Chapter 8

Greenhouse gas emissions from membrane bioreactors

G. Mannina[2], M. Capodici[1], A. Cosenza[1], D. Di Trapani[1] and M. C. M. van Loosdrecht[3]

[1]Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali, Università di Palermo, Viale delle Scienze, Ed. 8, 90128, Palermo, Italy

[2]Department of Earth and Environmental Engineering, Columbia University, 500 West 120th Street, New York, NY 10027, USA

[3]Department of Biotechnology, Delft University of Technology, Julianalaan 67, 2628 BC, Delft, Netherlands
E-mail corresponding author: giorgio.mannina@unipa.it

ABSTRACT

Nowadays, it is widely accepted that wastewater treatment plants (WWTPs) are significantly contributing to anthropogenic sources of greenhouse gas (GHG) emission. Among the GHGs emitted from WWTPs, nitrous oxide (N_2O) has been identified as the potentially major component, due to its high global warming potential (GWP) which is 298 times higher than that of carbon dioxide (CO_2) and also to its capability to react with stratospheric ozone, causing ozone layer depletion. Up until now, most of the experimental investigations aimed at assessing the key mechanisms of N_2O formation and the operational conditions that can enhance its emission, have been carried out on conventional activated sludge (CAS) processes, while the knowledge of N_2O emission from advanced technologies such as membrane bioreactors (MBRs) is still very limited. Moreover, the specific peculiarities of MBRs might hamper the direct transferability of data measured

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on CAS systems. Therefore, there is a need to increase the knowledge about N_2O emission from MBRs through experimental and mathematical modelling activities. The present chapter aims to provide some knowledge about GHG emissions from MBR systems, in particular regarding N_2O emissions, by reporting some experimental data carried out on pilot plant systems of different configurations. The effect of specific wastewater features and operational conditions on N_2O production/emission from MBRs are highlighted.

Keywords: Global warming, membrane filtration, nitrous oxide, wastewater treatment

8.1 INTRODUCTION

During the last decade the awareness of the fact that wastewater treatment plants (WWTPs) are responsible for greenhouse gas (GHG) emissions has increased considerably. This is evident from the large number of research papers published on the topic (among others, Kampschreur *et al.,* 2009; Foley *et al.,* 2010; Daelman *et al.,* 2012; Ni *et al.,* 2013; Kim *et al.,* 2015; Mannina *et al.,* 2016a, 2017a, 2018a,b).

The evaluations by the Intergovernmental Panel on Climate Change (IPCC), aimed at identifying the causes, impacts and possible response strategies for mitigating climate change, indicate that the waste and wastewater sector accounts for about 3% of the global GHG emissions (Forster *et al*., 2007; IPCC Climate Change, 2013). According to the United States Environmental Protection Agency (2013) water and wastewater facilities are amongst the largest energy consumers, thus significantly contributing to the overall GHG emissions, due to pumps, motors and equipment operating 24 hours a day and seven days a week. It is widely accepted in literature that WWTPs emit GHGs through three main sources, i.e., direct, indirect internal and indirect external (Global Water Research Coalition [GWRC], 2011). Direct GHG emissions are due to the biological processes occurring inside the WWTPs and represent the catabolite or obligate intermediates of reactions (CO_2, from microbial respiration; nitrous oxide, N_2O, from nitrogen removal processes, or methane (CH_4) from anaerobic processes). Indirect GHG internal emissions are mainly due to the consumption of electrical or thermal energy. Finally, indirect GHG external emissions are mainly related to sources not directly controlled within the WWTP (e.g., third-party biosolids hauling, production of chemicals and their transportation to the plant, etc.) (Mannina *et al.,* 2016e). Zeng *et al.* (2017) investigating 1079 urban WWTPs across China, have found that indirect GHG emissions could decrease by 32.2% if all plants worked efficiently.

The acquired awareness of "WWTP as source of GHG" has contributed to broaden the traditional operational goal of WWTPs to the minimization of GHG. Indeed, the traditional aim of WWTPs to achieve very stringent effluent limits now includes the GHG in terms of reduction of direct and indirect emissions (Flores-Alsina *et al.,* 2011a). In this regard, during recent years several efforts have

been made in order to identify the key issues surrounding the GHG emissions from WWTPs: (i) processes responsible for GHG emissions (Foley *et al.,* 2010; Daelman *et al.,* 2012); (ii) operating factors mainly affecting the GHG emissions (Kampschreur *et al.,* 2009); and (iii) strategies for predicting and reducing GHG emissions (Flores-Alsina *et al.,* 2011b; Corominas *et al.,* 2012; Kim *et al.,* 2015). Several research projects (i.e., SANITAS and ENERWATER, PRIN2012GHG) and a Task Group of the International Water Association have also been developed and promoted in order to better understand the key mechanisms of GHG emissions from WWTPs.

Among the GHGs emitted from WWTPs, N_2O has been identified as the one of greatest interest. The amount of N_2O emitted from WWTPs is considerably lower than that of CO_2 or CH_4. However, due to the high global warming potential (GWP) of N_2O, 298 times higher than that of CO_2, and its capability to react with stratospheric ozone it is required to be investigated (IPCC, 2007). Several studies have been performed with the aim of better understanding the core pathways of its formation (Kampschreur *et al.,* 2009; Law *et al.,* 2013; Ni *et al.,* 2013).

