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Chapter 6

Full-scale emission results (N_2O and CH_4)

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SUMMARY

This chapter reviews the studies from N_2O and CH_4 monitoring campaigns in full-scale wastewater treatment plants (WWTPs) and sewer networks. The focus is on greenhouse gas (GHG) emissions from WWTPs as more literature is available. The analysis classifies quantified N_2O and CH_4 emission factors (EFs), triggering operational conditions and formation pathways for different configurations. Control strategies to minimize N_2O emissions are proposed for different process groups. The main reasons for EF discrepancies are discussed. Overall, N_2O emission factors for processes treating low-strength wastewater streams range between 0.003 and 5.6% of the N-load (average equal to 0.9% of the N-load). Emissions higher than mainstream process average emissions have been reported in sequencing batch reactors (average equal to 3.6% of the influent N-load) and step-fed plug flow reactors. In full-scale sidestream processes, less than 15 monitoring campaigns have reported EFs (average equal to 2.5% of the N-load). Differences in the EFs among the process groups are partially attributed to disparities in the control strategies (i.e. aeration control), configuration, and operational and environmental conditions that favour the preferred enzymatic pathways. Overall, triggering operational conditions for elevated N_2O emissions in full-scale wastewater treatment processes include (i) increased NH_4^+ concentrations leading to a high ammonia oxidation rate (AOR) and increased production of intermediates (e.g. NH_2OH, NO^-, etc.), (ii) improper aeration control (i.e. inadequate aeration and non-aeration duration, over-aeration, under-aeration), (iii) NO_2^- accumulation triggering the nitrifier denitrification pathway, and (iv) sudden shifts in incomplete heterotrophic denitrification (i.e. due to excess dissolved oxygen (DO), chemical oxygen demand (COD) limitation etc.). The N_2O monitoring strategies can also influence the reliability of the quantified EFs. Due to temporal variation of N_2O emissions, short-term studies are not sufficient to quantify annual EFs. The analysis showed that the average EF for processes treating low-strength streams monitored for less than a week is 0.66% of the influent N-load. On the other hand, processes monitored over 6 months have an

average EF equal to 1.74%. Compared with N_2O, CH_4 quantification from full-scale WWTPs is less investigated, while it also contributes significantly to the overall plant carbon footprint. The results of full-scale CH_4 quantification studies are summarized in this chapter. Emissions of CH_4 in WWTPs mainly originate from the influent, anaerobic wastewater treatment and anaerobic sludge handling processes. The amount of CH_4 emissions varies greatly with different configurations of WWTPs. For WWTPs without anaerobic sludge handling processes, the CH_4 emissions can mainly be traced back to the CH_4 dissolved in the influent. When anaerobic treatment is applied in WWTPs for wastewater COD removal, its CH_4 emissions might substantially increase the overall plant carbon footprint. GHG monitoring campaigns carried out in WWTPs should include the monitoring of fugitive CH_4 emissions. Finally, CH_4 and N_2O emissions reported from sewer networks are also summarized in this chapter.

The last part of the chapter summarizes some mitigation strategies applied at full-scale to control fugitive CHG emissions from WWTPs and sewers.

Keywords: Full-scale greenhouse gas emissions, methane, nitrous oxide, sewer networks, wastewater treatment plants

TERMINOLOGY

Term	Definition
Activated sludge	Flocs of sludge particles containing microbes, which are formed in the presence of oxygen in aeration tanks.
Activated sludge process	The wastewater treatment process which applies activated sludge to speed up the decomposition of contaminants in wastewater. Oxygen is provided in the aeration tank in favour of the metabolization of activated sludge, to convert contaminants into harmless products. After the aeration tank, the mixed activated sludge goes to a clarifier to separate the sludge and treated water. The treated water will undergo further treatment.
Aeration	The introduction of air into the aeration tank for the oxidation of organic, nitrogenous and phosphorous compounds by microbes, and also for keeping the activated sludge suspended and well mixed.
Aerobic	Conditions with free oxygen in the wastewater.
Ammonia monooxygenase	An enzyme catalysing NH_4^+ oxidation to NH_2OH.
Anaerobic	Conditions without atmospheric or dissolved molecular oxygen in the wastewater.
Anoxic	Conditions of oxygen deficiency and presence of oxidized nitrogen species.
Biomass	A clump of organic material consisting of living organisms, which lives on the substrates in wastewater, or the dead organism debris.
Chemical oxygen demand	An indication of the amount of organic materials in wastewater. It refers to the amount of oxygen equivalent consumed in the chemical oxidation of organic matter by a strong oxidant such as potassium dichromate.
Dissolved oxygen	Molecular oxygen dissolved in wastewater.
Greenhouse gas	Gas that absorbs and emits radiant energy within the thermal infrared range and contributes to the global warming effect.
Heterotrophic denitrification	A series of reduction reactions from nitrate to nitrogen gas by heterotrophic denitrifiers under anoxic conditions, with organic carbon as the electron donor for the reactions.
Nutrient	Substances such as nitrogenous compounds and phosphorous or organic matter that can be assimilated by microbes to promote the metabolism and growth of microbes in the reactor.
Organic matter	The organic waste of plant or animal origin from homes or industry, mainly volatile fraction of solids.

Oxidation	Oxidation is the addition of oxygen, removal of hydrogen, or the removal of electrons from an element or compound. In wastewater treatment, organic matter is oxidized to more stable substances.
pH	An indication of the acidity or alkalinity of solutions.
Reactor	Containers of different size or design which can hold the activated sludge to conduct wastewater treatment processes.
Wastewater	The used water and solids from a community that flow into a treatment plant. Storm water, surface water, groundwater infiltration and a fraction of industrial wastewater also may be included.
EF	Emission factor

6.1 INTRODUCTION

Nitrous oxide (N_2O), is a potent greenhouse gas (GHG), 298 times stronger than CO_2 in terms of global warming potential (IPCC, 2013). N_2O can be generated in large amounts and stripped in the atmosphere during biological nutrient removal (BNR) at wastewater treatment plants (WWTPs). In the past few years, concern regarding the quantification and investigation of N_2O, from full-scale wastewater treatment processes has increased. There are three main biological pathways for N_2O production in BNR systems. N_2O can be formed during the autotrophic oxidation of ammonia to nitrite/nitrate through the activity of ammonia oxidizing bacteria (AOB) under aerobic conditions (nitrification/nitritation). The N_2O production by AOB can be due to the autotrophic denitrification of nitrite (nitrifier denitrification pathway) and due to incomplete oxidation of hydroxylamine (NH_2OH) (NH_2OH oxidation pathway). N_2O is also an intermediate during the reduction of nitrate/nitrite to nitrogen gas through the activity of heterotrophic denitrifying bacteria under anoxic conditions (heterotrophic denitrification pathway). There is a wide variety of different BNR processes applied at wastewater facilities to treat the incoming wastewater (i.e. with different numbers of compartments/zones for nitrification and denitrification, recirculation flows, flow-patterns and feeding strategies). Studies have shown that the direct N_2O emissions of BNR processes in WWTPs can contribute up to ~78% of the operational carbon footprint (Daelman *et al.*, 2013). There are recent studies reporting even higher percentages; for example, N_2O contributes up to 86% of the carbon footprint in the study of Kosonen *et al.* (2016), compared to direct methane emissions (CH_4).

Significant N_2O emissions have been reported from the biological treatment of high-strength wastewater streams. The anaerobic supernatant is a by-product from the treatment of the primary and secondary sludge via anaerobic digestion when the digestate is dewatered. This stream is small in volume (1–2% compared to the mainstream line), but very concentrated in nutrients and is conventionally recycled back to the primary treatment increasing the loads (and thus, the energy requirements and costs) of the mainstream biological treatment (i.e. contains 10–20% of the WWTP nitrogen load). For this purpose, BNR technologies (such as partial-nitritation-anaerobic ammonium oxidation (PN-anammox), nitritation-denitritation, etc.) have been developed to treat high-strength streams in a cost and energy efficient way (Lackner *et al.*, 2014; Zhou *et al.*, 2018). In the sidestream biological processes, favourable conditions for N_2O generation can prevail (i.e., NO_2^- accumulation, elevated NH_4^+ concentrations, etc.). Studies have shown that biological processes treating high-strength streams can contribute over 90% of the total direct N_2O emissions compared to the mainstream BNR processes (Schaubroeck *et al.*, 2015).

The recent mitigation roadmap to carbon neutrality in urban water published by the Water and Wastewater Companies for Climate Mitigation (WaCCliM) project and the International Water Association (IWA) (Ballard *et al.*, 2018), states that direct N_2O emissions in water utilities, should be considered for carbon footprint assessment, reporting and mitigation. However, in practice, the quantification of direct N_2O emissions at WWTPs via monitoring campaigns is not a regulatory requirement. Therefore, wastewater utilities usually estimate N_2O emissions via theoretical methods, that is based on the population equivalent of the WWTP (IPCC, 2006); the latter can significantly

underestimate the actual emissions (Cadwallader & VanBriesen, 2017). The 2019 IPCC Refinement of the 2006 IPCC Guidelines has significantly increased the suggested default EF; they propose a value equal to 1.6% of the influent N-load.

Full-scale monitoring campaigns have been implemented in full-scale BNR processes to provide insights into the dynamics and triggering mechanisms for N_2O generation. However, results were variable and there is still not a consensus to explain the exact causes. The application of different WWTP configurations and different biological treatments is a main reason that explains the variation in results. The sampling strategy and duration also play an important role. Most of the studies were performed over a short-term (days–weeks) showing only diurnal emission patterns. The sampling strategy (grabbing samples or online monitoring) is also a factor that can lead to an over or underestimation of the N_2O emissions. Additionally, N_2O fluxes were characterized by significant spatial and temporal variability due to the different interacting biological processes that consume or produce N_2O and the variation in operational conditions (Daelman *et al.*, 2015; Gruber *et al.*, 2020). Mechanistic process-based models have been developed over recent years aiming to integrate N_2O emissions generation of different processes in the design, operation and optimization of biological processes (Domingo-Félez *et al.*, 2017; Mannina *et al.*, 2016; Massara *et al.*, 2017). However, their online integration for the reliable quantitative estimation of N_2O emissions and offline integration for long-term quantitative purposes remain challenging (Haimi *et al.*, 2013; Mampaey *et al.*, 2019).

WWTPs also emit CH_4 (Daelman *et al.*, 2013; Ribera-Guardia *et al.*, 2019). Emissions of CH_4 in WWTPs mainly originate from the influent, anaerobic wastewater treatment and anaerobic sludge handling processes and can present large variations from plant to plant. For WWTPs without anaerobic sludge handling processes, the majority of the CH_4 emitted originates from the dissolved CH_4 in the influent formed in sewer networks. For WWTPs with anaerobic sludge handling processes, anaerobic sludge treatment and handling facilities contribute the most to the CH_4 emissions in plants. CH_4 emissions can substantially contribute to the carbon footprint of a WWTP, especially in those facilities with low N_2O emissions. Despite of its importance in the overall emitted GHG, there are only a few studies in the literature reporting CH_4 emissions from full-scale systems.

Finally, sewer systems also present fugitive greenhouse gas emission, with CH_4 being the main greenhouse gas produced although N_2O has also been reported. The reporting of emissions from sewers is much more scarce as compared to WWTPs but its important contribution to the overall CH_4 emissions of wastewater systems cannot be neglected.

