term

continuous monitoring but also create discrepancies between plant-wide and unit-level emission quantification (Daelman et al., 2013a; Moore et al., 2023; Ye et al., 2022). Therefore, plant-wide modelling can extend insights beyond what monitoring alone can provide, enabling the exploration of emission dynamics, testing scenarios, and the development of mitigation strategies.

Plant-wide models for GHG estimation can be divided into three categories: (i) empirical, (ii) steady-state, and (iii) dynamic-state models. Préndez & Lara-González (2008) projected that the WWTPs in the Santiago Metropolitan Area would contribute to nearly 50% of Chile's national GHG emissions by 2027, an order of magnitude higher than the actual contribution of WWTPs, highlighting the limitations of empirical models based solely on activity data as they overlook process configurations, operational complexity, and site-specific factors. Steady-state models relied on oversimplified assumptions, including (i) constant biogas losses or complete transformation of CH₄ to CO₂ during flaring (Bani Shahabadi et al., 2009), (ii) the equivalence of emissions across aerobic and anaerobic configurations, (iii) the equivalency of the performance of anaerobic and aerobic digesters (Monteith et al., 2005), (iv) identical primary sludge (PS) and waste activated sludge (WAS) degradation kinetics (Gori et al., 2011), and (v) collectively overlooking fugitive emissions from biosolids handling, leading to inaccurate estimates. Dynamic models provided greater resolution than steady-state models but were limited to virtual plants, neglecting fugitive CH₄ sources beyond AD and biosolids handling, and relied either on oversimplified or erroneous assumptions including (i) the adoption of the default Anaerobic Digestion Model No. 1 (ADM1) hydrolysis rate (i.e., $k_{\text{hyd}} = 10 \text{ d}^{-1}$), reducing the responsiveness of the model to volumetric changes in the digesters (Corominas et al., 2012), (ii) assumed mesophilic kinetics could be directly applied to thermophilic conditions, overlooking the need for temperature correction adjustments (Batstone et al., 2002; Flores-Alsina et al., 2014), and (iii) assumed CH₄ produced in the sewer network would be completely

released into the atmosphere at the plant's headworks due to high turbulence (Guo et al., 2012).

Further developments in plant-wide models expanded the scope of GHG accounting to include direct and indirect emissions from secondary treatment, anaerobic digestion, biosolids handling and storage, effluent disposal, and chemical and power use (Arnell et al., 2017; Flores-Alsina et al., 2014; Mannina et al., 2019; Solís et al., 2022). Although some of these models marked a progression from virtual to full-scale WWTPs, these full-scale implementations did not incorporate actual operational data (Arnell et al., 2017; Mannina et al., 2019). Additionally, several key modelling assumptions persisted, including (i) fixed biogas losses from AD and flaring, (ii) extended CH₄ production during storage for periods of up to 12 months, implicitly treating volatile solids as fully biodegradable, and (iii) the absence of ADM1 kinetic calibration.

Monitoring campaigns remain constrained by high resource demands, limited temporal resolution, and inherent uncertainty. At the same time, existing plant-wide models have largely focused on N₂O rather than CH₄, leaving CH₄ emissions comparatively under-addressed. This study addresses these gaps by developing a novel plant-wide modelling framework utilising operational data from a full-scale WWTP. The proposed framework explicitly captures CH₄ emissions across both the liquid and solids trains, enabling the dynamic estimation of fugitive CH₄ emissions from the influent wastewater, bioreactors, fermenters, and clarifiers under realistic operating conditions. Combined with uncertainty and sensitivity analyses, it identifies the dominant drivers of emissions and provides a generalisable, transferable framework for diagnosing, estimating, and mitigating fugitive CH₄ emissions.

2 Methodology

2.1 Site description

A WWTP in Canada with average and peak capacities of 396 ML/d and 1,069 ML/d, respectively, was evaluated in this study. Treatment is distributed across four parallel trains (i.e., Plants A–D) with a combined preliminary stage, followed by primary and secondary biological nutrient removal (BNR) stages, including chemical phosphorus (P) removal. Plant A has a Luzack-Ettinger configuration, Plant B has an A/O configuration preceded by a pre-anoxic zone, and Plants C and D have Westbank enhanced biological phosphorus removal (EBPR) configurations. The plant comprises four PS fermenters, where a portion of the PS is fermented to produce VFAs, serving as a supplemental carbon source for BNR processes. Each fermenter feeds into a downstream gravity thickener (GT). Since the fermenters are not heated, to ensure enough residence time during the winter, the hydraulic retention time (HRT) is decoupled from the SRT by recycling the thickened fermented PS to the inlet while sending a fraction to the anaerobic digesters. The WAS is thickened by dissolved air flotation (DAF), mixed with the thickened and fermented PS, and pumped into eight mesophilic anaerobic digesters. Biosolids are either dewatered on-site or transferred to an off-site lagoon, where they are ultimately applied to agricultural land. Details of the data collection and reconciliation procedures are provided in Section S1.

2.2 Model setup

Figure 2 depicts the plant's model setup. The model setup followed the procedure described by Rieger et al. (2012), from the model layout, model selection, model setup, and connections between sub-models. Sumo2, a plant-wide process model in SUMO24 (Dynamita, Fr), encompassing the main biological and chemical processes occurring at the plant, was used to simulate the WWTP, with the same modelling framework applied across all process units.

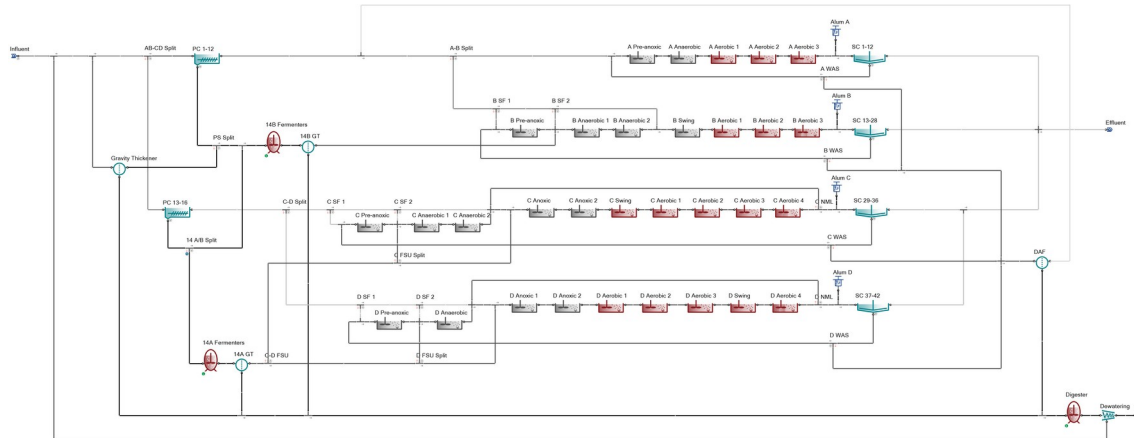


Figure 2. The WWTP's model setup.

Certain simplifications were applied to reduce model complexity and computational cost. These simplifications, along with their justification, are summarised in Table 1.

Table 1. Model simplifications and their rationale.