N_2O is mainly produced in the biological nitrogen removal (BNR) processes via nitrification and denitrification both from autotrophic and heterotrophic bacteria (Kampschreur *et al.,* 2009). In some cases, N_2O emissions have been found to contribute to over 80% of the total greenhouse gas footprint emitted from WWTPs (Daelman *et al.,* 2013a,b). Despite the knowledge on GHG emission from WWTPs being quite mature mainly regarding CO_2 and CH_4, for N_2O literature still reveals a huge variability in the N_2O measured data ranging between 0.01–1.8% (N_2O emitted relative to wastewater N-load) (Kampschreur *et al.,* 2009; Ahn *et al.,* 2010; Aboobakar *et al.,* 2013; Ye *et al.,* 2014; Rodriguez-Caballero *et al.,* 2015; Daelman *et al.,* 2015). Literature also shows several difficulties in measuring the real overall N_2O produced by WWTPs; the available literature data case studies are often specific and difficult to transfer to other systems (Marques *et al.,* 2016). This aspect is relevant because most of the studies reported in literature are related to conventional activated sludge (CAS) systems and the knowledge acquired may not be transferred into innovative systems such as membrane bioreactors (MBRs).

MBR systems have attracted increasing attention in recent years, due to several advantages compared with conventional processes (Judd & Judd, 2010). More specifically, MBR systems provide high effluent quality, small footprint and moderate sludge production rates compared to CAS systems (Stephenson *et al.,* 2000). However, MBRs are characterized by some specific peculiarities – biomass selection; absence of secondary clarifier – that can contribute to N_2O production. Moreover, the intensive aeration for fouling mitigation in membrane compartments can promote N_2O stripping. These issues may hamper a direct transferability of the results derived for CAS systems. The main goal of this chapter is to summarize the key operating factors influencing the GHG production/emission from MBR WWTPs. Since the acquired knowledge on CO_2 and CH_4 formation is well developed, attention is primarily focused on N_2O emission here.

8.2 GHG EMISSION MECHANISMS

8.2.1 Direct emissions

8.2.1.1 Carbon dioxide – CO_2

CO_2 is directly produced due to aerobic and anaerobic biological processes. During the aerobic biological processes, the cell growth leads to the oxidation of organic compounds into CO_2. During the anaerobic biological processes, the organic matter is transformed into biogas composed of CO_2 and CH_4. The amount of the fossil CO_2 emissions from WWTPs can vary with the inlet wastewater composition and the plant configuration (Law *et al.,* 2013).

8.2.1.2 Methane – CH_4

CH_4 has a GWP of 34 over a 100-year period (IPCC, 2013). It is mainly produced during the decomposition of a wide range of organic matter in anaerobic conditions. A large fraction of the volatile matter contained in the sludge entering the anaerobic digester is converted into CH_4 (around 60–70% for primary sludge). The process of anaerobic digestion consists of four main sequential steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Appels *et al.,* 2008).

Specifically, during the first hydrolysis step, both insoluble organic material and high molecular weight compounds such as lipids, polysaccharides, proteins and nucleic acids, are converted into soluble organic substances (e.g., amino acids and fatty acids). The products of the hydrolysis are further degraded during acidogenesis (second step). During the third step (acetogenesis), the organic acids and alcohols produced by acidogenesis are further digested to produce acetic acid as well as CO_2 and H_2. Finally, in the fourth step (methanogenesis) CH_4 is produced.

WWTPs, where anaerobic processes are implemented, are often a source of CH_4 (California Energy Commission [CEC], 2006; https://www.ncbi.nlm.nih.gov/pubmed/22575155). CH_4, produced during the anaerobic decomposition of organic substrate (activated by methanogenic bacteria), can be released to the atmosphere through the surface of open tanks (Mannina *et al.,* 2016b), or during storage and handling of the digested sludge. This methane emission can easily off-set the reduced fossil CO_2 emission associated with biogas energy production (https://www.ncbi.nlm.nih.gov/pubmed/22575155). Biogas, containing 55–65% of CH_4, can be used as an energy source and hence reduce the energy footprint (and consequently the GHG emissions) of the WWTP. Large amounts of CH_4 can be also produced due to the disposal of untreated sewage sludge to landfill (Czepiel *et al.,* 1993).

8.2.1.3 Nitrous oxide – N_2O

N_2O emissions from WWTPs are mainly related to the BNR processes (Kampschreur *et al.,* 2009; Law *et al.,* 2013), but also to processes that nitrify despite not being

designed as nitrification processes. In Figure 8.1 the key pathways related to the N_2O formation during nitrification and denitrification are summarized.

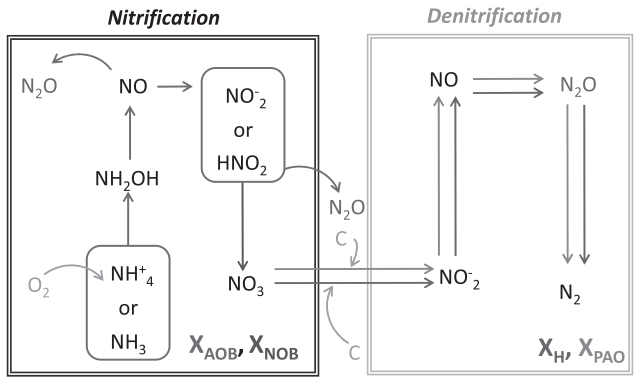

Figure 8.1 N_2O formation pathways during nitrification and denitrification process (X_{AOB} = ammonia oxidizing bacteria; X_{NOB} = nitrite oxidizing bacteria; X_H = heterotrophic bacteria) (Mannina *et al.* 2018c).