6.2 N_2O EMISSIONS FROM FULL-SCALE WWTP MONITORING RESULTS

This chapter reports emission factors (EFs) for the main BNR processes for wastewater treatment and proposes mitigation measures (Table 6.1). Monitoring campaigns to quantify and mitigate N_2O emissions have been performed over recent years in different WWTP configurations. Our observations to date confirm that due to differences in monitoring strategies (i.e. length of monitoring period) and design and operational conditions, universally acceptable configuration-based or performance based EF estimation modes are not yet available. The challenge of evaluating and mitigating N_2O emissions from BNR processes is further complicated by practical and technological hurdles that are related with the little field data regarding N_2O emissions for several BNR processes and other operational constraints.

Mainstream process groups include biological nutrient removal systems targeting N-removal (N-BNR) (aerobic/anoxic compartments), biological nutrient removal systems targeting both N and P removal (NP-BNR) (anaerobic/anoxic/aerobic compartments) and conventional activated sludge (CAS) systems (only aerobic reactors). Oxidation ditch (OD) reactor types and sequencing batch reactor (SBR) types have been considered as distinct process groups. Sidestream processes including partial-nitritation reactors, 1-step and 2-step PN-anammox and nitritation-denitritation configurations are also categorized as a distinct process group. Other processes with fewer than two case studies

Table 6.1 Methods and main findings of studies resulting in mitigation measures (The abbreviations are explained below*).

Process	EF range (% N-load)	Main findings	Mitigation measures	Source
Partial Nitritation – Anammox (1 reactor)	0.17–3.9	• Smoother aeration transitions during normal reactor operation connected with lower N_2O emissions; comparison with experiments • Prolonged anoxic periods leading to increased N_2O emissions • Over-aeration significantly impacting on N_2O emissions • Nitritation-denitritation SBR: the accumulation of N_2O at the end of the SBR anoxic phase is stripped in the subsequent aerobic phase and can have a significant impact on the amount of N_2O emitted • DO and conductivity have been linked with emissions in nitritation-denitritation SBR systems	• Optimize the aeration regime by introducing aeration control and ensuring smooth shift patterns in the aeration • Preferably operate under shorter cycles and short aeration intervals to avoid accumulation of NO_2^- • Step feeding and use of conductivity as a surrogate to estimate the effluent NH_4-N concentration of the reactor and optimize the anaerobic supernatant feeding load (avoid either FA accumulation or high AOR that trigger N_2O) • Frequent alternation of aerobic/anoxic phases to avoid nitrite accumulation	Castro-Barros *et al.* (2015); Kampschreur *et al.* (2009a, b); Weissenbacher *et al.* (2010); Joss *et al.* (2009); Christensson *et al.* (2013)
Partial Nitritation/–Anammox (2 reactors) and nitritation-denitritation systems	2.3–7.6	• Nitritation: N_2O formation higher during non-aerated periods • Splitting the anoxic period: average anoxic N_2O formation rate decreased • Shorter cycles can reduce the N_2O EF at the expense of higher NO_3^- concentrations • Anammox reactor: NO_2^- accumulation potentially increasing N_2O emissions	• Apply continuous aeration in nitritation reactor • Operate under lower DO setpoint and control the aeration rate. It is preferred that DO > 1.3 mg/L. Lower DO levels have been linked with elevated N_2O generation in nitritation-denitritation SBR systems. • Avoid anoxic phases in nitritation reactors • Operate a one-reactor nitritation-anammox process; potentially emitting less N_2O due to limited NO_2^- accumulation	Mampaey *et al.* (2016); Kampschreur *et al.* (2008); Vasilaki *et al.* (2020); Gustavsson and la Cour Jansen (2011); Ahn *et al.* (2010)

(Continued)

Table 6.1 Methods and main findings of studies resulting in mitigation measures (The abbreviations are explained below*) (*Continued*).

Process	EF range (% N-load)	Main findings	Mitigation measures	Source
N-BNR	0.018–4	• N_2O emissions have been correlated with increased abundances of AOB & lower counts of N_2O-reducers; AOB abundance favoured by higher NO_3^- & NO_2^-concentrations • DO exhibiting a significant influence on the N_2O production • N_2O production mainly in the aerated zones, minor N_2O consumption & minor stripping effect in the anoxic zones • N_2O emitted directly from the aeration basin: low COD:N ratio limiting denitrification & leading to 5-times higher N_2O emissions • N_2O dynamics not significantly influenced by DO variations (within the range of 1.5–2 mg/L) • Daily N_2O peaks occurring under higher aeration flow rates (more intense N_2O stripping) and under elevated bulk NO_2^- concentrations in the bioreactor and under poor plant aeration performance and insufficient DO • Low EF: diluted influent (groundwater infiltration) as the most probable reason	• Avoid NO_2^- accumulation, low temperatures & excess DO in the anoxic bioreactors to enable complete heterotrophic denitrification & hinder nitrifier denitrification • Apply proper control of DO in aerated compartments • Apply the BP-ANN model as a convenient & effective method for the description of N_2O emissions in an A/O • Studies in full-scale MLE reactors have not suggested process/study specific mitigation measures	Castellano-Hinojosa *et al.* (2018); Sun *et al.* (2017); Kosonen *et al.* (2016); Aboobakar *et al.* (2013); Samuelsson *et al.* (2018); Masuda *et al.* (2018); Rodriguez-Caballero *et al.* (2014); Pan *et al.* (2016); Ahn *et al.* (2010); Bellandi *et al.* (2018); Spinelli *et al.* (2018); Townsend-Small *et al.* (2011); Foley *et al.* (2010); Foley *et al.* (2015)

(Continued)

Table 6.1 Methods and main findings of studies resulting in mitigation measures (The abbreviations are explained below*) (*Continued*).

Process	EF range (% N-load)	Main findings	Mitigation measures	Source
NP-BNR	0.068–3.4	• N_2O emitted mainly from the oxic zone, with the emission levels increasing greatly from the beginning of the oxic zone towards the anoxic zone • NO_2^- accumulation directly triggering N_2O production • Both diurnal & seasonal N_2O emission levels fluctuating strongly; N_2O generated & emitted more in summer than in winter • Other factors influencing the N_2O emission: low DO/temperature • Microbial population & aeration strategy as key factors of N_2O generation & emission • Risk of elevated emissions in processes with plug-flow pattern with step feeding • Significant spatial variability of N_2O generation within the reactor	• Increase DO availability for both AOB & NOB and improve the growth conditions of AOB • Apply a step-stage aeration mode with varying aeration intensities (location-specific emission patterns for a plug-flow process) • Ensure better mixing via a higher horizontal plug-flow rate combined with an appropriate vertical airflow flux; the large cross-section widths reduced using partition walls to elevate flow velocities under a constant A^2/O tank working volume • Avoid incomplete/intermittent nitrification & over-aeration during the aerobic processes to achieve lower N_2O emissions • Apply uniform spatial DO profiles to promote SND that probably leads to less N_2O emissions • Perform flow equalization to control the peaking factor of the influent N-loading to the AS • Ensure a sufficiently long SRT to prevent NO_2^- accumulation during nitrification • Avoid the COD limitation of the denitrification process by minimizing the pre-sedimentation of organic carbon in the influent & dosing additional organic carbon • Avoidance of over-aeration (DO 1–2 mg/L) and control of mixed liquor recirculation rates to exceed 500% has been shown to reduce N_2O emissions	Wang *et al.* (2016b); Li *et al.* (2016); Ren *et al.* (2013); Foley *et al.* (2010); Foley *et al.* (2015); Yan *et al.* (2014); Zaborowska *et al.* (2019)

(Continued)

Table 6.1 Methods and main findings of studies resulting in mitigation measures (The abbreviations are explained below*) (*Continued*).

Process	EF range (% N-load)	Main findings	Mitigation measures	Source
SBR	0.58–5.6	• NH_4^+ accumulation leading to a high AOR during the aerobic SBR phases and, finally, to the increased production of intermediates (e.g. NH_2OH) • Low DO during nitrification majorly influencing N_2O production • Cycles with long aerated phases showing the largest N_2O emissions, with a consequent increase in the carbon footprint • Transient NH_4^+ & NO_2^- concentrations & transition from anoxic to aerobic possibly involved in the increased N_2O production • Spatial variability of N_2O generation within the reactor has been reported due to elevated NH_4^+ concentration in the feeding point	• Apply intermittent aeration and reduce the aerated periods to decrease the NO_2^- accumulation • Increase the aeration rate during the feeding period & decrease it to a proper level for nitrification in the aerobic stage • Alternatively, change the operational SBR mode (from feeding under synchronous aeration to feeding with anoxic stirring) to ensure enough COD provision/better utilization of influent COD for denitrification • Allow the system to consume N_2O through denitrification. Extend denitrification length or if required supply external carbon source during denitrification • Continuous aeration at DO equal to ~0.5 mg/L favouring simultaneous nitrification-denitrification can also reduce the N_2O	Ni *et al.* (2013); Rodriguez-Caballero *et al.* (2015); Sun *et al.* (2013); Duan *et al.* (2020); Gruber *et al.* (2020); Foley *et al.* (2010); Foley *et al.* (2015)
OD	0.03–2.8	• Both nitrifying & denitrifying zones are potential hotspots of N_2O production • Relatively low emissions due to strong dilution effect (relatively long HRT), AOB≈NOB (minor NO_2^- accumulation, less likely N_2O production via nitrifier denitrification), more uniform DO profile in the OD process (SND promoted) • Aerated zones: N_2O fluxes correlated with location-specific pH, AS mixed liquor temperature, DO, NH_4^+ & NO_2^- concentrations & interactive combinations • Anoxic zones: N_2O fluxes correlated with location-specific sCOD, pH, AS mixed-liquor temperature, DO, NO_2^- & NO_3^- concentrations & interactive combinations	• Essential to control DO at proper level during nitrification/denitrification & enhance the utilization rate of influent organic carbon for denitrification • Multivariate analysis can be applied (i.e. clustering, classification) to investigate the combined effect of operational variables on N_2O emissions	Sun *et al.* (2015); Ren *et al.* (2013); Daelman *et al.* (2015); Vasilaki *et al.* (2018); Ahn *et al.* (2010); Yan *et al.* (2014); Masuda *et al.* (2018); Chen *et al.* (2019); Foley *et al.* (2010); Foley *et al.* (2015); Ekström *et al.* (2017)

(Continued)

Table 6.1 Methods and main findings of studies resulting in mitigation measures (The abbreviations are explained below*) (*Continued*).