Process unit	Simplification	Justification
Primary clarifiers	Primary clarifiers 1–12 and 13–16 were modelled as single ideal clarifiers with a combined surface area equivalent to the sum of the individual clarifiers.	Settling characteristics and removal efficiencies were consistent across the clarifiers. Their influent and effluent were combined.
Bioreactors	Bioreactors 1–4, 5–8, 9–10, and 11–12 were modelled as a single lane with a combined volume equivalent to the sum of the individual bioreactors.	The flow distribution is equal across the bioreactors of each plant. Their influent and effluent were combined.
Fermenters	Fermenters 1–2 and 3–4 combined into single units. Modelled as chemostats with no PS recirculation.	The flow distribution is equal across the individual units, and the absence of operational data on PS recirculation.
Digesters	Digesters were combined into a single unit, with the working volume of the digesters out of service subtracted from the total volume.	Influent and effluent characteristics from the digesters are monitored as a single combined flow. Biogas measurements are similarly aggregated.
Secondary clarifiers	Secondary clarifiers 1–12, 13–28, 29–36, and 37–42 were modelled as single ideal clarifiers with a combined surface area equivalent to the sum of the individual clarifiers.	Settling characteristics and removal efficiencies were consistent across the clarifiers. Their influent and effluent were combined.
DAF and GTs	Modelled as volumeless point separators	Removal efficiencies and underflow flow rates are the

2.3 Model assumptions

1. Digested biosolids are conveyed exclusively to the dewatering unit, rather than the off-site lagoon, to account for on- and off-site emissions.
2. Elutriation water is typically fed to the fermenters to improve the recovery of biodegradable soluble COD (bsCOD) and VFAs from sludge layers, rather than increasing the oxidation reduction potential (ORP), suppressing not only methanogenesis but also fermentation, which typically requires an ORP below -100 mV (Bouzas et al., 2007; Pitman et al., 1992; Yin et al., 2016). Considering the underlying assumption of complete mixing within the model's process units, explicit modelling of elutriation was not considered.
3. A non-negligible portion (i.e., 15%) of the non-settled PS is conveyed to the bioreactors, where it continues to ferment, producing hydrogen (H_2) and VFAs. The presence of dissolved H_2 , even at low concentrations, is therefore considered a potential driver for CH_4 production through hydrogenotrophic methanogenesis in downstream processes (X. Chen et al., 2019).
4. Since the fermenters are not heated, they were assumed to operate at the same temperature as the wastewater influent.
5. Dissolved gases are emitted into the atmosphere only through stripping or gas-liquid exchange. Other potential pathways due to infrastructural defects or turbulence were not considered.

2.4 Model calibration and validation

A steady-state calibration was performed by adjusting selected model parameters to reproduce the median effluent quality, sludge production, and biogas production. Subsequently, the model was internally validated dynamically using the entire dataset to assess its performance in reproducing the digester's influent flow rates, as well as its influent and effluent solids COD, the key process variables governing the dynamics of CH₄ production in anaerobic digesters, and the variables of interest for this study (Vanrolleghem et al., 2003). The acceptable error ranges stipulated by Rieger et al. (2012) were applied as the evaluation criteria for the model's predictions in addition to the coefficient of determination (R^2) and the normalised mean absolute error (NMAE) detailed in Section S2. Additional model parameters, including influent characteristics and fractions, along with selected kinetic and physical parameters, were also adjusted to ensure an accurate prediction of sludge and biogas production, as described below.

2.4.1 Influent characteristics and fractions

The influent characteristics and fractions were adopted from a respirometric study carried out by the plant. The influent tool in SUMO was used to adjust the “To be estimated” fractions until a “good match” was achieved between the measured and estimated parameters. Here, a “good match” corresponds to differences within 5% for COD, volatile suspended solids (VSS), and total suspended solids (TSS), and within 10% for biochemical oxygen demand (BOD). The parameters obtained from the respirometric study and the changes in the influent tool are summarised in Tables S2 and S3, respectively.

2.4.2 Biokinetic parameters

The decay rate of the ordinary heterotrophic organisms (OHOs), which constitute the bulk of the WAS, was reduced from 0.62 to 0.2 d⁻¹, consistent with the value reported by Gujer et al. (1999) to match the plant's WAS production. The default decay rate of 0.62 d⁻¹ originates from the death-regeneration model adopted in the Activated Sludge Model No. 1 (ASM1); however, Sumo2 adopts the significantly different endogenous respiration model of ASM3, which typically results in a lower effective decay rate (Gujer et al., 1999; Henze et al., 2006). The kinetics of the ammonia oxidising bacteria (AOB) and the nitrite oxidising bacteria (NOB) obtained from the respirometric study did not differ significantly from the default parameters, as shown in Table S4; however, these minor adjustments were still applied. Methanogens ideally operate within a very narrow pH range of 6.8–7.2; however, their growth is significantly reduced below a pH of 6.5 and become increasingly susceptible to ammonia inhibition at a pH higher than 8.5 (Ward et al., 2008; Yenigün & Demirel, 2013). Hence, the default lower and upper pH limits for methanogenic activity, 4.5 and 9.5, respectively, were narrowed to a more physiologically relevant range of 6.5–8.5. This adjustment also prevents the model from predicting spurious CH₄ production in the fermenters, where low operational pH naturally suppresses methanogenic activity.

2.4.3 Anaerobic digesters/fermenters

The modifications described for the anaerobic digesters also apply to the fermenters, as both are represented using the same process unit. To avoid overestimating CH₄ production from the fermenters, bioreactors, and eventually digesters through hydrogenotrophic methanogenesis, the H₂ yield from fermentation had to be reduced by almost two orders of magnitude from 0.35 to 0.0032 g COD/g COD in line with the yield reported by Zhou et al. (2013).

The model treats CH_4 transfer as analogous to O_2 . However, in digesters, CH_4 is not diffused into the liquid phase like O_2 in aeration tanks, but produced biologically, often reaching supersaturated concentrations (Gupta & Goel, 2019). Moreover, the digesters' liquid phase is fully mixed under both actual operating conditions and in the model. Therefore, both the beta correction factor and the effective saturation depth fraction were adjusted from 0.3 and 0.1 to 1, respectively; otherwise, no driving force would exist for CH_4 transfer into the digester's headspace, and dissolved CH_4 concentrations in the digester, centrate, and dewatered solids would be underestimated.

A simplified model setup, including only the influent, primary clarification, fermenters, and their downstream gravity thickeners, was used for the calibration of the fermenters without sludge recirculation or elutriation, based on the continuous operation data reported by Bahreini et al. (2020) to establish the baseline performance. The hydrolysis rate and fermentation growth rate were adjusted to reproduce the fractionation of sCOD and VFAs in the fermented PS, respectively. Subsequently, the setup was extended to include recirculation, as depicted in Figure S2, with a regulated sludge wastage rate from the downstream gravity thickeners using the SRT tool. The model relies on the active biomass in the influent wastewater for hydrolysis; however, since that fraction is negligible, the hydrolysis rates of the fermenters were adjusted to account for the differences in operational HRTs, a previously noted limitation of activated sludge models (Ismail et al., 2024). Tables S4 and S5 summarise the changes applied to the global and local default parameters, respectively.