The nitrification process is divided into two main steps. In the first step, autotrophic ammonia oxidizing bacteria (X_{AOB}) aerobically oxidize NH_3 or NH_4^+ into NO_2^-. In the second step, autotrophic nitrite oxidizing bacteria (X_{NOB}) aerobically oxidize NO_2^- into NO_3^-. Denitrification leads to the reduction of NO_3^- into N_2 by means of heterotrophic bacteria growth (X_H).

N_2O is produced during the biological nitrogen removal processes due to both X_{AOB} and X_H (Kampschreur *et al.,* 2009; Ni & Yuan, 2015). X_{AOB} can produce N_2O as a product of the hydroxylamine oxidation (NH_2OH), identified as one of the major pathways, or nitrite (NO_2) reduction (X_{AOB} denitrification) (Ni *et al.,* 2013). Heterotrophic biomass produces N_2O as an obligate intermediate during nitrate (NO_3) reduction (Law *et al.,* 2013).

8.2.1.4 Liquid/gas mass transfer

The GHG emissions from WWTPs depend on the gas solubility and on operating and external factors influencing the GHG emission (e.g., stripping effect due to aeration or stirring).

Among the GHG emitted from a WWTP, CO_2 and N_2O are easily soluble in water; at 25°C and 0% salinity, the Henry's law constants of CO_2 and N_2O are 34 and 24 mM atm^{-1}, respectively (Weiss & Price, 1980). The Henry's law constants of CO_2 and N_2O are quite high compared with that of O_2 (1.3 mM atm^{-1}, at 25°C and 0% salinity). Therefore, an accumulation of CO_2 and N_2O in the liquid phase can occur, especially in the absence of external factors (e.g., non aerated tanks).

CH_4 has the same Henry's law constant as O_2, consequently the CH_4 produced inside the WWTP is mostly emitted into the atmosphere.

The main external factors influencing the GHG emission are: (i) temperature of the liquid phase, (ii) aeration, and (iii) stirrer effect. In particular, the temperature influences the coefficients of Henry's law, and the aeration and/or stirrer power promotes the stripping of GHG. Indeed, Ahn *et al.* (2010) have found that N_2O emissions are two to three orders of magnitude higher in aerated zones than in non-aerated ones.

8.2.2 Indirect emissions

8.2.2.1 Energy consumption

CO_2 emissions due to the energy consumption of WWTPs (internal indirect emission) represent important sources of GHG emissions from WWTPs. Pumps, motors, aeration and other equipment, operating 24 hours a day, seven days a week, make the water sector (which includes WWTPs) a large consumer of energy in a community (5–10 W/person) and potentially a large contributor to the community's total GHG emissions (US Environmental Protection Agency, 2013).

The energy (E_l) required for the mechanical devices such as pumps, motors, and aerators can be evaluated by using Equation 8.1 (Singh & Kansal, 2018).

$$E_l = \sum_{i=0}^{n} \frac{P_i \cdot T_i}{Q} \quad \left[\text{kWh m}^{-3}\right] \tag{8.1}$$

Where: P_i is the rated power of ith electrical equipment [kW]; T_i is the duration of daily operation of the ith electrical equipment [h d^{-1}]; and Q is the daily average sewage inflow to the WWTP [m^3 d^{-1}].

Energy for transporting sludge (E_d) can be evaluated by using Equation 8.2 (Singh & Kansal, 2018).

$$E_d = \frac{\sum_{i=0}^{n}\left(\frac{D_i}{E_i}\right) \cdot CF}{Q} \quad \left[\text{kWh m}^{-3}\right] \tag{8.2}$$

Where: D_i is the total distance travelled daily by ith vehicle [km/day]; E_i is the fuel efficiency of the ith vehicle [km L^{-1}]; and CF is the energy conversion factor for diesel to electricity (15.64 kWh L^{-1}).

The energy consumption due to the chemicals usage (E_{ch}) can be evaluated by using Equation 8.3.

$$E_{ch} = \frac{\left(\sum_{i=0}^{n} W_i \cdot E_{ci}\right)}{Q} \quad \left[\text{kWh m}^{-3}\right] \tag{8.3}$$

Where: E_{ci} is the unit energy consumption values of the *i*th chemical [kWh kg^{-1}]; and W_i is the consumption of the *i*th chemical [kg d^{-1}].

CO_2 emission per unit energy produced is of course related to the type of fossil fuel used and to the energy mix between renewable and non-renewable energy sources. Literature data suggest that the emission factor for the energy usage can vary between 0.45 $kgCO_2$ kWh^{-1} to 1.06 $kgCO_2$ kWh^{-1} (Central Electricity Authority [CEA], 2013).