Process	EF range (% N-load)	Main findings	Mitigation measures	Source
CAS	0.36–1.8	• Nitrification is the main driving force behind N_2O emission peaks • Compared to other parameters (e.g. sludge concentration/retention time), air flow-rate variations possibly influencing the N_2O emissions; high N_2O emissions under conditions of over-aeration or incomplete nitrification along with NO_2^- accumulation • The treatment of the anaerobic supernatant in mainstream CAS systems can trigger significant N_2O emissions	• Reduce the aeration rate to decrease the N_2O emission rate and energy consumption required for aeration • Add an anoxic zone & recirculation to a non-BNR system for nitrification; otherwise, high N_2O emissions expected in case of increased DO • Control the DO; dynamic changes in DO concentrations reported as being responsible for N_2O emission peaks • Avoid the concurrence of decreased DO & NO_2^- accumulation	Chen *et al.* (2016); Ribeiro *et al.* (2017); Ahn *et al.* (2010); Gruber *et al.* (2020); Brotto *et al.* (2015)
Other/ generic	0.004–2.8	• Investigate possible links between WWTP operating conditions & N_2O emission fluxes • Aerobic zones: N_2O fluxes correlated with location-specific pH, AS mixed liquor temperature, DO, NH_4^+ & NO_2^- concentrations & interactive combinations • Anoxic zones: N_2O fluxes correlated with location-specific sCOD, pH, AS mixed-liquor temperature, DO, NO_2^- & NO_3^- concentrations & interactive combinations • In cases of low external C-source availability, internally stored compounds (e.g. polyhydroxyalkanoates (PHAs)) can be alternatively utilized. The latter is likely to increase the N_2O production during denitrification	• BNR processes: Avoid high NH_4^+ & NO_2^- & DO concentrations & transients • Aerobic processes: avoid incomplete/ intermittent nitrification & over-aeration • Rely on more uniform spatial DO profiles to promote SND • Minimize peak N-flow (flow equalization) • pH maintained $6 \leq pH \leq 7$ • Provision of sufficient C-source to increase the possibility of N_2O consumption through denitrification. • DO must be controlled at approximately 2 mg/L while aeration minimized to avoid stripping • Perform advanced N-removal (e.g. nitritation-denitritation or partial nitritation-anammox) only after optimizing the process parameters. • BP-ANN and data-driven models suitable for the description of N_2O emissions in other WWTPs with different configurations (e.g. A^2/O, SBR & nitrification-anammox), if influent/environmental parameters & N_2O emission data can be investigated through full-, pilot- or lab-scale experiments	Wang *et al.* (2016a); Ahn *et al.* (2010); Samuelsson *et al.* (2018); Kosonen *et al.* (2016); Mello *et al.* (2013); Filali *et al.* (2013); Foley *et al.* (2010); Foley *et al.* (2015); Baresel *et al.* (2016); Gruber *et al.* (2020)

*SBR: sequencing batch reactor; DO: dissolved oxygen; FA: free ammonia; AOR: ammonia oxidation rate; AOB: ammonia oxidizing bacteria; NOB: nitrite oxidizing bacteria; COD: chemical oxygen demand; BP-ANN: back propagation-artificial neural network; A/O: anoxic/oxic reactor; MLE: modified Ludzack-Ettinger; N-BRN: nitrifying – biological nitrogen removal; NP-BNR: biological nitrogen and phosphorus removal; A2/O: anaerobic/anoxic/oxic reactor; SND: simultaneous nitrification denitrification; AS: activated sludge; SRT: sludge retention time; HRT: hydraulic retention time; OD: oxidation ditch; sCOD: soluble chemical oxygen demand; CAS: conventional activated sludge.

which do not belong to the aforementioned process groups are categorized separately. These include intermittently aerated or simultaneous nitrification-denitrification reactors (i.e., Filali *et al.*, 2013; Gruber *et al.*, 2020; Mello *et al.*, 2013), systems with external carbon dosage (Ahn *et al.*, 2010) and biofilm reactors for C (i.e. Townsend-Small *et al.*, 2011) or N removal (i.e., Bollon *et al.*, 2016).

In total ~67% of the analysed mainstream reactors, have reported the quantified EFs in terms of the %N-load. Approximately 12% of the studies have reported the EFs in terms of N-removed.

There is a significant variation in the N_2O emissions of full-scale wastewater treatment processes. The N_2O emissions range reported in literature is between 0.003% of the influent N-load for a mainstream BNR system treating municipal low-strength wastewater, diluted by groundwater and marine intrusions and 7.6% of the NH_4-N load for a sidestream short cut enhanced nutrient abatement (SCENA) SBR treating anaerobic digestion supernatant. Generally, BNR processes treating high strength streams have been associated with high risk of elevated N_2O emissions. This is mainly due to the high ammonia oxidation rate (AOR) and NO_2^-accumulation typically observed in such systems (Desloover *et al.*, 2011; Gustavsson & la Cour Jansen, 2011; Kampschreur *et al.*, 2008). Discrepancies in the EFs observed in the different process groups can, to some extent, be attributed to variations in operational characteristics and control parameters. In addition to reactor configuration, emission rates depend on the operational/environmental conditions and preferred enzymatic pathways (Wan *et al.*, 2019).

Figure 6.1 shows boxplots of the observed EFs (with respect to the influent N-load) of mainstream processes in different countries. The width of the violin plot outlines surrounding the boxplots represents the data kernel density distribution of the EFs. Overall, ~60% of the monitoring campaigns in processes treating low-strength streams have been performed in China (18%), the United States (18%), Australia (14%) and Sweden (10%). Overall, the highest EFs have been reported in Australia. The median EF in Australia is 1.35% of the N-load (average equal to 1.6%). The lowest EFs have been

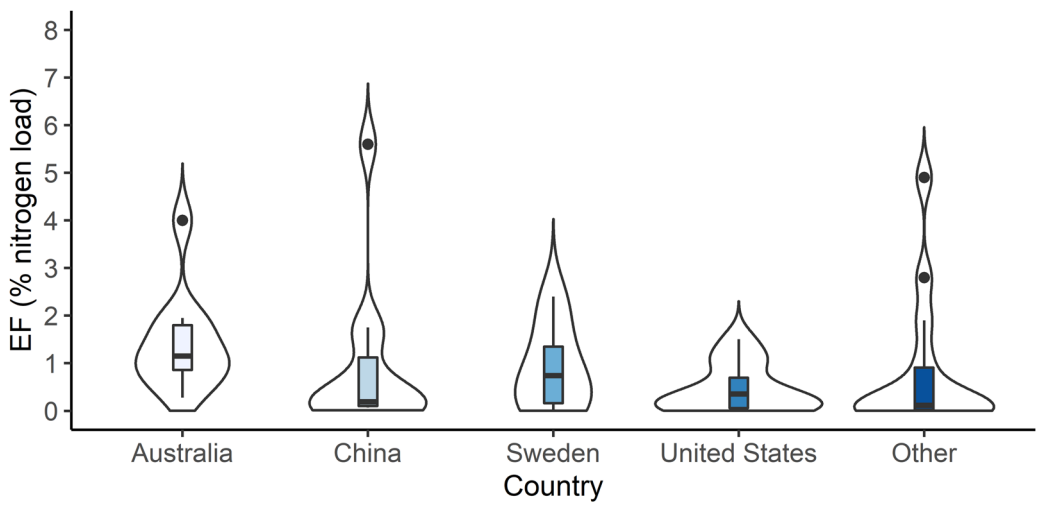

Figure 6.1 Boxplots of the reported EFs (% N load) with respect to the WWTP in different countries using violin plot outlines. The rectangles represent the interquartile range. The median is denoted by the black horizontal line dividing the box into two parts. The dots represent the values exceeding 1.5 times the interquartile range. The upper and lower whiskers stand for values higher or lower than the interquartile range, respectively (within 1.5 times the interquartile range above and below the 75th and 25th percentile, respectively). The violin plot outlines show the kernel probability density of the EF in mainstream and sidestream processes; the width of the violin plot outlines represents the proportion of the data located there.

reported in China; the median EF is equal to 0.2% of the N-load (average 0.8% of the N-load). In the United States the median EF is 0.3%, while in Sweden the median EF is 0.74% of the N-load (averages equal to 0.4% and 0.9% of the N-load, respectively.)

The majority of the processes monitored in Australia are step-feed reactors. Higher than average N_2O emissions have been reported for step-feed reactors. Moreover, the majority of the WWTPs studied in China do not have anaerobic digestion on-site. The anaerobic supernatant is a by-product from the treatment of the primary and secondary sludge via anaerobic digestion when the digestate is dewatered. This stream is small in volume (1–2% compared to the mainstream line), but very concentrated in nutrients and is conventionally recycled back to the primary treatment increasing the loads (and thus, the energy requirements, costs and potentially the N_2O emissions) of the mainstream biological treatment. The majority of the studied processes in Sweden and Australia belong to WWTPs with anaerobic digestion on-site. It is possible that WWTPs that recycle anaerobic supernatant that contains 10–20% of the WWTP nitrogen load, have a higher risk of increased N_2O emissions. The sampling protocols and duration of monitoring campaigns also vary significantly between the different countries. For instance, long-term monitoring of N_2O emissions (>6 months) has been performed mainly in China via grab-samples collected bi-monthly. Vasilaki *et al.* (2019) showed that low-frequency (i.e. bimonthly) grab-sampling might underestimate emissions due to limitations in sampling duration (i.e. it does not occur during night-time) or due to short-term process perturbations triggering elevated emissions not coinciding with the sampling days.

Figure 6.2 shows the EF range for the different groups of mainstream processes and sidestream processes. As a general remark, the majority of the EFs in processes treating low-strength wastewater

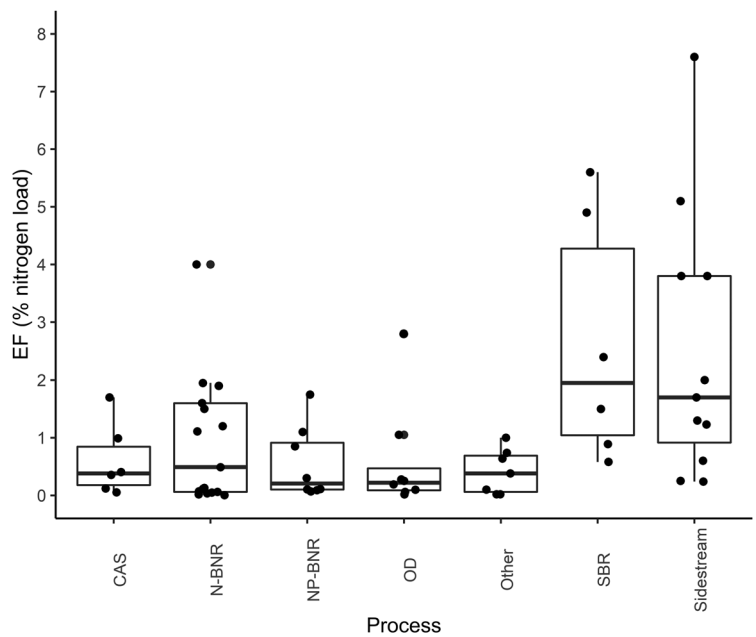

Figure 6.2 Boxplots visualizing the EF range for the different groups of mainstream processes and sidestream processes (adapted from Vasilaki *et al.* 2019). The rectangles represent the interquartile range. The median is denoted by the black horizontal line dividing the box into two parts. The dots represent values exceeding 1.5 times the interquartile range. The upper and lower whiskers represent values higher or lower the interquartile range, respectively (within 1.5 times the interquartile range above and below the 75th and 25th percentile, respectively).

range from 0.1% to 2% of the influent N-load. Higher than average emissions have been reported in SBRs and step-fed plug-flow reactors. The potential for N_2O emissions from reactors treating high-strength wastewater streams is considered higher compared to the mainstream BNR processes. This is mainly because the nitritation/partial-nitritation occurring during sidestream treatment is linked with higher ammonia oxidation rate (AOR) and NO_2^- accumulation (Desloover *et al.*, 2011; Gustavsson & la Cour Jansen, 2011; Kampschreur *et al.*, 2008).