2.5 Emissions sources

2.5.1 Primary sources

The primary emission sources included CH_4 emissions from the primary contributing sources:

(i) anaerobic digesters, (ii) bioreactors, and (iii) biosolids handling. Emissions from fermenters were excluded since the plant typically feeds elutriation water into the fermented sludge line to maintain a positive ORP and suppress methanogenesis. Since no sampling was carried out, potential emissions from the influent wastewater were not considered. Biogas losses from the anaerobic digesters were assumed to be the difference between the measured and predicted biogas production. Emissions from the bioreactors and biosolids handling represent the CH₄ produced within or conveyed to these processes and are fully released into the atmosphere.

The predicted biogas was validated whenever influent and effluent sampling coincided with Equation 1.

$$Q_{\text{biogas}} = Q_{\text{dig}} \times (\text{COD}_{\text{inf}} - \text{COD}_{\text{eff}}) \times Y_{\text{CH}_4} \times \frac{273.15+T}{273.15} \times \frac{1}{f_{\text{CH}_4}} \quad (1)$$

Where Q_{biogas} is the calculated biogas flow rate (m³/d), Q_{dig} is the digesters' influent flow rate (m³/d); COD_{inf} and COD_{eff} are the digesters' influent and effluent total COD concentrations (kg COD/m³), respectively. Y_{CH_4} is the theoretical CH₄ yield at standard temperature and pressure (0.35 m³ CH₄/kg COD; Metcalf & Eddy, 2014); T is the digesters' operating temperature (°C); and f_{CH_4} is the CH₄ content in the biogas.

2.5.2 Potential sources

2.5.2.1 Fermenters

To evaluate the impact of sludge retention on CH₄ generation, SRTs ranging from 3 to 7 days were investigated in accordance with the plant's operations report, with elutriation excluded from the fermenters' feed.

2.5.2.2 Secondary clarifiers

Analyses of COD, nitrogen (N), and P species were carried out to identify COD losses that may contribute to fugitive CH₄ emissions. Changes in soluble species within the sludge blanket denoted as ΔS were calculated using Equation 2, where S_{MLSS} and S_{RAS} are the concentrations of any variable in the mixed liquor suspended solids (MLSS) from the bioreactors (i.e., secondary clarifier influent) and in the return activated sludge (RAS; g/m³), respectively.

$$\Delta S = S_{MLSS} - S_{RAS} \quad (2)$$

VSS solubilisation was estimated from changes in ammonia using Equation 3, where VSS_{sol} is the solubilised VSS (g VSS/m³), ΔNH_x-N is the change in ammonia (g N/m³), and pN/VSS is the solids' particulate N to VSS ratio (g N/g VSS).

$$VSS_{sol} = \Delta NH_x-N \times VSS / pN \quad (3)$$

The resulting change in soluble COD was calculated using Equation 4, where $\Delta sCOD$ is the change in soluble COD (g COD/m³) and $pCOD/VSS$ is the solids' particulate COD to VSS ratio (g COD/g VSS).

$$\Delta sCOD = VSS_{sol} \times pCOD / VSS \quad (4)$$

Changes in soluble P concentrations due to solubilisation were determined using Equation 5, where ΔsP_{sol} is the change in soluble P due to VSS solubilisation (g P/m³) and pP/VSS is the solids' particulate phosphorus to VSS ratio (g P/g VSS).

$$\Delta sP_{sol} = VSS_{sol} \times pP / VSS \quad (5)$$

2.5.2.3 Sewers

To account for the wide variation in influent CH₄ concentrations, particularly from systems receiving septic tank, cesspool, or greywater effluents and typical municipal sewers, two scenarios comprising a lower and upper bound of concentrations were developed. Dissolved CH₄ concentrations from gravity sewers and WWTP inlets adopted from the literature, as summarised in Table S6. The upper bound ranged from 0.04 to 13.1 g CH₄/m³, while the lower bound ranged from 0.001 to 2.59 g CH₄/m³.

2.6 Uncertainty and sensitivity analyses

The uncertainty in fugitive CH₄ emissions and EFs was evaluated using the model, described by Equations 6–15 and detailed in Table 2. The model included primary and potential emission sources that could be evaluated with the plant-wide model or Monte Carlo simulations, including the influent wastewater, fermenters, bioreactors, digesters, and downstream biosolids handling. The bioreactors' volume is treated as a variable due to the presence of multiple swing zones.

The uncertainty was evaluated using Monte Carlo simulations, following the procedure described by Sin et al. (2009) using Python 3.15 (Python Software Foundation, USA). Input variables were assigned truncated probability distributions based on measurements, model outputs, or the available literature to avoid sampling negative values. A total of $N = 10^6$ samples of the model's input variables were generated to propagate their uncertainty to the corresponding model outputs. A sufficiently large number of samples was used to ensure convergence, minimise Monte Carlo error, and reduce variation in results across repeated simulations (Koehler et al., 2009). The sensitivity analysis using the same model was carried out using the Sobol method, following the procedure described by Al et al. (2019) and implemented in MATLAB R2025a (MathWorks, USA). The Sobol method was chosen as it

distinguishes between first- and higher-order effects by decomposing the variance of the model output into contributions of each variable and their combinations. The first-order Sobol index (S_i) accounts for the individual contribution of variable i to the output variance, whereas the total-order index (S_{Ti}) accounts for its overall contribution, including its interactions with other variables (Saltelli et al., 2008, 2010). The same number of Monte Carlo iterations was employed for consistency.

$$E_{total} = E_{inf} + E_{cent} + E_{bioreactors} + E_{ferm} + E_{dig} + E_{ds} \quad (6)$$

$$E_{inf} = Q_{inf} \times S_{inf} \quad (7)$$

$$E_{cent} = Q_{cent} \times S_{cent} \quad (8)$$

$$E_{ferm} = M_{CH_4,ferm} + Q_{fsu} \times S_{fsu} \quad (9)$$

$$E_{bioreactors} = r_p \times V_r \quad (10)$$

$$E_{dig} = M_{CH_4,dig} \times f_{leaked} \quad (11)$$

$$E_{ds} = Q_{ds} \times S_{cent} \quad (12)$$

$$r_p = r_{su} \times \frac{Mw_{CH_4}}{4 \times Mw_{H_2}} \times \frac{1}{COD_{H_2}} \quad (13)$$

$$r_{su} = \frac{r_n + b}{Y} \quad (14)$$

$$EF = \frac{E_{total}}{Q_{inf} \times COD_{inf}} \quad (15)$$

Table 2. Uncertainty and sensitivity analyses model variables.