8.2.2.2 Chemicals usage

Chemicals used during the operation of the WWTPs embody energy which leads to the CO_2 emission (Singh & Kansal, 2018). Thus, knowing the amount of chemicals used during the plant operation, it is possible to evaluate the CO_2 emission due to their usage on the basis of the emission factor. For example, the emission factors due to the used polymer and disinfectant are 13.54 and 1.124 $kgCO_2\,kg^{-1}$, respectively (Haas, 2009; Zhang *et al.,* 2010; Singh & Kansal, 2018). Therefore, the total GHG emissions due to chemicals (G_{ch}) can be evaluated by using Equation 8.4.

$$G_{ch} = \frac{\left(\sum_{i=0}^{n} W_i \cdot EF_i\right)}{Q} \qquad \left[\mathrm{kgCO_{2eq}m^{-3}}\right] \tag{8.4}$$

Where: EF_i is the emission factor of the *i*th chemical [$kgCO_2\,kg^{-1}$].

8.3 GHG FROM MBR: LITERATURE OVERVIEW

As mentioned above, the issue related to GHG emission from WWTPs has emerged significantly in recent years. Table 8.1 reports some literature data, in terms of N_2O emission, from activated sludge and biofilm systems.

From the observation of Table 8.1, it is possible to notice the huge variability of the N_2O emission factors (expressed as percentage of the influent N loading rate), depending on operational conditions as well as plant configuration.

Concerning the GHG emissions from MBRs specifically, limited information has been reported in literature so far. MBRs are characterized by specific peculiarities (biomass selection independent of settling properties, lack of final settling tank, intensive aeration for fouling mitigation, etc.) that can contribute to GHG production/emission (referring in particular to N_2O). Thus results achieved for conventional activated sludge systems should not be directly transferred to MBR systems. Table 8.2 reports a summary of some results achieved for MBR systems in terms of N_2O emission.

Table 8.1 N_2O emission factor (as % of influent load) in different WWTP configurations.

Reference	N_2O Emission (% of N-Loading)	Type of WWTP	Configuration	Remarks
Zheng *et al.* (1994)	2.3–16%	Nitrifying activated sludge	Lab-scale plant fed with artificial wastewater	N_2O emission increased with decreasing oxygen concentration and SRT
Czepiel *et al.* (1995)	0.04%	Activated sludge	Full-scale plant (11,000 pe)	
Wicht and Beier (1995)	0–14.6% (average: 0.6%)	Activated sludge	25 full-scale plants	N_2O increased with increasing nitrogen load
Sümer *et al.* (1995)	0.00%	Activated sludge	Full-scale plant (60,0000 pe)	N_2O emission increased with nitrite + nitrate concentrations
Osada *et al.* (1995)	1–35%	Oxic-Anoxic SBR	Lab-scale plant fed with real high strength wastewater	N_2O emission higher with longer aeration period in one SBR cycle, probably related to increased nitrite levels
Kimochi *et al.* (1998)	0.01–0.08%	Activated sludge	Full-scale plant (1000 pe)	N_2O emission decreased with proportionally shorter aeration periods
Park *et al.* (2000)	0.2–4.5%	Nitrifying and denitrifying activated sludge	Lab-scale plant fed with real wastewater	N_2O emission decreased after methanol addition
Park *et al.* (2000)	0.2–3%	Aerated biofilm filter	Lab-scale	N_2O emissions increased without substrate addition
Itokawa *et al.* (2001)	0.5– > 20%	Oxic-anoxic SBR activated sludge	Lab-scale plant fed with artificial high strength wastewater	N_2O emission increased with C/N decrease

Zeng *et al.* (2003)	90%	Anaerobic-anoxic SBR activated sludge	Lab-scale plant fed with artificial wastewater	N_2O emission increased with increased nitrite concentration – N_2O might be major product of denitrification by GAO
Rezić *et al.* (2007)	3–25%	Rotating tube	Lab-scale	Inverse relationship of N_2O emissions to RPM
Kampschreur *et al.* (2008)	4%	Nitrification stage of activated sludge plant	Full-scale plant (620,000 pe)	
Ahn *et al.* (2010)	0.01–3.3%	Several plant configurations: separate-stage BNR, four-stage Bardenpho, step-feed BNR, step-feed non-BNR, plug-flow, oxidation ditch	Full-scale plants	High nitrite, ammonium, and dissolved oxygen concentrations positively correlated with N_2O emissions from aerobic zones. High nitrite and dissolved oxygen concentrations positively correlated with N_2O emissions from anoxic zones.
Aboobakar *et al.* (2013)	0.01–0.036%	Plug-flow nitrifying activated sludge process	Full-scale plant (210,000 pe)	Emissions were shown to be negatively correlated to dissolved oxygen
Lochmatter *et al.* (2013)	1–9%	Granular sludge	Lab-scale plant fed with synthetic wastewater	Inverse relationship between COD load and N_2O emissions
Kong *et al.* (2013)	2.70%	SBBR	Lab-scale plant fed with synthetic ammonium-rich wastewater	N_2O emissions likely related to intermittently aerated partial nitrification

(*Continued*)

Table 8.1 N_2O emission factor (as % of influent load) in different WWTP configurations. (*Continued*)