The benchmarking of the EF for groups of processes remains challenging, mainly due to differences in the strategies applied during monitoring, the operational and environmental conditions and the duration of monitoring campaigns. Additionally, limited information exists on the N_2O emissions for several other processes (e.g. biofilm-based processes or partial-nitritation-anammox systems, etc.) (Sabba *et al.*, 2018; Vasilaki *et al.*, 2019).

Process characteristics, EFs, N_2O triggering mechanisms, operational conditions and mitigation measures for processes treating low-strength and high-strength wastewater streams are analysed in Sections 6.2.1 and 6.2.2, respectively.

High sensitivity of the quantified EF between different monitoring strategies and monitoring campaign durations has been reported (Vasilaki *et al.*, 2019). When considering the duration of the monitoring campaign, studies lasting over a year result in a median EF equal to 1.7% of the N-load. On the other hand, most of the monitoring campaigns lasting less than one month have reported EFs less than 0.3% of the N-load. Therefore, short-term monitoring periods may fail to capture underlying seasonal variations in the N_2O formation (or be affected by short-term process perturbations) and, consequently, result in unreliable EFs. Similarly, the studies monitoring N_2O emissions in mainstream wastewater processes continuously (i.e. online via gas analysers), have quantified higher N_2O EFs than studies monitoring N_2O emissions discontinuously (i.e. offline via grab samples). The average EFs of mainstream wastewater processes monitored continuously and discontinuously are 1.2% and 0.44% of the N-load, respectively. Low-frequency sampling campaigns have a high risk of not sufficiently capturing short-term changes in pollutant concentrations, operational conditions and system disturbances impacting N_2O generation.

The reliability of the monitoring campaigns also depends on the amount and location of the sampling points (Gruber *et al.*, 2020). Significant spatial variations of the N_2O emissions have been reported in complete mixing reactors (Duan *et al.*, 2020). The variability was attributed to gradients in the nutrients within the reactor and elevated NH_4^+ concentrations close to the feeding area causing increased AOR and triggering N_2O emissions. The use of one gas chamber for N_2O emissions collection in complete mixing reactors might result in unreliable quantification of N_2O EFs. The latter can have significant implications, since one gas chamber is conventionally used for sampling in complete mixing reactors, whereas several sampling points are suggested for reactors operating in plug-flow mode (Duan *et al.*, 2020). On the other hand, Gruber *et al.* (2020) observed negligible spatial variability of N_2O emissions in a complete mixing reactor monitored with three gas chambers in different locations within the reactor. Therefore, additional studies are required to determine the optimum N_2O sampling points and understand under which conditions nutrient gradients are observed.

Differences in the N_2O emissions have been also reported in parallel reactors. Chen *et al.* (2019), studied parallel OD reactors and observed deviations in the N_2O emissions behaviour under similar NH_4^+, NO_3^- and dissolved oxygen (DO). They suggested that the reliable quantification of WWTP N_2O EFs requires monitoring of all plant reactors. The opposite has been reported by Daelman *et al.* (2015) who observed similar N_2O emission patterns in two parallel OD reactors.

Generally, the quantification of reliable annual EFs requires sampling campaigns lasting at least 1 year. Additionally, a decision tree for the selection of the monitoring strategy has been developed by Gruber *et al.* (2020). They define specific criteria for the selection of sampling points and location. Influent compositions, feeding locations and homogeneity, and the key performance indicators (i.e. removal efficiencies) should be considered to decide whether similar N_2O emissions are expected in parallel reactors. Similarly, plug-flow type reactors featuring spatial variability of concentrations and aeration intensity require multiple sampling points.

The variability of EF reported in full-scale wastewater treatment processes can be attributed to complex relationships between emitted N_2O and operational conditions and different configurations (i.e., SBR, continuous systems), loads (i.e., NH_4^+ concentrations), feeding strategies and operational control (i.e., DO set-points).

The conditions leading to elevated N_2O emissions or N_2O generation are usually associated with N-forms build-up in the reactor (i.e., NH_4^+, NH_2OH, NO-, NO_2^-). Depending on the BNR process and the acclimatized biomass in the reactor, the accumulation of N intermediates does not necessarily have to be very high to trigger N_2O pathways. The accumulation mainly depends on the influent dynamics or on improper process operation and/or design.

During nitrification, NH_3/NH_4^+ concentration can significantly affect the N_2O emissions (Law *et al.*, 2012; Wunderlin *et al.*, 2012). High NO_2^- accumulation, that is the toxic product of aerobic NH_3 oxidation in AOB, has also been linked with elevated N_2O emissions, especially under low DO concentrations (Desloover *et al.*, 2011; Kampschreur *et al.*, 2008; Law *et al.*, 2012; Massara *et al.*, 2017; Peng *et al.*, 2015; Tallec *et al.*, 2006). Different N_2O production dynamics can be potentially triggered under the same NO_2^- concentration depending on the type of AOB. It has been also reported that AOB can adapt to different environments with different NO_2^- concentrations. Overall, N_2O generation has been associated with higher NO_2^- concentrations in wastewater treatment processes (Foley *et al.*, 2010). DO is also considered an important parameter affecting N_2O emissions (Kampschreur *et al.*, 2009b), with sub-optimum DO concentrations generally increasing N_2O emissions. AOB can use nitrite instead of oxygen as an electron acceptor (Kampschreur *et al.*, 2009a, b), in oxygen limiting conditions, generating N_2O emissions. At present, establishing a generic optimum DO concentration threshold to minimize N_2O emissions for nitrifying systems is not possible since other compounds (i.e. N compounds discussed above) have a simultaneous effect on N_2O generation. An optimal DO level for minimal N_2O emissions can be established for each system taking into consideration the concentration of other compounds that affect these emissions. Overall, in aerated reactors/zones, higher emissions are expected under high NH_4^+ concentrations, high AOR, sub-optimum DO (under or over-aeration) or NO_2^- build-up (Desloover *et al.*, 2011; Kampschreur *et al.*, 2008). Sub-optimum pH and short solids retention times (SRTs) have been reported to influence N_2O production in AOB.

Additionally, feeding mainstream reactors with high-strength streams (i.e., anaerobic supernatant) can create peak nutrient loadings increasing the risk of elevated N_2O emissions. In the studied processes, WWTPs that have anaerobic digestion on-site have median EFs equal to 1.5% of the N-loading (average equal to 1.47%). On the other hand, processes that are not fed with anaerobic supernatant (i.e., WWTPs applying sludge dewatering and drying) have a median EF equal to 0.11% of the N-load (average 0.47% of the N-load).

Sub-optimum DO, chemical oxygen demand (COD), pH and SRT can also result in nitrite and N_2O accumulation during denitrification (Schulthess *et al.*, 1994; Yang *et al.*, 2012). Low values of COD/N can result in incomplete denitritation and, therefore, N_2O accumulation via the heterotrophic denitrification pathway (Wunderlin *et al.*, 2012).

Seasonal environmental variations, can influence the bacterial community structure in WWTPs (Flowers *et al.*, 2013) and the N_2O emissions. Temperature can significantly affect the AOB specific growth rate during nitrification (Van Hulle *et al.*, 2010). The higher temperature also decreases the N_2O solubility, thus intensifying the N_2O stripping to the atmosphere (Reino *et al.*, 2017). Adouani *et al.* (2015) reported an increased sensitivity of the N_2O reductase activities at lower temperatures compared to other denitrification enzymes and, therefore, to incomplete denitrification. Other seasonal variations (e.g., influent loading, wet and dry season) can affect the enzymatic reactions and the emissions. Vasilaki *et al.* (2018) observed peaks of N_2O emissions coinciding with precipitation events, at low temperatures. Further investigation is required to understand the impact of seasonal effects on the N_2O emissions (Gruber *et al.*, 2020; Vasilaki *et al.*, 2019).

Disturbances in the process can affect short-term (i.e., 1 day) or even longer period (i.e., >1 week) N_2O generation (Vasilaki *et al.*, 2018). Gruber *et al.* (2021) observed in an SBR reactor, that N_2O

emission peaks, nitrification failure, poor activated sludge settleability and high turbidity of treated effluent, were all linked to a less diverse microbial community and changes in community mixture. Specifically, a decrease in abundance of filamentous and nitrite oxidizing bacteria was reported.

6.2.1 Processes treating low strength streams

6.2.1.1 N-BNR and NP-BNR processes

This section discusses findings regarding N_2O generation in BNR processes. The Modified Ludzack-Ettinger (MLE) process is the most studied N-removal configuration. In total, 41% of the N-BNR systems are MLE processes. The MLE process consists of anoxic and aerobic tanks and a secondary settler. The influent wastewater is first fed to the anoxic tank for denitrification and next to the aerobic zone for nitrification. The process uses an internal recycle flow from the aerobic tank to the head of the anoxic tank providing nitrate for denitrification. After anoxic and aerobic processes, the wastewater is fed to the secondary settler. A part of the sludge, the return activated-sludge, returns to the head of the anoxic zone to increase the mixed liquor volatile suspended solids (MLVSS) concentration in the reactor. In total, the N-BNR configurations consist of a broad category of processes with anoxic and oxic compartments. Step-feed plug-flow reactors with alternating anoxic/oxic zones and reactors with small anoxic compartments (for predenitrification) and aerobic compartments with and without recirculation of nitrates belong to this category.

Similarly, the anaerobic/anoxic/aerobic (A^2/O) process is the most studied N and P-removal configuration. In total 64% of the NP-BNR systems are A^2/O processes. The A^2/O process is a modification of the MLE process. The process consists of an anaerobic zone followed by the same configuration of MLE. The return activated sludge goes to the head of the anaerobic tank. The anoxic tank is used to decrease the amount of nitrate, in the anaerobic tank, that returns from the activated sludge. Overall, the NP-BNR process group includes configurations with anaerobic, anoxic and aerobic compartments, such as reversed-A^2/O configurations (A^2/O systems where the anaerobic and anoxic compartments are reversed) or A^2/O systems with a predenitrification zone.

The median EF of N-BNR processes is 0.5% of the influent N-Load, while the median EF of NP-BNR processes is 0.2% of the influent N-Load. In N-BNR configurations, the N_2O emissions range between 0.003% and 4% of the influent N-load (Foley *et al.*, 2010; Spinelli *et al.*, 2018). In NP-BNR configurations, the N_2O emissions range between 0.07% and 1.75% of the influent N-load (Wang *et al.*, 2016b; Yan *et al.*, 2014). MLE and A^2/O are the most studied configurations; around 54% of the monitoring campaigns have been performed in these two systems.

Overall, in N-BNR and NP-BNR systems, N_2O emission peaks have been reported during the transition from non-aerated to aerated zones/compartments (i.e. Rodriguez-Caballero *et al.* 2014; Sun *et al.* 2017). This can be partially due to incomplete denitrification and accumulation of dissolved N_2O under anoxic conditions. Elevated emissions have been also linked with excess DO in anoxic compartments, inhibiting complete denitrification (Castellano-Hinojosa *et al.*, 2018). Therefore, process control in the anoxic compartments should target the minimization of NO_2^- accumulation and excess DO and the avoidance of COD limitation. This will facilitate complete heterotrophic denitrification and N_2O consumption.