Variables	Description	Unit
Simulation output variables		
Q_{cent}	Centrate flow rate	m ³ /d
Q_{ds}	Dewatered solids flow rate	m ³ /d
S_{cent}	Dissolved CH ₄ concentration in the centrate	kg CH ₄ /m ³
$M_{CH_4,dig}$	CH ₄ mass flow rate from digesters	kg CH ₄ /d
$M_{CH_4,ferm}$	CH ₄ mass flow rate from fermenters	kg CH ₄ /d
Q_{fsu}	Fermenter supernatant flow rate	m ³ /d
S_{fsu}	Dissolved CH ₄ concentration in the fermenter supernatant	kg CH ₄ /m ³
r_n	Net hydrogenotrophic methanogens growth rate	kg COD/m ³ ·d
Measured or estimated variables		
Q_{inf}	Influent flow rate	m ³ /d
S_{inf}	Dissolved CH ₄ concentration in the influent	kg CH ₄ /m ³
COD_{inf}	Influent COD concentration	kg COD/m ³
Constants		

Mw_{CH_4}	Molecular weight of CH_4	g/mole
Mw_{H_2}	Molecular weight of H_2	g/mole
COD_{H_2}	COD equivalent of H_2	g COD/g H_2
b	Decay rate of hydrogenotrophic methanogens	d^{-1}
Y	Hydrogenotrophic methanogens' biomass yield	g COD/g COD
Calculated variables		
f_{leaked}	Estimated fraction of CH_4 leaking from digesters	%
r_p	CH_4 production rate	kg $CH_4/m^3 \cdot d$
V_r	Bioreactor volume	m^3
r_{su}	Maximum specific substrate utilisation rate	kg COD/ $m^3 \cdot d$
Evaluated variables		
E_{total}	Total fugitive CH_4 emissions per day	kg CH_4/d
E_{inf}	Emissions from influent wastewater	kg CH_4/d
E_{cent}	Emissions from the centrate	kg CH_4/d
$E_{bioreactors}$	Emissions from bioreactors	kg CH_4/d
E_{ferm}	Emissions from the fermenters	kg CH_4/d
E_{dig}	Emissions from the digesters	kg CH_4/d
E_{ds}	Emissions from the dewatered solids	kg CH_4/d
EF	Emission factor	kg CH_4/kg COD

3 Results and discussion

3.1 Model calibration and validation

Table 3 summarises the steady-state calibration results, presenting the median of the measured values with their standard deviations (σ) alongside the corresponding predicted effluent characteristics, digesters' influent and effluent COD concentrations, and sludge flow rates. Deviations in measured and predicted effluent quality concentrations ranged from 0.04 to 1 g/m^3 , remaining well within the most stringent acceptable error recommended by Rieger et al. (2012). Errors in predicted influent and effluent sludge COD concentrations were below 10%, substantially lower than the acceptable deviations of 20% and 40% for steady- and dynamic-state calibrations, respectively (Ezzahraoui & Hamza, 2024). Similarly, errors in the predicted flow rates ranged from 0.1 to 5.5%.

Table 3. Steady-state calibration results.

Measured variable	Median	σ	Predicted variable	Absolute error	Acceptable error
Effluent characteristics					
Total suspended solids (TSS)	6.3	1.8	6	0.3 g/m ³	10 g/m ³
COD	44	12.4	45	1 g/m ³	3 g/m ³
Total nitrogen (TN)	17.6	2	17.5	0.1 g/m ³	0.5 g/m ³
Nitrite and nitrate (NO _x)	15	2.1	14.78	0.22 g/m ³	0.5 g/m ³
Total ammonia (NH _x)	0.5	0.6	0.59	0.09 g/m ³	0.5 g/m ³
Total phosphorus (TP)	0.6	0.2	0.66	0.06 g/m ³	0.5 g/m ³
Soluble phosphorus (sP)	0.25	0.23	0.21	0.04 g/m ³	0.5 g/m ³
Sludge quality					
Digesters' influent COD	54,550	8,442	55,391	1.5%	–
Digesters' effluent COD	24,500	4,301	22,584	7.8%	–
Flow rates					
Gravity thickener underflow	609	109	604	0.9%	–
Fermenters 1 and 2 underflows	252	77	245	2.7%	–
Fermenters 3 and 4 underflows	479	51	478	0.1%	–
Plant A WAS	2,112	535	2,118	0.3%	–
Plant B WAS	2,350	535	2,388	1.6%	–
Plant C WAS	1,475	288	1,440	2.4%	–
Plant D WAS	1,248	353	1,267	1.5%	–
Thickened WAS	1,300	245	1,298	0.1%	–
Sludge blend	2,580	364	2,639	2.3%	–
Biogas	47,003	14,894	44,406	5.5%	–

The results of the dynamic validation, including the digesters' influent flow rates and influent and effluent COD loads, are depicted in Figures S3, 3, and 4, respectively. Dynamic predictions showed minimal errors (NMAE < 11%), well within acceptable performance ranges, considering no noise filtering was carried out (Géron, 2022). This demonstrates the model's strong ability to reproduce the dynamics of the anaerobic digesters, thereby providing confidence in the reliability of its predictions, including biogas production. Parity plots of the

digesters' influent flow rates, influent and effluent COD concentrations, and validated biogas production, depicted in Figures S5–S8, showed an excellent fit between the measured and predicted data with R^2 values exceeding 0.98.

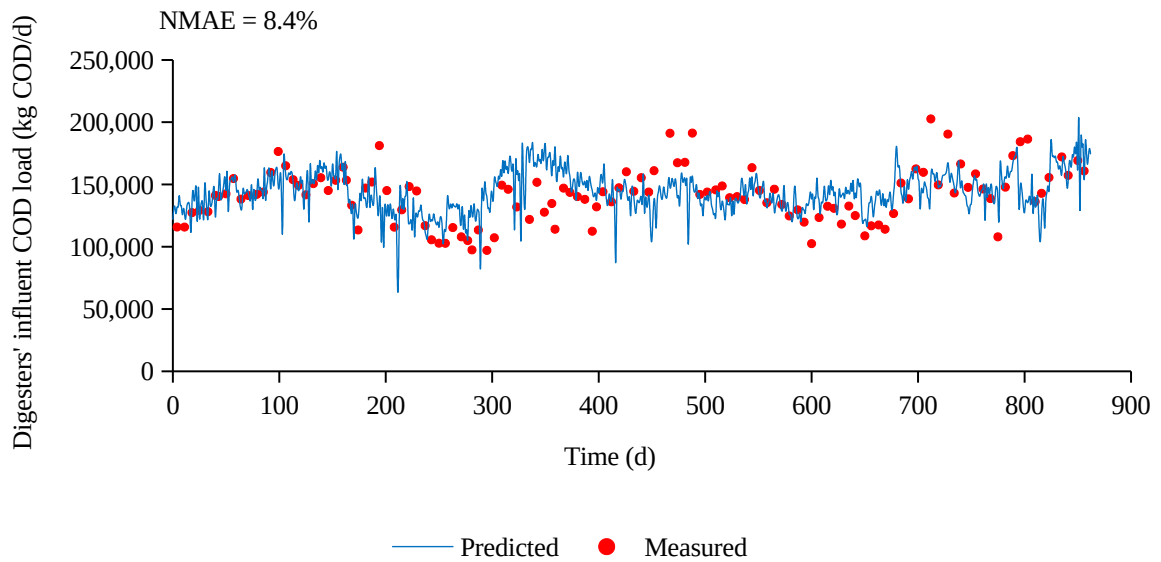


Figure 3. Dynamics of the measured and predicted digesters' influent COD load.