Reference	N_2O Emission (% of N-Loading)	Type of WWTP	Configuration	Remarks
Eldyasti *et al.* (2014)	0.6–1.9%	Fluidized bed reactor	Lab-scale plant	N_2O emissions increased with the C/N decrease
Daelman *et al.* (2015)	2.8–11%	Plug flow reactor in series with two parallel Carrousel reactors	Full-scale plant	Seasonal peaks in the nitrite concentration correlated with the N_2O emission. The diurnal variability of N_2O emission depends on the trend of the nitrite and nitrate concentrations in the tank.
Ma *et al.* (2015)	0.5–1.5%	MBBR nitritation-anammox bioreactor	Lab-scale plant	N_2O emissions increased with the increase of inorganic carbon limitation
Todt and Dörsch (2015)	0.7–8.5%	MBBR	Lab-scale plant	N_2O peaks coincided with NO_2 accumulation peaks
Baresel *et al.* (2016)	0.3–0.4%	Activated Sludge Process in the UCT-configuration	Full-scale plant	Measurements of dissolved N_2O required low maintenance and N_2O emission monitoring based on such measurements might therefore be considered as a significant practical improvement
Pan *et al.* (2016)	0.68–3.5%	Step-fed, plug-flow activated sludge reactors	Full-scale plant	The step-feed configuration had a substantial influence on the N_2O emissions

Note: SRT = solids retention time; SBR = sequencing batch reactor; GAO = glycogen-accumulating organisms; COD = chemical oxygen demand; pe = population equivalent; SBBR = sequencing batch biofilm reactor; MBBR = moving bed biofilm reactor; UCT = University of Cape Town

Table 8.2 N_2O emission factor (as percentage of influent load) from MBRs.

Reference	N_2O emission (% of N-loading)	Type of WWTP	Configuration	Remarks
Nuansawan *et al.* (2016)	0.04–0.18%	Two stage anaerobic-aerobic MBR	Lab-scale plant fed with municipal waste leachate	N_2O emissions reduced with sludge recirculation
Mannina *et al.* (2016a)	0.18–5.11%	SB-MBR	Pilot-scale plant, anoxic-aerobic MBR, subjected to salinity increase	N_2O emissions increased with the salinity increase
Mannina *et al.* (2016b)	0–92%	DN-MBR	Pilot-scale plant MBR, in a pre-denitrification scheme, treating saline wastewater contaminated by hydrocarbons	N_2O emissions significantly affected by the joint effect of salt and hydrocarbons
Mannina *et al.* (2017b)	3.82–10.26%	UCT-MBR	Pilot scale plant MBR in a UCT configuration subjected to C/N variation	N_2O emissions increased with the C/N decrease
Mannina *et al.* (2018b)	0.0002–4.01%	UCT-IFAS-MBR	Pilot scale plant IFAS-MBR in a UCT configuration operated at different C/N ratios	Highest N_2O emission related to the presence of free ammonia that caused nitrite accumulation
Mannina *et al.* (2017c)	0.6–38%	UCT-IFAS-MBR	Pilot scale plant IFAS-MBR in a UCT configuration operated at different SRTs	N_2O emissions increased significantly in the MBR compartment with the increase of the air flow rate (for fouling mitigation)
Mannina *et al.* (2018a)	0.6–8.9%	UCT-IFAS-MBR	Pilot scale plant IFAS-MBR in a UCT configuration operated at different HRT/SRTs	N_2O emissions decreased with the decrease of HRT/SRT

Note: SB = sequencing batch; DN = denitrification; IFAS = integrated fixed-film activated sludge; HRT = hydraulic retention time.

Even for MBRs, the literature data show a significant variation for the N_2O emission factor, depending on system configuration, features of feeding wastewater and operational conditions. Due to the increasing recurrence of MBR processes in recent years, it is important to increase the knowledge about GHG production/emission from such systems, by investigating the effect of wastewater features, operational conditions and plant layout on the GHG emissions in ad-hoc experimental campaigns.

8.4 MAIN FACTORS AFFECTING GHG EMISSIONS

The GHG emission from WWTPs has been widely investigated in order to identify its key parameters and its relationship with the operational conditions of the treatment plant.

With reference to N_2O, the emission has been related to the carbon source used during denitrification as well as with the nitrate concentration in the effluent (among others Park *et al.,* 2000; Li *et al.,* 2008; Kampschreur *et al.,* 2009; Yan *et al.,* 2014). The deficiency of dissolved oxygen during nitrification, as well as elevated nitrite concentrations and the incorrect balancing of COD vs nitrogen ratio have been identified as the key factors affecting the N_2O emission (Kampschreur *et al.,* 2009). Hence, the operational conditions play a significant role in N_2O emission (see for instance Figure 8.2).