In aerobic compartments, peak N_2O fluxes have coincided with peak nutrient loads and low DO concentrations (Wang *et al.*, 2011, 2016b); the integration of flow equalization can control the influent N-loading peaks to the systems. Moreover, close to the inlet of aerobic compartments with a plug-flow pattern, AOB abundances and high NO_2^- concentrations can result in an increase in the N_2O emissions. Risk of elevated emissions has also been reported in processes with plug-flow pattern and step feeding. Pan *et al.* (2016) showed an EF equal to 0.7% of the influent N-load in the first step of a plug-flow reactor and 3.5% in the second step. The increased N_2O emissions in the second step were attributed to the recirculated stream being directed only at the first step causing dilution; the MLVSS concentration in the second step was 40% lower than that in the first step (70% less biomass compared to the first step). The higher specific AOR in this stage triggered the N_2O generation. It is

important to note that in reactors with plug-flow pattern, the effect of the N-load, DO concentration and temperature on N_2O emissions varies along the reactor (Aboobakar *et al.*, 2013). Thus, the dominant N_2O triggering conditions can also vary.

Low EFs have been reported in reactors treating diluted low-strength wastewater (i.e. due to groundwater infiltration) (Bellandi *et al.*, 2018; Spinelli *et al.*, 2018). Low EFs have also been reported in the majority of the A²/O and reversed A²/O processes, with the median N_2O EF ~0.11% of the influent N-load. However, it must be noted that the seasonal variability of the N_2O emissions in A²/O rectors has not been studied adequately. The majority of the monitoring campaigns lasted less than 3 months. Wang *et al.* (2016b) showed that the EF of an A²/O process has strong temporal patterns and varied between 0.1 and 3.4% of the influent N-load between different months within 1 year. The effect of environmental conditions on N_2O generation is discussed in Section 6.2.

Both the nitrifier denitrification pathway and the NH_2OH oxidation pathway have been suggested as major contributors to the N_2O emissions in aerated compartments/zones. The nitrifier denitrification pathway is considered the main triggering mechanism in aerobic compartments (i) when NO_2^-, NH_4^+ and O_2-limiting conditions co-exist (Wang *et al.*, 2016b), (ii) when NO_2^- is correlated with N_2O emissions, (iii) when increasing N_2O emissions are observed under DO limitation where sufficient O_2 is provided to the AOB for the oxygenation of NH_3 to NH_2OH but not for aerobic respiration; NO_2^- is potentially used as alternative electron acceptor to complete nitrification (Aboobakar *et al.*, 2013; Castellano-Hinojosa *et al.*, 2018; Sun *et al.*, 2017; Wang *et al.*, 2011), and (iv) under shock loads of toxic compounds, where the AOB likely activate their denitrification pathway (Rodriguez-Caballero *et al.*, 2014). In anoxic compartments, the nitrifier denitrification pathway has been suggested as the main contributor to N_2O generation, when excess DO is observed (Castellano-Hinojosa *et al.*, 2018). The NH_2OH oxidation pathway is significantly promoted at higher DO concentrations (Blomberg *et al.*, 2018; Zaborowska *et al.*, 2019) and when N_2O emissions increase together with the AOR increase (Ni *et al.*, 2015; Pan *et al.*, 2016). Finally, heterotrophic denitrification is mainly triggered under carbon-limiting conditions (low COD/N ratio) and excess DO in anoxic compartments (Andalib *et al.*, 2017; Wunderlin *et al.*, 2012).

6.2.1.2 Sequencing batch reactors (SBR)

The SBR process uses a fill-and-draw complete mixing reactor operating in batch reaction steps. The biological removal and clarification occur in the same tank.

Mainstream SBRs have reported higher N_2O emissions compared to the other mainstream process groups. EFs range between 0.89% of the influent N-load for an SBR that receives the anoxic selector effluent and operating under feeding (intermittent aeration), aerobic (intermittent aeration), settling and decanting sequences (Duan *et al.*, 2020) and 5.6% of the influent TN-load for an SBR operating under aerated feeding, aerobic and anoxic settling and decanting sequences (1 h each) (Sun *et al.*, 2013). The average EF from SBR reactors is 3.6% of the influent N-load (median: 3.65% of the influent N-load).

Overall, elevated emissions are attributed to (i) NH_4^+ accumulation leading to high AOR during the aerobic SBR phases and to increased production of intermediates (e.g., NH_2OH, NO^-, etc.), (ii) long aerated cycles, (iii) transitions from anoxic to aerobic phases possibly triggering increased N_2O production, (iv) rapid changes in the NH_4^+ and NO_2^- concentrations within the cycle, (v) accumulation of dissolved N_2O during anoxic settling and decanting that is stripped in the subsequent aerobic phase and (vi) accumulation of NO_2^-.

Intermittent aeration and short aerated periods have been suggested to reduce the NO_2^- accumulation in SBR systems and subsequently N_2O emissions. Duan *et al.* (2020), however, showed that elevated DO concentrations (up to 8 mg/L) during intermittent aeration can also be responsible for elevated emissions in the SBR systems and should be avoided. The authors used a multi-pathway N_2O model (Peng *et al.*, 2016) to design a mitigation strategy that was implemented in the studied system. They showed that continuous aeration at DO equal to ~0.5 mg/L that favours simultaneous

nitrification-denitrification (SND) can be an effective operational strategy for SBR reactors. The SND operation mode resulted in 35% reduction of the N_2O emissions compared to intermittent over-aeration. The reduction was due to the reduction of DO concentration during feeding and aerated phases that can enhance denitrification during aerated periods and minimize NO_2^- accumulation.

Additionally, in SBR reactors the supply of an external carbon source during denitrification can secure sufficient COD provision and better utilization of influent COD for denitrification (promoting complete heterotrophic denitrification). This allows the system to consume N_2O during denitrification and avoid stripping of residual liquid N_2O in the subsequent aerated phases, thus, reducing N_2O emissions. A cycle configuration with a sequence of aerobic phases (adjusted on site) followed by short non-aerated periods has been proposed as an effective control mechanism to reduce N_2O generation (Rodriguez-Caballero *et al.*, 2015).

In SBR reactors, elevated N_2O emissions are attributed to the NH_2OH pathway when elevated DO is observed during feeding and when high NH_4^+ concentrations are observed without simultaneous NO_2^- increase in the aerated phases. The nitrifier denitrification pathway is the main N_2O triggering mechanism when low DO concentrations in aerobic phases are linked with the N_2O generation and when certain NO_2^- accumulation under aerobic conditions is observed in the reactor. In cases where N_2O generation continues when the aeration finishes, both the nitrifier denitrification and heterotrophic denitrification can contribute to the N_2O formation in the reactor. Finally, the correlation between N_2O emission and influent COD/N, indicates that the incomplete heterotrophic denitrification is mainly responsible for the N_2O generation.

6.2.1.3 Oxidation ditch (OD)

An OD is a modified activated sludge biological treatment process; the removal of biodegradable organics is achieved by applying long SRTs. ODs are considered to approach complete mixing systems, but they can also operate in plug-flow mode.

The N_2O emissions of OD reactor types range from 0.03% of the N-load for an OD reactor favouring simultaneous nitrification denitrification (Ahn *et al.*, 2010) to 2.8% of the N-load for a system consisting of an anaerobic/anoxic/oxic plug-flow reactor followed by two parallel Carrousel reactors (Daelman *et al.*, 2015). The median EF is equal to 0.2% of the influent N-load (average equal to 0.3% of the N-load).

Overall, relatively low emissions have been reported in OD systems; this is attributed to the strong dilution effect (relatively long hydraulic retention time), to the abundance of AOB and nitrite oxidizing bacteria (NOB), and to the more uniform DO profile in the OD process especially when SND is promoted (Li *et al.*, 2016). Abundance of NOB and denitrifiers has been reported in OD systems as contributing to the consumption of NO_2^- during nitrification. The latter reduced NO_2^- accumulation and facilitated complete heterotrophic denitrification (Sun *et al.*, 2015). It is important to note, though, that the majority of the OD reactors have been monitored with gas hoods. The use of floating hoods to monitor GHG emissions in OD systems when aerated with surface aerators has been criticized due to the turbulence commonly observed at the surface affecting the capturing of the emissions in the hood (Ye *et al.*, 2014).

Elevated emissions have been linked to NH_4^+ concentration peaks. In a simulation study, Ni *et al.* (2013) observed that more than 90% of the N_2O emissions were attributed to aerated zones with DO >2 mg/L and NH_4-N concentration peaks (up to $\sim$9 mg/L). Inadequate anoxic zones, inhibiting complete denitrification have been also reported in OD systems. OD systems with surface aerators are prone to developing zones with reduced DO, inhibiting complete nitrification, that results in nitrite accumulation and increased N_2O emissions.

A similar N_2O emissions pattern has been reported in two OD reactors operating under different control and design (Chen *et al.*, 2019; Daelman *et al.*, 2015). Both systems were monitored over a long term; an increasing trend in N_2O emissions coincided with increase in water temperature whereas, low emissions were observed under lower water temperature. Further studies are required

to understand the exact triggering mechanisms at decreasing temperatures and investigate if this N_2O pattern is process-specific.

All N_2O generation pathways have been reported in OD reactors. Incomplete heterotrophic denitrification has been attributed to the competition of the denitrification steps and the preference of the heterotrophic denitrifiers to reduce NO_3^- instead of N_2O under electron donor limitation (Pan *et al.*, 2013). Additionally, heterotrophic denitrification and nitrifier denitrification are the main N_2O triggering mechanisms at insufficient anoxic conditions. Under these conditions NO_2^- accumulation is expected. The NH_2OH oxidation pathway will be triggered in periods with influent NH_4^+ concentration peaks, high ammonia oxidation rate and elevated DO concentrations. Vasilaki *et al.* (2018), showed that the relationships between N_2O emissions and other variables monitored in an OD (i.e. NH_4^+, NO_3^-, DO) are dynamic and affected by seasonal variations. The preferred N_2O pathways were found to be dependent on time and operational conditions.

6.2.1.4 Conventional activated sludge systems

CAS systems consist of aerobic reactors (1-step feed or multiple-step feed) without anoxic compartments. They are characterized by a median EF equal to ~0.4% of the influent N-load (average equal to 0.71%). The NH_4^+ removal is between 38% and 53%. The EF in CAS systems ranges from 0.05% of the N-load (translated to 9% of the NH_4-N removed) (Chen *et al.*, 2019) to 1.7% of the N-load (Gruber *et al.*, 2020).

Peak loads and recirculation of the anaerobic supernatant can be responsible for the N_2O fluxes observed in CAS systems, whereas high aeration rates have been reported, enhancing N_2O stripping (Chen *et al.*, 2016). Additionally, the spatial variation of nutrients in step-fed CAS systems can result in incomplete denitrification and affect the AOR during nitrification (due to uneven substrate-biomass distribution in all feeding points), hence, increasing the total N_2O emissions (Pan *et al.*, 2016). The treatment of the anaerobic supernatant in mainstream CAS systems has been reported to trigger significant N_2O emissions. Gruber *et al.* (2020), monitored the N_2O emissions in two parallel CAS systems and found that elevated emissions were observed solely in the reactor treating the anaerobic supernatant. N_2O emissions can be reduced by up to 80% when influent N-loads are reduced by 30%.