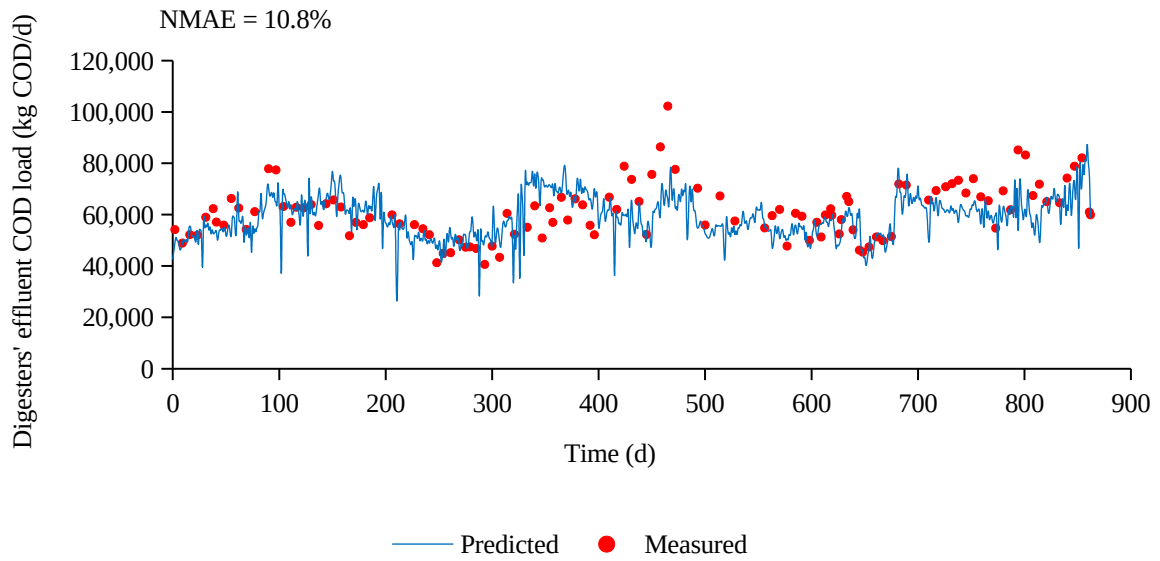


Figure 4. Dynamics of the measured and predicted digesters' effluent COD load.

3.2 Primary sources

3.2.1 Anaerobic digesters

Discrepancies between the predicted and measured biogas production ranged from 0.04% to 38%. These deviations were sporadic, as shown in Figure 5, with other periods exhibiting close agreement between predicted and measured values. Such discrepancies are indicative of underlying operational disturbances or instrumentation issues such as flow metre drifts, maintenance, pipeline modifications or even the use of unmonitored pipelines, several of which occurred during the commissioning of the plant's cogeneration facility during the study period (i.e., 2021–2024). However, they may also reflect actual biogas losses resulting in fugitive CH₄ emissions, all of which warrant further investigation. These deviations therefore serve as valuable diagnostics of plant performance, highlighting periods where additional scrutiny is required to distinguish between true emissions and operational or instrumentation artefacts.

The magnitude of these discrepancies exceeded the previous assumptions of either complete transformation of CH_4 to CO_2 during flaring or losses within 2 to 5% (Bani Shahabadi et al., 2009; Flores-Alsina et al., 2011). The latter assumption primarily reflected the limited accuracy of large-scale biogas flow metres, which typically cannot measure flow rates with errors lower than 5% (Gori et al., 2011). The estimated discrepancies fell within the range reported by Fredenslund et al. (2023), of 2 to 39.4% in full-scale anaerobic digesters across 25 Danish WWTPs, primarily due to issues with pressure relief valves, gas-bearing components, inspection hatches, pipe connections, mixer axles, and soft covers. The discrepancies in CH_4 corresponding to those in the biogas were $3,428 \pm 2,067 \text{ kg CH}_4/\text{d}$.

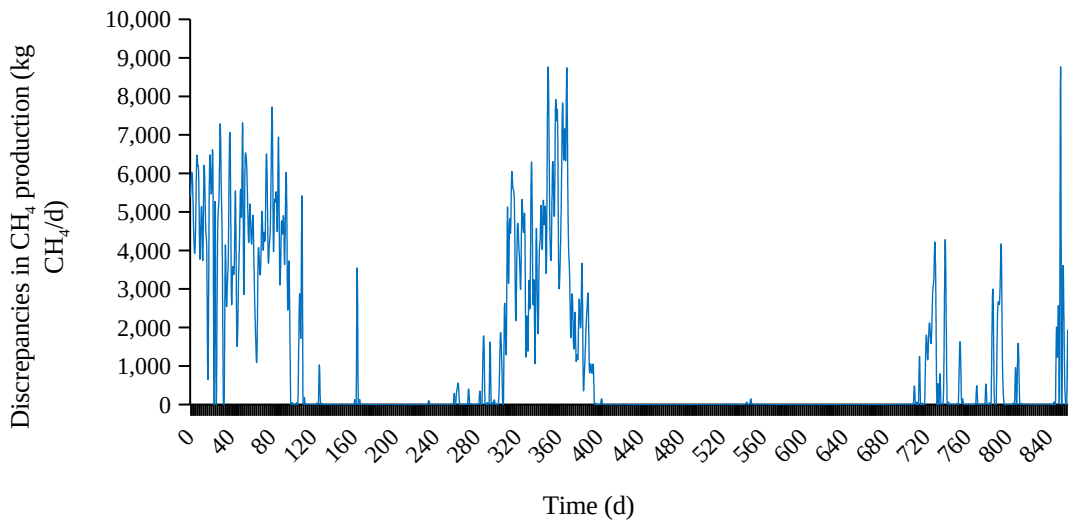


Figure 5. Dynamics of the discrepancies in CH_4 production from the anaerobic digesters.

3.2.2 Bioreactors

Emissions from the bioreactors were $245 \pm 19 \text{ kg CH}_4/\text{d}$, exclusively through hydrogenotrophic methanogenesis, while no acetoclastic methanogenesis activity was observed. This was expected, as hydrogenotrophic methanogens exhibit a higher growth rate relative to that of acetoclastic methanogens (1.3 vs 0.3 d^{-1}). Additionally, hydrogenotrophic methanogens have a lower half-saturation concentration ($K_s = 0.00125 \text{ g H}_2/\text{m}^3$), enabling them to utilise H_2 at very