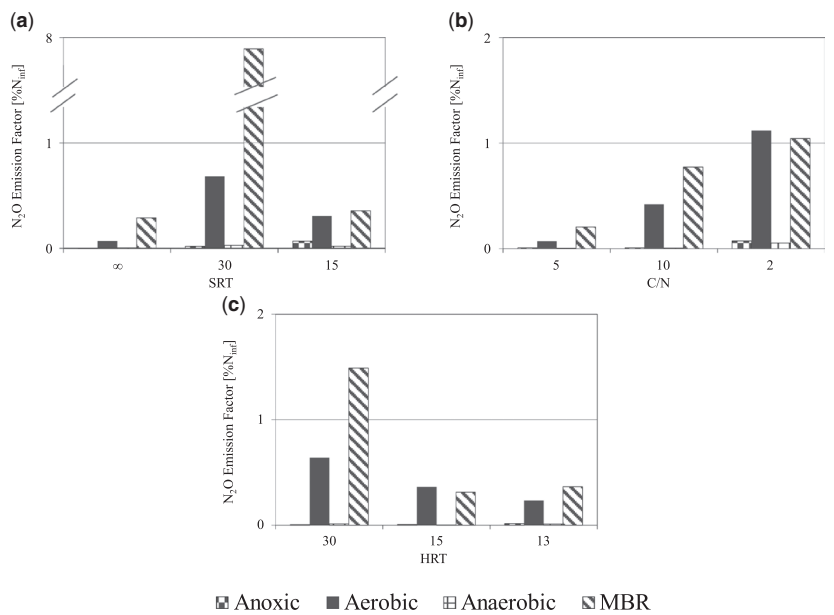

Figure 8.2 N_2O emission factor from a UCT-IFAS-MBR by varying SRT (a); C/N (b); HRT (c) (Mannina *et al.,* 2017a).

Mannina *et al.* (2017a) investigated University of Cape Town (UCT) integrated fixed film activated sludge (IFAS) membrane bioreactor (MBR) (referred to as UCT-IFAS-MBR) pilot plant fed with real wastewater with dosed organic supplements and equipped with funnel shaped covers over all reactors for nitrous oxide collection. The experiments were divided in three phases and aimed at investigating the influence of SRT, influent carbon to nitrogen concentration (C/N) ratio and hydraulic retention time (HRT) operational conditions on the nitrous oxide emission factor. Each experimental phase was divided in three experimental cycles by varying the operational conditions in each phase.

In Figure 8.2a the effect exerted by SRT variation, from indefinite SRT to 15 d is shown; in detail, in each cycle the highest N_2O emission occurred from the aerobic and MBR reactors, thus confirming the crucial role played by the aeration devices in enhancing the emission from WWTPs. In particular, the cycle carried out with SRT = 30 d resulted in the highest emission. The effect of influent C/N ratio, depicted in Figure 8.2b was highest during the third cycle (C/N = 2). During this last cycle, the emission from the aerobic reactor was higher than from the MBR reactor. This is likely ascribable to incomplete denitrification in the anoxic reactor due the organic carbon deficiency that leads to an increase in N_2O production. The N_2O produced in the anoxic reactor was conveyed to the aerobic reactor contributing to the high emission. The effect of combined HRT-SRT variation, depicted in Figure 8.2c, resulted in high emission during the longest HRT (30 h), while no significant differences were found by comparing HRT in the second and third cycles.

The relationship between N_2O and dissolved oxygen concentration was also investigated in Mannina *et al.* (2016a). These authors reported the results of a batch fed membrane bioreactor (SBR-MBR) treating saline wastewater. During the experimentation the authors also investigated the influence exerted by DO concentration on nitrous oxide formation, comparing the results achieved with NaCl concentrations equal to 0 and 10 g L^{-1}. The results are depicted in Figure 8.3.

The DO concentration, together with salinity, significantly affected the N_2O production during the nitrification process. As demonstrated in Figure 8.3a there is a fairly strong exponential correlation, proven by the high value of R^2, between the average DO and N_2O concentration in the aerobic tank. Furthermore, the salt concentration (Figure 8.3c,d) also influenced the pattern of DO and N_2O concentration profiles. Indeed, when no salt was present in the treated wastewater, the nitrification activity lead to an initial decrease of DO promoting an increase in nitrous oxide production. When the nitrification activity was completed, the DO concentration increased and the nitrous oxide concentration reached its lowest value. Conversely, at 10 g NaCl L^{-1}, the DO consumption decreased due to the lower nitrification activity caused by the shock exerted on autotrophic strains by salinity. Such circumstances led to an incomplete nitrification as well as to nitrous oxide formation an order of magnitude higher than that measured during the period carried out with no salt.

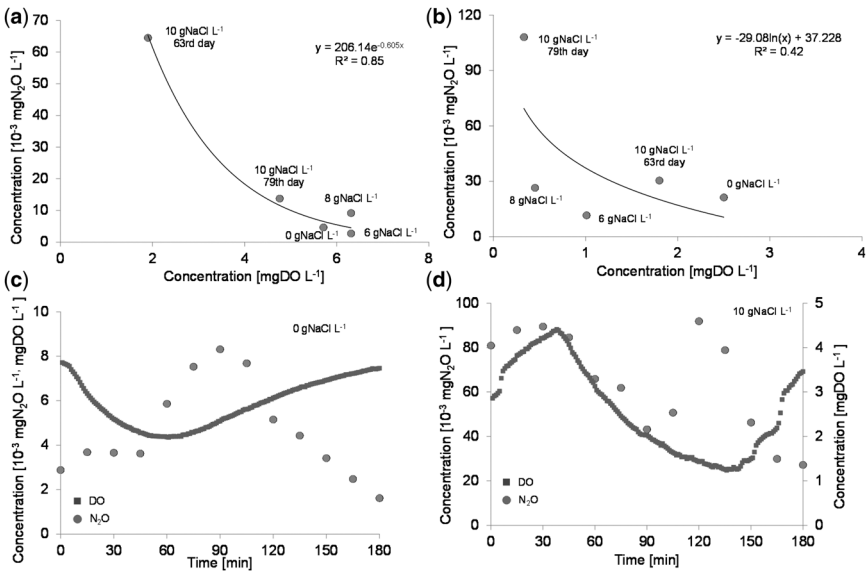

Figure 8.3 Average N_2O concentration in the gas samples withdrawn from the aerobic (a) and anoxic tank (b) in a batch fed membrane bioreactor (SBR-MBR) vs DO concentration; DO and N_2O concentration in the gas samples withdrawn from the aerobic tank during the cycle time at 0 g NaCl L^{-1} (c) and 10 g NaCl L^{-1} (d) (Mannina *et al.,* 2016a).