Tumendelger *et al.* (2014) reported that the NH_2OH oxidation pathway was responsible for up to 90% of the N_2O formation under high DO (~2.5 mg/L at the middle and close to the outlet of the aerobic tank) in a CAS system (site preference (SP) isotopic analysis). Both AOB pathways contributed almost equally to N_2O emissions generation at DO levels of ~1.5 mg/L, whereas nitrifier denitrification dominated at DOs lower than 1.5 mg/L. Overall, in activated sludge systems the reduction of aeration rates can decrease the N_2O fluxes stripped and the control of DO has been proposed as a key measure to mitigate N_2O emissions. Additionally, the addition of an anoxic zone to avoid the concurrence of decreased DO and NO_2^- accumulation can have a positive impact on the N_2O generation.

6.2.2 Processes treating high strength (high nitrogen loading) streams

Sidestream processes, such as the partial-nitritation-anammox and nitritation-denitritation are emerging for the low-cost treatment of high-strength municipal wastewater streams (Lackner *et al.*, 2014; Zhou *et al.*, 2018). In the nitritation-denitritation process, ammonium is firstly oxidized to nitrite (nitritation) and then it is reduced to nitrogen gas (denitritation) under anoxic conditions. In the partial-nitritation-anammox process, ammonium is partially oxidized to nitrite and then ammonia and nitrite are converted to nitrogen gas and nitrate under oxygen-free conditions by anaerobic ammonium oxidizers (anammox).

N_2O monitoring studies have been performed in less than 15 sidestream processes. There is a need to improve the understanding of N_2O generation in sidestream processes. For instance, the N_2O emissions were equal to 7.6% of the NH_4-N load in a SCENA process and contributed up to 97% of the operational carbon footprint of the process (Vasilaki *et al.*, 2020). Additionally, the seasonal variation (~1 year) of N_2O emissions in sidestream reactors has not been assessed.

The average EF from full-scale nitritation and partial-nitritation reactors is equal to 4.3% of the influent N-load. One-stage granular anammox reactors have an average EF of 1.1% of the influent N-load. Zhuang *et al.* (2020) showed that in a high-rate anammox granular sludge reactor, N_2O emissions were mainly generated in anammox flocs (~10% total biomass) compared to anammox granules. They reported that the N_2O reduction in flocs was inhibited due to the accumulation of NO. Anammox bacteria concentrations were higher in granules and scavenged NO that was inhibiting the N_2O reduction. In comparison, emissions in lab and pilot-scale single-stage granular anammox reactors ranged from 0.1 to 12.19% of influent N-load (Wan *et al.*, 2019). Therefore, additional studies are required to establish reliable ranges of EFs in sidestream processes and gain insights into the mitigation of N_2O emissions. Low emissions have been also reported in moving bed biofilm reactor (MBBR) annamox technologies. Christensson *et al.* (2013) reported that ~0.75% of the N-reduced were emitted as N_2O at a full-scale deammonification MBBR. Process disturbances and a DO concentration lower than 1 mg/L can increase the N_2O emissions. The authors concluded that stable operation at DO equal to 1 mg/L can result in average daily N_2O of 0.06% of N-reduced. In pilot-scale MBBR-anammox and integrated fixed-film activated sludge (IFAS) – anammox systems Liu *et al.* (2014) reported N_2O EFs equal to 0.52% and 1.7% of the total Kjeldahl nitrogen (TKN) load, respectively.

In the sidestream reactors, the rate of aeration and the DO concentration can significantly impact both the N_2O emissions generation and the N_2O mass fluxes stripped in the atmosphere (Harris *et al.*, 2015; Rathnayake *et al.*, 2015). The influence of the aeration regime on the N_2O generation varies; this can be partially due to the different configurations. For example, Mampaey *et al.* (2016) and Stenström *et al.* (2014) reported an increase of N_2O emissions with lower DO concentrations in a PN-anammox system and a sidestream nitrification-denitrification SBR, respectively. Vasilaki *et al.* (2020) observed increased dissolved N_2O concentration peaks at DO levels lower than 1 mg/L in a SCENA SBR system. The authors reported a Spearman's correlation coefficient between dissolved N_2O concentration and DO equal to −0.7. On the other hand, Kampschreur *et al.* (2009a) could not identify a relationship between the N_2O increase and the higher aeration flowrate during a prolonged aeration experiment in a single-stage nitritation-anammox reactor. As a general remark, it is suggested to have DO concentrations higher than 1 mg/L.

In one-stage PN-anammox reactors, elevated N_2O emissions have been reported during shifts from low to high aeration and linked with high NH_4^+ concentrations and high AOR. Additionally, in nitritation-denitritation SBRs the aerobic dissolved N_2O concentration has been correlated with the decrease of the average aerobic conductivity rate (Spearman's correlation coefficient equal to 0.7) and the changes of conductivity between sequential cycles. Higher emissions have been also linked with high ammonia removal efficiencies (Vasilaki *et al.*, 2020). This means that elevated emissions are due to AOR or higher than average NO_2^- accumulation. N_2O emissions have also increased due to the stripping of the accumulated N_2O in the previous anoxic cycle (accumulated due to incomplete denitritation). In that case, step-feeding, control of initial NH_4^+ concentrations and aeration duration can mitigate the N_2O peaks.

In anammox reactors, a non-negligible generation of N_2O emissions has been reported. Kampschreur *et al.* (2008) observed an EF equal to 0.6% of the influent N-load for the anammox compartment of a full-scale two-stage PN-anammox system treating anaerobic supernatant. Given that N_2 is recognized as the end-product of the anammox process (Jetten *et al.*, 2005), the authors assumed that AOB from the nitritation compartment infiltrated the anammox reactor. Yan *et al.* (2019) observed, via laboratory experiments, that the increase of the COD/N ratio from 0 to 1 can decrease the N_2O generation by 16.7% in a CANON process coupled with denitrification. Therefore, low carbon dosage can be a mitigation strategy for the CANON process or anammox reactors infiltrated with AOB from the nitritation compartment in two-stage PN-anammox processes.

It must be noted, though, that N_2O generation depends not only on a single operational variable but also on the combined effect of several variables (temperature, NH_4^+, NO_2^-, DO, aeration rate). This is supported by Wan *et al.* (2019) who found that higher temperatures resulted in increased N_2O

emissions in the presence of COD and in decreased N_2O emissions in the absence of COD in a one-stage PN-anammox reactor. The latter was attributed to increased anammox activity and reduction of NO_2^- accumulation at higher temperature.

N_2O emissions elevated during shifts from low to high aeration. Under these operational conditions the NH_2OH pathway has been reported as a main generation mechanism (Castro-Barros *et al.*, 2015). At elevated NH_4^+ or DO in the reactor, N_2O production by nitrifier denitrification is enhanced, while NH_2OH oxidation is relatively unimportant (Harris *et al.*, 2015). Both NH_2OH oxidation and nitrifier denitrification can be the main contributors to N_2O accumulation across a range of conditions with varying concentrations of NH_4^+, O_2, and NO_2^-. Harris *et al.* (2015) concluded that when N_2O emissions are relatively low under optimal reactor operation the current understanding of N_2O production and isotopic fractionation is incomplete and needs further investigation.

6.3 CH_4 EMISSIONS FROM FULL-SCALE WWTPs

Compared with N_2O, CH_4 emissions from full-scale WWTPs is less investigated, while it contributes significantly to the overall plant carbon footprint. The results of full-scale CH_4 quantification studies are summarized in Table 6.2. Emissions of CH_4 in WWTPs mainly originate from the influent, anaerobic wastewater treatment and anaerobic sludge handling processes. CH_4 emissions thus vary greatly with different WWTP configurations. For WWTPs without anaerobic sludge handling processes, the majority of the CH_4 may be traced back to the dissolved CH_4 in the influent, which was likely formed in sewer networks. For WWTPs with anaerobic sludge handling processes, anaerobic sludge treatment and handling facilities may contribute the most to CH_4 emissions in plants. When anaerobic treatment is applied in WWTPs for wastewater COD removal, its CH_4 emissions might substantially increase the overall plant carbon footprint.

6.3.1 WWTPs without anaerobic sludge handling

In WWTPs without anaerobic sludge treatment, the largest CH_4 emission source is often the aerobic tank and headworks (especially aerated grit chamber) via the stripping of CH_4 dissolved in the influent. The biological generation of CH_4 requires strict anaerobic conditions. Due to the short residence time, and periodical exposure to oxygen and nitrate or nitrite, it is often not believed that CH_4 can be produced from the headworks or from the aerobic/anoxic wastewater treatment processes (Ribera-Guardia *et al.*, 2019). Instead, it is more likely to be generated in pressurized sewer mains (see next section). By measuring liquid and gas CH_4 concentration, mass balance analyses have been performed in some studies (Daelman *et al.*, 2013; Noyola *et al.*, 2018; Yan *et al.*, 2014), suggesting dissolved CH_4 in the influent could be the main source of CH_4 emissions in WWTPs without anaerobic sludge treatments. In two studied WWTPs in China without sludge stabilization processes, Yan *et al.* (2014) observed 80–98% of total CH_4 was emitted from the wastewater treatment line, and the remaining from headworks. With mass balance analysis, it was concluded that the majority of the CH_4 emissions originated from the CH_4 dissolved in the influent. Similar observations were reported by Daelman *et al.* (2013). In two Dutch WWTPs without anaerobic sludge digestion, 86% and 77% of the total methane emissions stemmed from the influent. Nevertheless, in some cases, CH_4 may be generated during the wastewater treatment processes. A WWTP in Japan without anaerobic sludge digestion saw its CH_4 mainly (86.4%) emitted from the aerobic tank. Considering the relatively small amount of CH_4 in the influent, the CH_4 emitted is likely formed during the wastewater treatment processes under anaerobic conditions (Masuda *et al.*, 2015). Wang *et al.* (2011) also reported CH_4 formation during the wastewater treatment processes, emitting a significant amount of CH_4.

6.3.2 WWTPs with anaerobic sludge handling

Anaerobic sludge digestion is a commonly practised technology for sludge stabilization. During anaerobic sludge digestion, biodegradable organic matters are degraded in the absence of oxygen, to

Table 6.2 A summary of CH_4 quantification results in full-scale WWTPs.

WWTP	Wastewater treatment process	Influent organic strength (mgO_2/L)	Sludge treatment process	Contribution from Headworks (%)	Contribution from secondary treatment (%)	Contribution from sludge management (%)	Emission factor (kg CH_4/kg $COD_{influent}$)	Contribution of total CH_4 emissions to the overall carbon footprint	Source
Durham WWTP, USA	Aerobic treatment	BOD: 250	Aerobic sludge digestion	36	51	13	0.16% (BOD)	Not measured	Czepiel *et al.* (1993)
Jinan WWTP, China	Anaerobic/ anoxic/ oxic (AAO) process	COD: 200	Sludge dewatering, drying	9.3	80% (40% from anaerobic tank, and 40% from aerobic tank)	9.5	0.08%	Not measured	Wang *et al.* (2011)
Papendrecht WWTP, Netherlands	Anaerobic tank followed by anoxic/ oxic carousel reactors	Not available	Sludge dewatering	50	47	3	0.87%	17%	Daelman *et al.* (2013); Daelman *et al.* (2012)
Kortenoord WWTP, Netherland	Anaerobic tank followed by anoxic/ oxic carousel reactors	Not available	Sludge dewatering	45	45	10	0.53%	13%	Daelman *et al.* (2013); Daelman *et al.* (2012)
Kralingseveer WWTP, Netherlands	Anoxic/ aerobic plug flow followed by carousel reactors with surface aerators	COD:339	Anaerobic sludge digester; digestate stored for up to 5 days	<31	Not provided	72 (50% from dewatered sludge storage and buffer tank)	0.8–1.2% (seasonal variation)	5–36%	Daelman *et al.* (2013); Daelman *et al.* (2012)
Granollers WWTP, Spain	Anoxic/oxic plug–flow reactors	COD:730	Anaerobic sludge digestion	Not provided	Not provided	Not provided	0.016%	Not measured	Rodriguez-Caballero *et al.* (2014)

(Continued)

Table 6.2 A summary of CH_4 quantification results in full-scale WWTPs. (*Continued*).