low concentrations. In contrast, the slower growth rate and the higher acetate half-saturation concentration ($K_s = 400 \text{ g COD/m}^3$) of acetoclastic methanogens prevent them from outcompeting other acetate-utilisers such as denitrifiers, phosphorus accumulating organisms (PAOs), and sulphate reducing bacteria (SRB) to eventually produce CH_4 . Several studies have reported H_2 generation by *Candidatus Accumulibacter* during anaerobic acetate contact and its uptake for polyhydroxyalkanoate (PHA) synthesis, serving as part of the redox balance in EBPR systems (Leonor et al., 2020; Oyserman et al., 2016). Randall et al. (1992) also reported anaerobic COD losses in EBPR systems where fermentable substrates were used instead of acetate, partly due to CO_2 production during fermentation, but also due to H_2 evolution, as trace concentrations of H_2 were measured in the off-gas of properly functioning systems. Dissolved H_2 present in the fermenter supernatant, along with that produced during EBPR and in situ fermentation in anaerobic and anoxic selectors, could be a potential source for CH_4 emissions. Yan et al. (2014) and Wang et al. (2011) reported CH_4 emissions ranging from 74.4 to 147.7 kg CH_4/d and from 24 to 49 kg CH_4/d , respectively, from the bioreactors of BNR plants in China, operating at average COD loads that were 47% and 73.6% lower than those of the plant in this study. It is noteworthy that it was not possible to distinguish between the emissions produced in the bioreactors and those conveyed from upstream processes. However, when applying the CH_4 production rates reported by Ren et al. (2013) (i.e., 0.006 to 0.011 kg $\text{CH}_4/\text{m}^2\cdot\text{d}$ across anaerobic, anoxic, and aerobic zones) to the surface areas of the bioreactors in this study, emissions exclusively from the bioreactors ranged from 221 to 385 kg CH_4/d , well-aligned with the model's results, demonstrating the value of rigorous calibration, particularly the reduction in the H_2 fermentation yield, given that default values would have inflated the model's predictions by two orders of magnitude.

3.2.3 Biosolids handling

Emissions from the dewatered solids and the recycled centrate, depicted in Figure 6, were 10 ± 2 and 76 ± 10 kg CH₄/d, respectively. Since gas–liquid exchange is not modelled in the dewatering unit, the dissolved CH₄ concentration in the digester effluent is assumed to remain equal in both the centrate and the dewatered solids, which will eventually be stripped into the atmosphere. Consequently, the higher emissions from the centrate are primarily due to its flow rate, which is more than twice that of the dewatered solids. Daelman et al. (2012) reported CH₄ emissions from biosolids of 168 kg CH₄/d, albeit with an uncertainty of almost 100%, and carried out at a smaller plant not directly comparable in magnitude; it remains one of the few studies explicitly reporting emissions from biosolids handling emissions. Nonetheless, the model’s predictions remain consistent with the general magnitude of those measurements.

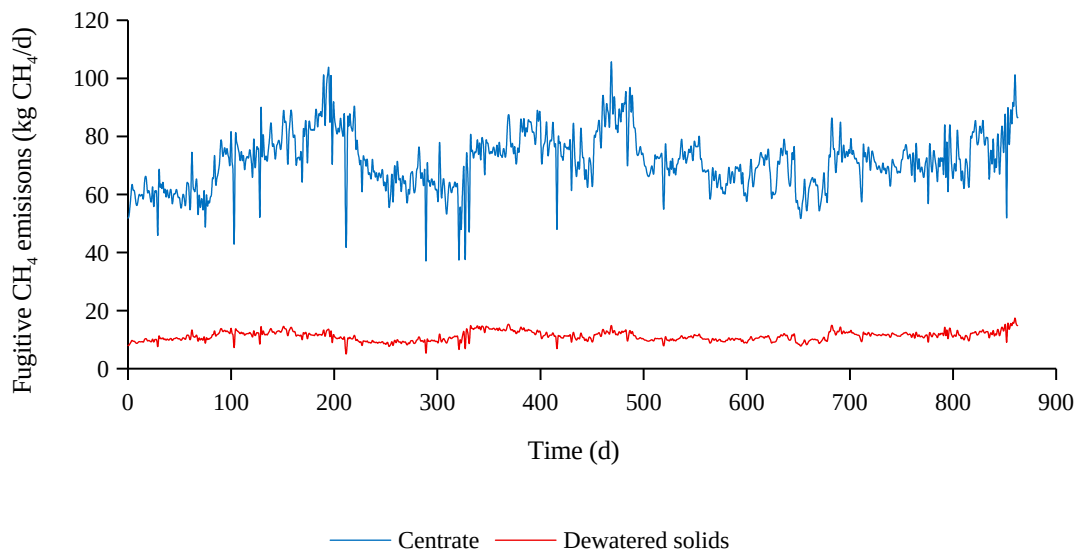


Figure 6. Daily CH₄ emissions from biosolids handling units.

3.2.4 Overall emissions

Overall emissions over the study period were $1,111 \pm 1,932$ kg CH₄/d, reflecting temporal variability exceeding 100% during the study period, translating to EFs of 0.0047 ± 0.0081 kg

CH₄/kg COD and 0.012 ± 0.02 kg CH₄/kg BOD. EFs from the primary sources were consistent with the ranges reported by Moore et al. (2023) of 0.001 to 0.4 kg CH₄/kg BOD across 63 full-scale WWTPs in the United States. The results are also consistent with other full-scale studies of WWTPs with AD, which report EFs ranging from 0.023 to 0.064 CH₄/kg BOD (Daelman et al., 2013b; Delre et al., 2017). The average EF was 70% higher than the Canadian EF for BNR plants (0.0036 kg CH₄/kg BOD) but 33% lower than that of the Intergovernmental Panel on Climate Change (IPCC; 0.018 kg CH₄/kg BOD), highlighting that existing national EFs may not adequately represent CH₄ emissions from centralised WWTPs (Baasansuren et al., 2019). The influent BOD load was used as the reference metric, as it is the conventional organic loading parameter adopted by the IPCC and is more routinely monitored across WWTPs than COD.

3.3 Potential sources

The primary sources were constrained by the routine measurements available at the plant; however, as was previously demonstrated in Figure 1, additional CH₄ sources may be relevant. Therefore, this section addresses these potential sources to evaluate their significance and ensure they are considered in the uncertainty analysis.

3.3.1 Sewers

CH₄ formation in sewer systems, often reaching supersaturated concentrations, was previously reported by Guisasola et al. (2008). However, it was not until 2019 that the 2006 IPCC Guidelines for National Greenhouse Gas Inventories were refined to acknowledge this issue. Even then, the guidelines only considered emissions from stagnant sewers, assuming those from free-flowing waters to be negligible, a stance that has remained unchanged (IPCC, 2022;

Lambiasi et al., 2024). Earlier concerns regarding the potential magnitude of CH₄ emissions from sewers were raised a decade earlier by Foley et al. (2009), who reported dissolved CH₄ concentrations ranging from 1 to 9.29 g CH₄/m³ in a downstream wet well of a rising main in Gold Coast, Australia, concluding that, contrary to the IPCC's assumptions, sewers represent a significant source of CH₄ emissions.

Based on the distributions of the data in Table S6, the higher bound of sewer-induced emissions was estimated to be $2,726 \pm 1,516$ kg CH₄/d, ranging from 0.009 to 11,754 kg CH₄/d, while the lower bound was estimated to be 476 ± 211 kg CH₄/d, ranging from 0.002 to 1,870 kg CH₄/d. While emissions from sewers and the influent wastewater have been quantified in full-scale studies, they have rarely been incorporated into plant-wide modelling frameworks to assess their contribution to plant-wide emissions. The results indicate they are far from negligible and, in some cases, can exceed emissions from digester leaks, representing a significant but often overlooked source of CH₄ emissions.