8.4.1 Direct emissions

With the aim to partially fill the knowledge gap related to GHG emissions from MBR systems, under the Italian research project PRIN2012 entitled "Energy consumption and GreenHouse Gas (GHG) emissions in the wastewater treatment plants: a decision support system for planning and management" a number of experiments have been carried out over 2 years (Mannina *et al.,* 2016a,b, 2017a,b,c, 2018a,b). The main aim was to assess the effect on the N_2O production/emission of different MBR configurations, influent wastewater characteristics (municipal or industrial), operational conditions (SRT, influent C/N ratio, HRT) and type of membrane modules (Mannina, 2017). In the following, a brief description of the pilot plants as well as the main operational features is reported, whilst in Figure 8.4 the schematic lay-out of the pilot plants used is shown.

Pilot plant No.1, referred to as SB-MBR, was designed according to a pre-denitrification scheme in a sequential feeding mode. It consisted of two in-series reactors: one anoxic (volume: 45 L) and one aerobic (volume: 224 L), followed by an MBR compartment (volume: 50 L). The experimental campaign was divided into six phases, each characterized by a different salt concentration in the feeding

wastewater. The salt concentration was gradually increased from 0 to 10 g NaCl L^{-1} (Phase I: no salt addition; Phase II: 2 g NaCl L^{-1}; Phase III: 4 g NaCl L^{-1}; Phase IV: 6 g NaCl L^{-1}; Phase V: 8 g NaCl L^{-1}; Phase VI: 10 g NaCl L^{-1}).

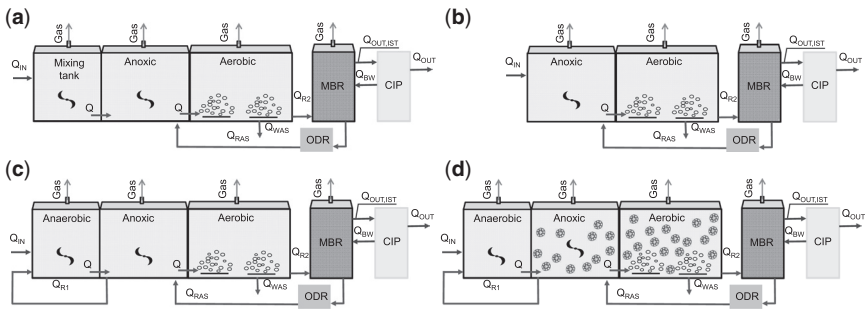

Figure 8.4 Schematic layout of the investigated pilot plants: (a) SB-MBR, (b) pre-denitrification MBR, (c) UCT-MBR, and (d) UCT-IFAS-MBR (Mannina *et al.,* 2016a,b, 2017a,b,c, 2018a,b). (ODR = oxygen depletion reactor; CIP = clean-in-place; RAS = recycle activated sludge; WAS = waste activated sludge).

Pilot plant No.2, referred to as DN-MBR, was characterized by one anoxic (volume: 45 L) and one aerobic (volume: 224L) in-series reactor. The experimental campaign had a duration of 90 days and was divided in two Phases, characterized by different features of the inlet wastewater. In Phase I the salinity of the influent was increased from 10 g NaCl L^{-1} up to 20 g NaCl L^{-1}, while in Phase II the inlet wastewater had a constant salinity (20 g NaCl L^{-1}) and diesel fuel dosage.

Pilot plant No.3, referred to as UCT-MBR was characterized by one anaerobic (volume: 62 L), one anoxic (volume: 102 L), and one aerobic (volume: 211 L) in-series reactor, according to the University of Cape Town (UCT) scheme (Ekama *et al.,* 1983). The UCT-MBR pilot plant was fed with a mixture of real and synthetic wastewater, the latter comprising sodium acetate, glycerol, di-potassium hydrogen phosphate and ammonium chloride. The experimental campaign was divided in two Phases, each characterized by a different value of the influent C/N ratio – in Phase I a C/N of 10 (duration: 41 days) and in Phase II a C/N of 5 (duration: 39 days).

Pilot plant No.4, referred to as UCT-IFAS-MBR, was characterized by one anaerobic (volume: 62 L), one anoxic (volume: 102 L), and one aerobic (volume: 211 L) in-series reactor, according to the University of Cape Town (UCT) scheme (Ekama *et al.,* 1983). The pilot plant was realized according to the IFAS-MBR (integrated fixed-film activated sludge membrane bioreactor) based on the combination of a moving bed biofilm reactor (MBBR) and an activated sludge based membrane bioreactor configuration with the presence of both activated

Table 8.3 Summary of literature studies on N_2O emissions from MBR plants.