WWTP	Wastewater treatment process	Influent organic strength (mgO_2/L)	Sludge treatment process	Contribution from Headworks (%)	Contribution from secondary treatment (%)	Contribution from sludge management (%)	Emission factor (kg CH_4/kg $COD_{influent}$)	Contribution of total CH_4 emissions to the overall carbon footprint	Source
Beijing WWTP1, China	Oxidation ditch process	COD: 306–689	Sludge thickening, drying and storage	1%	98% (mainly from influent stripping)	Likely negligible	0.17–0.39%	19%	Yan *et al.* (2014)
Beijing WWTP2, China	Reversed AAO process	COD: 353–687	Sludge thickening, drying	11%	89% (mainly from influent stripping)	Likely negligible	0.10–0.19%	15.8%	Yan *et al.* (2014)
Beijing WWTP2, China	AAO process	COD: 353–687	Sludge thickening, drying	19.8%	80% (mainly from influent stripping)	Likely negligible	0.06–0.11%	6.1%	Yan *et al.* (2014)
Sendai WWTP, Japan	Pseudo Anoxic-oxic process	COD: 110	Sludge dewatering, storage	8.2	86.4	<5.4	1.0%	8.3%	Masuda *et al.* (2015)
La Roca del Vallès WWTP, Spain	SBR for COD and N removal	COD: 600	No sludge stabilization	N/A	N/A	N/A	0.02%	Not measured	Rodriguez-Caballero *et al.* (2015)
Akiu WWTP, Japan	Oxidation ditch	BOD: 130	Sludge thickening, storage		97.7 (Grit chamber + OD)	<1	1.3% (BOD)	<4%	Masuda *et al.* (2018)
Hirosegawa WWTP, Japan	Anoxic-oxic process	BOD: 210	Sludge thickening, storage	<75	23.5	Not clear	0.98% (BOD)	<5%	Masuda *et al.* (2018)
Kamiyagari WWTP, Japan	Pseudo anoxic-oxic process	BOD: 150	Sludge thickening, storage	68.1	22.6	<5.6	0.3% (BOD)	<5%	Masuda *et al.* (2018)
Girona WWTP, Spain	Modified Ludzack-Ettinger (MLE) configuration	COD: 410	Anaerobic digestion	N/A	N/A	N/A	0.28–0.49%	45–57%	Ribera-Guardia *et al.* (2019)

CH_4-rich biogas, which can be captured for energy recovery. Undesirable leaks of the generated CH_4 could contribute significantly to the plant overall carbon footprint. In WWTPs with anaerobic sludge digestion, its related CH_4 emissions could contribute the majority of the total CH_4 emissions. Daelman *et al.* (2012) found 72 ± 23% of the total CH_4 emissions originated from the anaerobic sludge handling facilities: the gravitational thickener for the primary sludge, the centrifuge, the buffer tank for the effluent of the digester, the storage tank that contains the dewatered sludge and methane leakage from the gas engines. Recent studies focusing on methane losses from 23 biogas plants, including those from WWTP facilities, found an average CH_4 emission rate of 10.4 $kgCH_4/h$ with an average loss of 4.6% of the produced CH_4 (Scheutz and Fredenslund, 2019; Tauber *et al.*, 2019). Importantly, Pan *et al.* (2016) identified that the anaerobic sludge drying lagoon could also produce a large amount of CH_4. During a long-term sludge drying process, the degradable organics are converted to CH_4 under anaerobic conditions. Without capturing the produced biogas, the CH_4 emissions from a long-term sludge drying lagoon would represent a quarter to two-thirds of the overall GHG emissions from the investigated WWTP.

6.3.3 WWTPs with anaerobic wastewater treatment technologies

While most WWTPs rely on anoxic/aerobic technologies for COD removal, anaerobic technologies (e.g., upflow anaerobic sludge blanket reactor and anaerobic lagoon) are also applied in WWTPs for COD removal. The anaerobic COD removal wastewater treatment processes often lead to substantial CH_4 emissions. During anaerobic wastewater treatment, biodegradable organics are converted to CH_4. Methane is regarded poorly soluble in water with a relatively high Henry's Law constant. It was previously believed that dissolved methane was saturated at equilibrium with the gas phase methane concentration. However, studies have found dissolved methane is often supersaturated in bulk liquid, and can be several times higher than the predicted equilibrium concentration (Hartley and Lant, 2006). The ratio of the actual dissolved methane concentration to the calculated value from Henry's Law is used to describe the extent of methane supersaturation. For anaerobic treatment systems receiving municipal wastewater, the degree of methane supersaturation measured in many studies falls in the range of 1.34 to 6.9, with a median value of 1.64 (Crone *et al.*, 2016; Hartley and Lant, 2006). Inadequate liquid-to-gas mass transfer of methane due to the lack of mixing and low liquid velocities inherent to the reactor design, results in the observed supersaturation of methane (Crone *et al.*, 2016).

The relatively high dissolved CH_4 concentration in the anaerobic treatment effluent leads to substantial release of CH_4 in downstream processes. Existing quantification studies are mostly conducted in lab-scale and pilot-scale reactors. According to the data summarized by Crone *et al.* (2016), nearly half (49%) of the total CH_4 generated during the anaerobic wastewater treatment is lost in the effluent, which is subject to release in downstream processes. The aerobic activated sludge process is reportedly able to remove 80% of the dissolved CH_4 (Daelman *et al.*, 2012). With COD removal efficiency of anaerobic treatment technologies in the range of 55–80%, the dissolved CH_4 in the anaerobic treatment effluent could lead to CH_4 emissions of about 1.4–2% of the influent COD ($kgCH_4/kgCOD_{influent}$). In comparison, for WWTPs without anaerobic wastewater treatment, the total CH_4 emissions account for 0.02–1.2% of the influent COD (Table 6.2). The anaerobic wastewater treatment process could produce CH_4 emissions higher than an entire WWTP implementing anoxic/aerobic wastewater treatment processes. The CH_4 emissions resulting from the anaerobic wastewater treatment process is still one of the major obstacles for its wide application.

It is clear that CH_4 emissions represent a significant portion of the overall carbon footprint in WWTPs while rarely being the dominant one. The contribution of CH_4 emissions varied mostly from 4% to 19% of the overall carbon footprint (Table 6.2). In cases when N_2O emissions are particularly low, the CH_4 emissions could be the dominant source (45–57%) of overall GHG emissions, as reported by Ribera-Guardia *et al.* (2019). Overall, CH_4 emissions from WWTPs should be monitored, especially in facilities where anaerobic treatment is implemented.

6.4 GHG EMISSIONS FROM SEWER NETWORKS

6.4.1 Reported CH_4 emissions from sewer networks

Anaerobic conditions in sewer pipes together with the high biodegradable COD concentration in the sewage favour the accumulation of methane as the end-product of the methanogenic archaea present in the sewer networks. There are not many studies focusing on the quantification of the overall CH_4 emissions from full-scale sewer systems, probably due to the complexity of the monitoring and the limited accessibility of some parts of the network. To date, overall methane emission data is only available for single pipe rising main and gravity sewers, calculated through the dissolved methane concentration data and following the methods explained in Chapter 4.

The overall methane emission potential of the monitored rising main sewers varies substantially, ranging from 0.04 to 0.32 kg CO_2-equivalent/m^3 with an average value of 0.18 kg CO_2-equivalent/m^3 of wastewater transported. Table 6.3 summarizes the studies reporting CH_4 emissions from sewer networks in the literature.

The majority of the methane formed in rising mains will be eventually stripped to the atmosphere via ventilation in gravity sewers or at WWTPs during the treatment of wastewater, mainly because methane oxidation in sewers is expected to be a slow process (Valentine & Reeburgh, 2000). Therefore, rising main data can be used to calculate potential overall emission rates from sewer systems.

In some other studies, the quantification of overall CH_4 emissions has been carried out by direct measurement of methane emission rate from a discharge manhole (Shah *et al.*, 2011). However, this methodology is expected to underestimate emissions as CH_4 could also be emitted at other locations in the network.

6.4.2 Reported N_2O emissions from sewer networks

Studies providing N_2O emission data from sewer networks are sparse, with very few studies published to date. In 2014, Short *et al.* reported the dissolved N_2O concentrations from the inlet of three WWTPs in Australia during an 8 month monitoring campaign. They found that average levels in the raw wastewater were relatively consistent among the three WWTPs monitored at around 7–10 μg N-N_2O/L. Combining these results with wastewater parameters they were able to calculate presumptive per capita N_2O emission factors, resulting in 1.39–1.84 g N_2O/person year and 0.009–0.02 kg N-N_2O/kg TN.

Another study conducted in the sewer network of the Cincinnati municipality (Fries *et al.*, 2018) reported that its wastewater collection system was a non-point source of N_2O. Based on their results, they estimated approximately an average rate of 151.2 ± 326 g N_2O/d for the whole city.

As the authors from both studies mentioned, all these numbers should be taken with caution as further investigations are needed to better understand the magnitude of sewer N_2O emissions.

6.5 MITIGATION STRATEGIES APPLIED IN FULL-SCALE SYSTEMS

6.5.1 GHG mitigation in WWTPs

There is no standardized methodology for the establishment of N_2O mitigation strategies in full-scale systems. Table 6.1 summarizes the main mitigation strategies that have been proposed or tested in full-scale wastewater treatment processes.

Testing different operational modes is regarded as one of the most effective ways to identify measures for emission mitigation. Several studies have modified the aeration intensity and/or strategy, and optimized the DO set-point and cycle duration to investigate the effect on N_2O emissions in full-scale BNR processes (Castro-Barros *et al.*, 2015; Duan *et al.*, 2020; Kampschreur *et al.*, 2009a, 2009b; Mampaey *et al.*, 2016; Rodriguez-Caballero *et al.*, 2015). For instance, Mampaey *et al.* (2016) achieved a reduction in the N_2O emissions of 56% when the cycles in a one-stage granular SHARON reactor were shortened by 1 h. Rodriguez-Caballero *et al.* (2015) tested different operational conditions in a full-scale SBR. They suggested an optimum control strategy for the minimization of N_2O

Table 6.3 Dissolved methane concentrations and methane emission in rising mains (adapted from Liu *et al.* 2015b).