3.3.2 Fermenters

Considering the fermenters' off-gas is pumped directly into the bioreactors, any CH₄ present in this stream would be considered fugitive. Emissions from the fermenters were 25 ± 99 , 37 ± 157 , 396 ± 438 , 1183 ± 186 , and 1482 ± 287 kg CH₄/d across SRTs of 3, 4, 5, 6, and 7 days, respectively. Despite the relatively short HRTs of the fermenters, decoupling the HRT from the SRT allows not only hydrogenotrophic methanogenesis to occur, but also acetoclastic methanogenesis, since the minimum SRT required to prevent their washout is 4 days (Rittmann & McCarty, 2001). Considering that the temperatures investigated in this scenario, ranging from 9.9 to 18.8 °C, were well below the optimal range for methanogenesis, it is likely that, in heated fermenters, the onset of CH₄ production would occur over a shorter duration, with the

cut-off potentially falling below 5 days. Overall emissions from the fermenters' off-gas and supernatant are depicted in Figure 7.

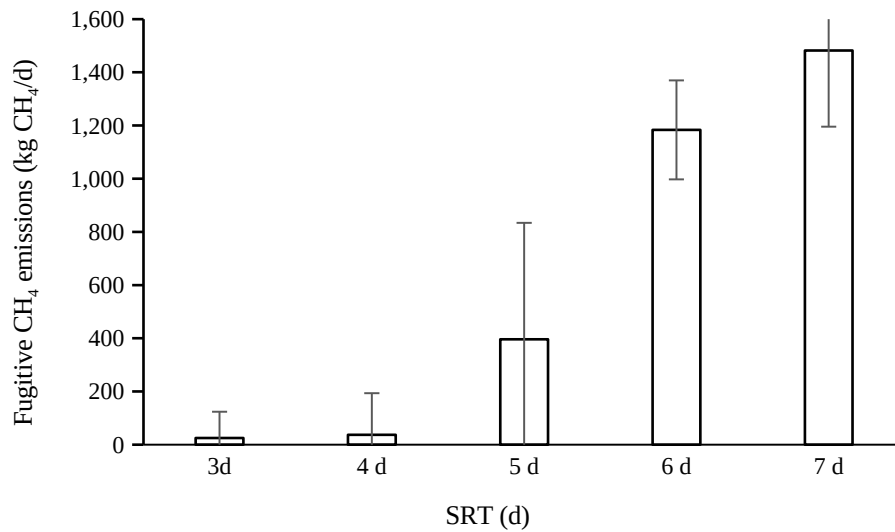


Figure 7. Fugitive CH₄ emissions from the fermenters at different SRTs.

3.3.3 Secondary clarifiers

Since fermentation in sludge blankets, whether intentional or not, can create conditions conducive to methanogenesis, secondary clarifiers represent a potential unaccounted source of CH₄ (Metcalf & Eddy, 2014). Due to data limitations, emissions were estimated using manual calculations. Analysis of the secondary clarifiers revealed that complete removal of NO_x, accompanied by an increase in NH_x and sCOD concentrations in the sludge blanket, reaching 36.8 g N/m³ and 261 g COD/m³, respectively, indicative of fermentation. Considering the pN/VSS and pCOD/VSS ratios of the WAS being 0.095 g N/g VSS and 1.46 g COD/g VSS, respectively, it was estimated that on average 137 g VSS/m³ were solubilised, releasing 201 g COD/m³. The COD consumed for denitrification was estimated to be 14.3 g COD/m³, based on an average COD/N consumptive ratio of 4.5 (Metcalf & Eddy, 2014). Meanwhile, the concentration of orthophosphate (PO₄) increased significantly, from an average of 0.07 to 66.1

g P/m³. Considering the pP/VSS ratio of the WAS being 0.034, the amount of PO₄ released from fermentation only amounted to 4.7 g P/m³, and the residual COD after denitrification was insufficient for phosphorus release by PAOs. Additionally, due to fermentation, low pH pockets may have formed, shifting the aluminium phosphate (AlPO₄) precipitation–dissolution equilibrium toward dissolution (Metcalf & Eddy, 2014). Consequently, approximately 79 g COD/m³ remain unaccounted for, which may have been released as either CH₄ or CO₂ or both, depending on the prevailing microbial pathways.

Emissions from clarifiers are associated with substantial uncertainty and a lack of data to properly evaluate them. Daelman et al. (2012) reported emissions from primary and secondary clarifiers of 24 ± 96 and 24 ± 120 kg CH₄/d, while Yan et al. (2014) reported no emissions from the clarifiers of 3 different WWTPs. One of the key limitations of the model was the inability to estimate emissions from primary clarifiers, specifically, due to insufficient data on the PS characteristics. Additionally, clarifiers are typically modelled as non-reactive ideal separation units, while reactive clarifier models are computationally demanding, and the necessary data from full-scale plants for calibration are non-existent. Hence, the reliance on manual calculations was the only way available to evaluate any COD losses.

3.4 Uncertainty and sensitivity analyses

The first- and total Sobol indices of this scenario are summarised in Table 4. Fugitive CH₄ emissions and the EFs from the primary sources were estimated to be $3,845 \pm 1,774$ kg CH₄/d and 0.018 ± 0.008 kg CH₄/kg COD, respectively, with uncertainties of 46.1% and 44.4% reflecting substantial variability. The sensitivity analysis showed that f_{leaked} and M_{CH_4} were the most sensitive variables, accounting for 86.7% and 9.7% of the output variance, respectively. This was expected given the limited number of contributing variables in this scenario and the

magnitude of their associated uncertainty. Small numerical errors can arise from the truncation of Monte Carlo approximations used in Sobol's method; therefore, slightly negative indices are assumed to be equal to zero (Tang et al., 2007).

In the scenario representing the upper bound of influent CH₄ concentrations, fugitive CH₄ emissions and the EFs were $7,643 \pm 2,440$ kg CH₄/d and 0.034 ± 0.012 kg CH₄/kg COD, with uncertainties of 31.9% and 35.3%, respectively. S_{inf} was the most sensitive variable, accounting for 83.5% of the output variance, followed by Q_{inf} and f_{leaked} , contributing 10.9% and 1.5%, respectively. The influence of S_{inf} substantially reduced the relative sensitivity of f_{leaked} , from 86.7% from the primary sources to 1.5%. This reflects not only the influence of the relatively high concentrations but also the high flow rates exhibited by the plant, which reached 661,200 m³/d during the study period.

In the scenario representing the lower bound of influent CH₄ concentrations, fugitive CH₄ emissions and the EFs were $5,393 \pm 1,925$ kg CH₄/d and 0.024 ± 0.009 kg CH₄/kg COD, with uncertainties of 35.7% and 37.5%, respectively. Similar to the upper bound scenario model, S_{inf} was the most sensitive variable, contributing 58% to the total variance, followed by f_{leaked} , Q_{inf} , $M_{CH_4,dig}$ and S_{fsu} contributing 25%, 8%, 2.7%, 1.5% to the output variance, respectively. Table S7 summarises the overall uncertainty in fugitive CH₄ emissions and EFs from each scenario, including minimum, mean (μ), standard deviation, and maximum values.

Across all scenarios, the first- and total-order Sobol indices were very similar, indicating that the model behaves nearly additively with respect to a variable. In such cases, the variable's effect on the output is largely independent, contributing to the variance primarily through its main effect rather than through interactions with other variables (Saltelli et al., 2008).