Country	Name	Type	Length (m)	Diameter (mm)	A/V (m^{-1})	HRT (h) average (min–max)	WWT (°C)	Dissolved CH_4 (mg/L) average (min–max)	Daily flow (m^3/day)	Production ($kgCH_4$/day)	Overall emissions ($kgCO_2eq/m^3$)	References
Australia	UC09	Rising main	828	150	26.7	2.5 (3.1–4.6)	27.7	5.3 (4.4–6.1)	200	1.1	0.11	Foley *et al.* (2011)
Australia	C16	Rising main	1100	300	13.3	2.6 (3.9–11.0)	22.5	15.3 (11.3–3.0)	707	9.8	0.32	Foley *et al.* (2011)
Australia	C16	Rising main	1100	300	13.3	2.6 (3.9–11.0)	23.5	5.2 (3.4–6.6)	707	2.6	0.11	Foley *et al.* (2009)
Australia	C27	Rising main	4400	525	7.6	9.1	24.6	9.1 (5.0–15.0)	2840	24.6	0.19	Liu *et al.* (2015b)
Australia	C27	Rising main	4400	525	7.6	9.1	20.3	7.1 (3.5–12.0)	2840	19.0	0.15	Liu *et al.* (2015b)
Australia	PerthB	Rising main	15 000	900	4.4	–	–	4.8	11 000	52.8	0.10	Liu *et al.* (2015b)
Thailand	RV	Gravity	1000	1000	–	27.9 (22–31.4)	33.3	10.1 (8.0–13.7)	–	–	–	Chaosakul *et al.* (2014)
Thailand	RV	Gravity	1000	1000		7.8 (0–12)	30.2	4.6 (0.1–11.4)	–	–	–	Chaosakul *et al.* (2014)
Australia	CO16 PS	Pumping station	–	–	–	–	23.5	1.5 (1.0–1.92)	707	–	–	Foley *et al.* (2009)
Australia	OR3 PS	Pumping station	–	–	–	–	–	0.51	2000	–	–	Liu *et al.* (2015b)
Spain	Radin	Rising main	2930	500	8.0	4.7 (2.9–6.8)	16.0	1.95 (1.3–2.7)	4210	8.2	0.04	Personal communication
Spain	Collet	Rising main	4800	556	3.6	12.4 (7.3–15.5)	25.4	3.0 (1.9–4.01)	2700	8.1	0.06	Personal communication

emissions based on the application of short aerobic-anoxic cycles (20-min aerobic phase and short duration of anoxic stage).

Activated sludge models have been also applied to identify potential N_2O mitigation strategies in BNR systems. Ni *et al.* (2015) developed a mechanistic model utilizing the data from a two-step plug-flow reactor (Pan *et al.*, 2016) showing that the biomass specific N-loading rate is linked with the elevated N_2O emissions observed in the second step of the process. Different operational conditions were tested with the model demonstrating that lower N_2O emissions (<1% of the N-load) can be achieved if 30% of the total return activated sludge (RAS) stream is recirculated to the second step of the plug-flow reactor (Table 6.1). However, it is unknown whether the suggested mitigation strategy was demonstrated in the system. Similarly, Zaborowska *et al.* (2019) used multiple-pathway activated sludge modelling to investigate N_2O mitigation strategies in an A^2/O reactor. They showed that DO concentrations between 1 and 2 mg/L and mixed liquor recirculation rates above 500% could minimize N_2O emissions and energy consumption during aeration without compromising TN removal in the studied A^2/O reactor. Duan *et al.* (2020) used a multiple-pathway model to test different N_2O mitigation strategies in an SBR reactor. Based on the simulation results, they modified the aeration control of the system. They showed that SND operation mode can result in 35% reduction of the N_2O emissions compared to intermittent over-aeration.

Overall, the main techniques for mitigating the N_2O emissions in wastewater treatment processes target (i) the reduction of the diurnal variation of NH_4^+ loads and avoidance of NH_4^+ peaks and NH_4^+ and NO_2^- build-up (i.e. integration of equalization tanks, recycling steps, optimization of anaerobic supernatant feeding), (ii) the increase of the MLVSS concentration to lower the specific N-loading (i.e. optimization of the RAS or SRT increase), (iii) the facilitation of complete reactions by providing sufficient electron donors (COD) during denitrification (i.e. supply of additional carbon source to ensure complete denitrification) and electron acceptors (O_2) during nitrification, and (iv) the facilitation of N_2O consumption during denitrification (i.e. increasing anoxic duration, lowering DO to enhance SND).

Reports on mitigation of methane from WWTPs are very scarce. Some technologies have been proposed for the removal of dissolved methane from anaerobic effluents, one for the most effective being the application of a degassing membrane (Bandara *et al.*, 2011). However, their application is very limited and no studies for their application in full-scale WWTPs have been found.

Sludge storage also contributes significantly to the fugitive methane emissions from WWTPs as digested sludge has a significant residual methane potential (Daelman *et al.*, 2012). The authors proposed the use of the ventilation air from the buffer tank as combustion air in the gas engines of the cogeneration plant, receiving the biogas produced in the digesters. This would result in less diluted methane streams going to the cogeneration plant, but this should be adapted to handle methane concentrations that exceed the lower explosive limit of methane in air.

Finally, it is important to highlight the need for good housekeeping and regular maintenance of the anaerobic digestion facilities present in WWTPs for sludge digestion, to avoid fugitive CH_4 emissions from these reactors.

6.5.2 GHG mitigation from sewers

CH_4 is the main GHG emitted from sewers and it is usually biogenically formed together with hydrogen sulfide under anaerobic conditions (Chapter 5). The wastewater industry uses several chemical-dosing approaches to mitigate sulfide emissions including the addition of nitrate, oxygen, ferric salts, hydroxide (pH elevation) and free nitrous acid (FNA) (Zhang *et al.*, 2008). But those can also suppress CH_4 formation from sewers because the methanogens are slow growers and are very sensitive to environmental conditions as compared with sulfate reducing bacteria (SRB) (Guisasola *et al.*, 2008). Also, in contrast to SRB, methanogens usually inhabit the deeper zone of sewer biofilms or sediments and are usually protected due to limited penetration of the dosed chemical. Thus, for effective control of methanogens, a higher dosage of chemicals may be needed to achieve full penetration during the

Table 6.4 Summary of the CH_4 mitigation studies conducted in full-scale sewer networks.

Chemical	Dosing levels	Dosing plan	CH_4 reduction (%)	CH_4 production recovery	Reference
Nitrate	17 kg N-NO_3^-/ML	One shock	13	100% in 2 days	Shah *et al.* (2011)
Nitrate	50 kg N-NO_3^-/ML	One shock	27	100% in 2 days	Shah *et al.* (2011)
Hydroxide	pH 11.5	Shock for 6 h	97	3% in 15 days	Gutierrez *et al.* (2014)

initial dosing period, when overall bacterial activity is high. However, continuous dosing, as required for sulfide control with most chemicals, may not be necessary. Table 6.4 summarizes the mitigation studies conducted in full-scale sewer networks.

Today, the current practice of selecting chemicals and design of dosing locations/rates is still mainly based on an individual's experience (Ganigue *et al.*, 2011; Liu *et al.*, 2015a). Constant, flow-paced and profiled dosing rates are currently applied during chemical dosing, again based on experience. Instead, the approach should be based on specific features of the sewer in question. In this respect, the SeweX model (Sharma *et al.*, 2008) consists of an empowering tool in supporting decision-making. Concentrations of methane, sulfide and flows show significant temporal and spatial dynamics in sewers. The rudimentary current methods could be ineffective in methane control, resulting in over-dosing of chemicals during periods with low methane and sulfide production, and conversely underdosing during other periods.

6.6 CONCLUDING REMARKS

Currently, operational strategies at WWTPs do not consider the mitigation of GHG emissions. New objectives, New objectives, including environmental and carbon neutrality targets, in the water industry require approaches to dynamically integrate new parameters (i.e. GHG emissions sensors, energy meters) into the process monitoring, control and decision-making.

Process-based N_2O EF benchmarking is challenging due to (i) differences in the N_2O generation triggered by the site-specific operational characteristics, environmental conditions and control parameters, and (ii) the sensitivity of the quantified EF to differences in monitoring strategies and duration of monitoring campaigns. The quantification of reliable annual EFs requires sampling campaigns lasting at least 1 year. Additional campaigns are required for specific groups of processes (i.e., processes treating high strength streams, biofilm technologies) that have received less attention until now.

Guidelines for N_2O mitigation measures for different process groups have been developed. Further research is required to develop practical approaches to help utilities to quantify, understand and report the N_2O EF and develop dynamically evolving mitigation measures based on the operational conditions. Future research can explore the possibility of coupling artificial intelligence (AI) techniques with multiple-pathway process models for full-scale applications, to facilitate the fast and adaptable online implementation of model predictive control and forecasting decision support tools.

GHG monitoring campaigns carried out in WWTPs should include the monitoring of fugitive CH_4 emissions, which contribute significantly to the overall plant carbon footprint. CH_4 emissions mainly originate from the influent, anaerobic sludge handling processes and anaerobic wastewater treatment in WWTPs. For WWTPs without anaerobic sludge handling processes, the CH_4 emissions can mainly be traced back to the CH_4 dissolved in the influent. The implementation of anaerobic sludge handling processes may contribute the most to CH_4 emissions in WWTPs. When anaerobic treatment is applied in WWTPs for wastewater COD removal, its CH_4 emissions might substantially increase the overall plant carbon footprint.

Finally, more attention should be paid to fugitive GHG emissions from sewer networks. Several studies suggest CH_4 emissions could be important in some parts of the sewer networks, with most of the

monitoring campaigns being conducted in pressurized sewer mains. However, very little information is reported for full-scale gravity sewers and very scarce data is available for N_2O emissions from sewer networks.

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NOMENCLATURE

A/O	Anoxic/aerobic
A^2/O	Anaerobic/anoxic/aerobic
AMO	Ammonia monooxygenase
Anammox	Anaerobic ammonium oxidation
AOA	Ammonia oxidizing archaea
AOB	Ammonia oxidizing bacteria
AOR	Ammonia oxidation rate
BNR	Biological nutrient removal
CANON	Completely autotrophic nitrogen removal over nitrite
CAS	Conventional activated sludge
CO_2	Carbon dioxide
COD	Chemical oxygen demand
Comammox	Complete ammonium oxidizer
CuO	Copper oxide
dGAO	Denitrifying glycogen accumulating organisms
DO	Dissolved oxygen
dPAO	Denitrifying polyphosphate accumulating organism
EF	Emission factor
FA	Free ammonia
FNA (HNO_2)	Free nitrous acid
GHG	Greenhouse gas
H_2S	Hydrogen sulphide
HRT	Hydraulic retention time
MLE	Modified Ludzack-Ettinger
MLVSS	Mixed liquor volatile suspended solids
N_2	Nitrogen gas
N_2O	Nitrous oxide

N_2O_4	Nitrogen tetroxide
NaR	Nitrate reductase
NH_2OH	Hydroxylamine
NH_3	Ammonia
NH_4^+	Ammonium
NiR	Nitrite reductase
NO	Nitric oxide
NO_2^-	Nitrite
NO_3^-	Nitrate
NOB	Nitrite oxidizing bacteria
NOH	Nitrosyl radical
NoR	Nitric oxide reductase
NoS	Nitrous oxide reductase
OD	Oxidation ditch
PN	Partial nitrification
RT-qPCR	Real time quantitative polymerase chain reaction
SBR	Sequencing batch reactor
SCENA	Short cut enhanced nutrient abatement
SP	Site-preference
WWTPs	Wastewater treatment plants