Table 4. First- and total-order Sobol indices of all scenarios.

Sources	Primary sources	Primary and secondary sources
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Variable			Upper bound scenario		Lower bound scenario	
	S_i	S_{Ti}	S_i	S_{Ti}	S_i	S_{Ti}
Q_{inf}	–	–	0.109	0.145	0.08	0.1
S_{inf}	–	–	0.835	0.873	0.58	0.6
Q_{cent}	5.83×10^{-5}	6.07×10^{-5}	1.02×10^{-4}	1.02×10^{-4}	1.73×10^{-3}	1.79×10^{-3}
S_{cent}	1.65×10^{-6}	3.02×10^{-6}	2.77×10^{-5}	2.13×10^{-5}	3.37×10^{-4}	3.75×10^{-4}
$M_{CH_4,dig}$	0.097	0.13	1.59×10^{-3}	2.1×10^{-3}	0.027	0.037
f_{leaked}	0.869	0.90	0.015	0.01	0.25	0.26
$M_{CH_4,ferm}$	–	–	-2.05×10^{-7}	3.12×10^{-7}	8.42×10^{-6}	5.52×10^{-6}
Q_{fsu}	–	–	4.5×10^{-4}	5.9×10^{-4}	7.8×10^{-3}	0.01
S_{fsu}	–	–	7.7×10^{-4}	9.82×10^{-4}	0.015	0.017
Q_{ds}	1.23×10^{-6}	1.27×10^{-6}	2.19×10^{-4}	2.05×10^{-4}	3.63×10^{-3}	3.63×10^{-3}
r_p	1.18×10^{-4}	1.01×10^{-4}	1.74×10^{-4}	1.64×10^{-4}	2.99×10^{-3}	2.91×10^{-3}
V_r	1.03×10^{-6}	1.14×10^{-5}	1.59×10^{-5}	1.86×10^{-5}	2.76×10^{-4}	3.28×10^{-4}

3.4.1 Synopsis

The primary reason previous plant-wide models have focused on N₂O rather than CH₄, aside from the substantial difference in their global warming potentials (273 vs. 27), is the significant spatial and temporal variability of N₂O emissions observed in full-scale monitoring campaigns, which can range from 0 to 90% of the influent nitrogen load, in addition to the uncertainty in its production pathways (IPCC, 2022; Kampschreur et al., 2009; Vasilaki et al., 2019). In contrast, CH₄ emissions were long assumed to be static, originating primarily from leaks in anaerobic digesters and typically estimated at only 2 to 5%. However, the uncertainty and sensitivity analyses showed that CH₄ emissions can also be highly variable, with uncertainties approaching 50%, and amounting to 13.6% of the total influent COD load, far beyond IPCC's estimate of 0.75% for centralised aerobic plants (Eggleston et al., 2006). These results also underscore that even strictly aerobic plants may exhibit significant fugitive CH₄ emissions, considering bioreactors contributed negligibly to the overall emissions. The variables with the largest influence were the influent flow rate, influent CH₄ concentrations, the amount of CH₄ produced in anaerobic digesters, and the amount leaked from the digesters' headspace into the atmosphere.

It is important to note that, while influent wastewater characteristics and fractions are inherent sources of uncertainty in modelling, they were not propagated in this analysis. This decision was supported by the historical stability of the studied plant's influent; however, this source of uncertainty should be carefully considered when applying the framework to facilities with more variable influent quality. Frameworks for propagating influent uncertainty in plant-wide models have been proposed (e.g., Ramin et al. (2022)), and could be incorporated where influent variability is significant.

3.5 Practical implications

Capturing the diurnal and seasonal variability of emissions through dedicated monitoring campaigns is costly, labour-intensive, and time-consuming. Moreover, such campaigns often fail to resolve temporal variations in emissions and provide limited process-level insight to support mitigation, particularly when municipalities and WWTPs are not required to carry out monitoring for regulatory compliance. In contrast, a rigorously calibrated and validated plant-wide model can identify emission hotspots, quantify emissions, estimate uncertainties, and inform targeted mitigation strategies at a much lower cost. Nevertheless, model performance, like that of all models, is conditioned by the quality and frequency of the data used for hydraulic and mass balance calculations, calibration, and validation.

Biogas production predictions, supported by COD mass balance calculations, were sufficient to reveal discrepancies indicative of operational disturbances, instrumentation issues, or biogas losses, without requiring additional sampling beyond routine monitoring. Therefore, the framework does not attempt to directly predict factors contributing but rather identifies

inconsistencies in the COD-to-CH₄ mass balance that signal potential methane losses within the system.

The model provided key process insights into CH₄ formation across the fermenters and bioreactors. In the fermenters, the operational SRT governed both the onset and magnitude of CH₄ production, with longer SRTs, even at colder temperatures, increasing emissions by orders of magnitude. In the bioreactors, the model revealed that CH₄ formation occurred primarily through hydrogenotrophic methanogenesis, persisting even under alternating aerated and non-aerated conditions.

Additionally, while emissions from sewers were estimated using published data, confirming the presence of dissolved CH₄ in the influent would require limited targeted sampling, which remains far less resource-intensive than plant-wide measurement campaigns and can be incorporated into routine influent monitoring.

Across all primary sources, including anaerobic digesters, bioreactors, and biosolids handling, the dynamically estimate emissions aligned with values reported in plant-wide measurement campaigns. This demonstrates that the model provides a practical alternative for continuous plant-wide assessment, as calibration and validation rely primarily on routine plant data. While additional targeted efforts, such as influent characterisation, may be required, the overall resource demand remains substantially lower than that of comprehensive, long-term plant-wide monitoring campaigns. Moreover, the framework enables dynamic predictions, visualisation, and the identification of atypical operational behaviour that can guide targeted mitigation efforts, capabilities that are seldom captured through monitoring campaigns.

4 Conclusions

This study presents a plant-wide modelling framework that enables quantification of fugitive CH₄ emissions, evaluation of uncertainty, and identification of key emission hotspots in full-scale WWTPs. The main findings are as follows:

- Fugitive CH₄ emissions are substantially underestimated when assumed to originate solely from anaerobic digesters and when the fugitive fraction is assumed to be constant and not quantified based on operational data.
- Thorough model calibration is essential, as default model parameters can lead to either under- or overestimation of emissions.
- Monte Carlo simulations indicated uncertainties ranging from 39.1% to 46.1% in both CH₄ emissions and emission factors.
- The sensitivity analysis revealed that the influent flow rate, dissolved influent CH₄ concentrations, CH₄ production in anaerobic digesters, and the fraction leaked into the atmosphere are the largest contributors to fugitive emissions.
- A rigorously calibrated and validated plant-wide model can effectively predict CH₄ emissions without the need for resource-intensive monitoring campaigns.

While the framework provides a practical tool for plant-wide assessment of fugitive CH₄ emissions, its performance remains dependent on the availability and quality of operational data. Future work should focus on improving the predictive capability of plant-wide models for process units that are not readily identifiable as emission hotspots and may require more detailed calibration or a refined process representation, such as clarifiers.

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