Configuration	HRT [h]	Influent COD/N Ratio [mg COD $mg^{-1}TN$]	SRT [d]	Membrane Typology	Brief Process Description
Sequencing batch operation	20	8	Indefinite (no sludge withdrawal)	Ultrafiltration hollow fibre GE Zenon ZW10®	Evaluation of the effect of a gradual salinity increase in the short term. Experiment divided into six phases (Mannina *et al.,* 2016a)
MBR in a pre-denitrification scheme	16	7	Indefinite (no sludge withdrawal)	Ultrafiltration hollow fibre GE Zenon ZW10®	The joint effect of the salinity and hydrocarbons (20 mg TPH L^{-1}) in the short term was investigated (Mannina *et al.,* 2016b)
MBR coupled to UCT configuration for carbon and nutrient removal	20	10, 5	Indefinite (no sludge withdrawal)	Ultrafiltration hollow fibre PURON®	Evaluation of C/N ratio effect in a BNR process integrated with a membrane module for solid/liquid separation phase (Mannina *et al.,* 2017b)
Hybrid moving bed biofilm membrane bioreactor coupled to UCT configuration for carbon and nutrients removal	30, 15, 13	10, 5, 2	Indefinite (no sludge withdrawal), 30, 15	Ultrafiltration hollow fibre PURON®	Evaluation of the SRT effect on the performance of a UCT-IFAS-MBR pilot plant, evaluating the bio-kinetic activity of the bacterial species (Mannina *et al.,* 2018b)
CAS + MBR	–	–	–	–	Full-scale plant treating domestic and industrial wastewater (Singh & Kansal, 2018)
Activated sludge with sequenced aeration followed by MBR	–	–	–	–	Full-scale plant treating domestic wastewater (GWRC, 2011)
Anaerobic + aerobic pilot plant	5, 2.5	15–17 (anaerobic reactor); 9–16 (aerobic reactor	–	Mitsubishi Rayon, PVDF, 0.4 μm pore size, 0.077 m^2 surface area	Evaluation of the HRT and sludge recirculation effect on CH_4 and N_2O emission from a pilot plant treating fresh leachate mixed with tap water (1:1.5 v/v) (Nuansawan *et al.,* 2016)

sludge and biofilm (Ødegaard, 2017). The suspended plastic carriers for biofilm growth were added to the anoxic and the aerobic reactors, with filling fraction of 15 and 40%, corresponding to specific area of 75 and 200 m^2 m^{-3}, respectively. The experimental campaign had a duration of 340 days and was aimed at investigating the influence of operational variables (namely, SRT, influent C/N ratio and HRT-SRT) on N_2O production and emission.

For further details on the pilot-plant description as well as on experimental campaigns the reader is referred to Mannina *et al.* (2016a, 2017a).

Table 8.3 summarizes the few studies found in literature on N_2O emissions from MBR plants including the MBRs described above operated by Mannina *et al.* (2016a, 2017a), in which a wide range of N_2O emission factors under the different operations were found.

Singh and Kansal (2018) evaluated the total GHG emissions (expressed in terms of equivalent CO_2 emissions) from different WWTPs by adopting a simplified model. Among these plants, four were MBR systems treating domestic wastewater. They found an average GHG emission of 0.85 kg CO_{2eq}/m^3.

Within the work performed by the Global Water Research Coalition (GWRC, 2011) one MBR full-scale plant located in France was monitored in terms of N_2O emissions. An emission factor in terms of N_2O of 0.0011 $kgN_2O\text{-}N\ kgTKN_{influent}^{-1}$ was observed.

Nuansawan *et al.* (2016) investigated an anaerobic – aerobic MBR pilot plant treating leachate under different HRTs (2.5 and 5 days) and with the presence and absence of sludge recirculation from the anaerobic to the aerobic reactor. The main objective of this study was to evaluate the GHG emissions (CH_4 and N_2O) under the two different HRT operation conditions. They found the highest CH_4 (8.26% of the inlet carbon) and N_2O (0.18% of the inlet N) emissions took place from the anaerobic reactor under HRT of 5 days and without sludge recirculation.

By varying the experimental MBR system layout, an intensive campaign (Mannina *et al.,* 2016a,b, 2017a,b,c, 2018a,b) aimed at evaluating the N_2O production was carried out over almost two years (see Figure 8.5). The aim was to create a robust dataset to better understand the N_2O production and emission mechanisms.

Headspace data are representative of the N_2O concentration confined between the liquid surface and the funnel shape cover over the reactors, while the dissolved concentration data are representative of the N_2O concentration in the liquid bulk of each reactor. The data depicted in Figure 8.5 are representative of the aerobic and anoxic reactors where the core part of the nitrogen transformation process occurs.

The data collected reveal a huge variability of N_2O concentrations measured; indeed, the N_2O concentration ranged within six orders of magnitude (from 10^{-1} $\mu g\ N_2O\text{-}N\ L^{-1}$ up to 10^5 $\mu g\ N_2O\text{-}N\ L^{-1}$). This N_2O concentration variability yielded a wide range of the emission factors (EF) measured during the experimentation. In Figure 8.6 the average values of the EF (assessed as percentage of the total nitrogen influent emitted as N_2O according to Tsuneda *et al.* (2005)), are depicted (Mannina *et al.,* 2016a,b, 2017a,b,c, 2018a,b).

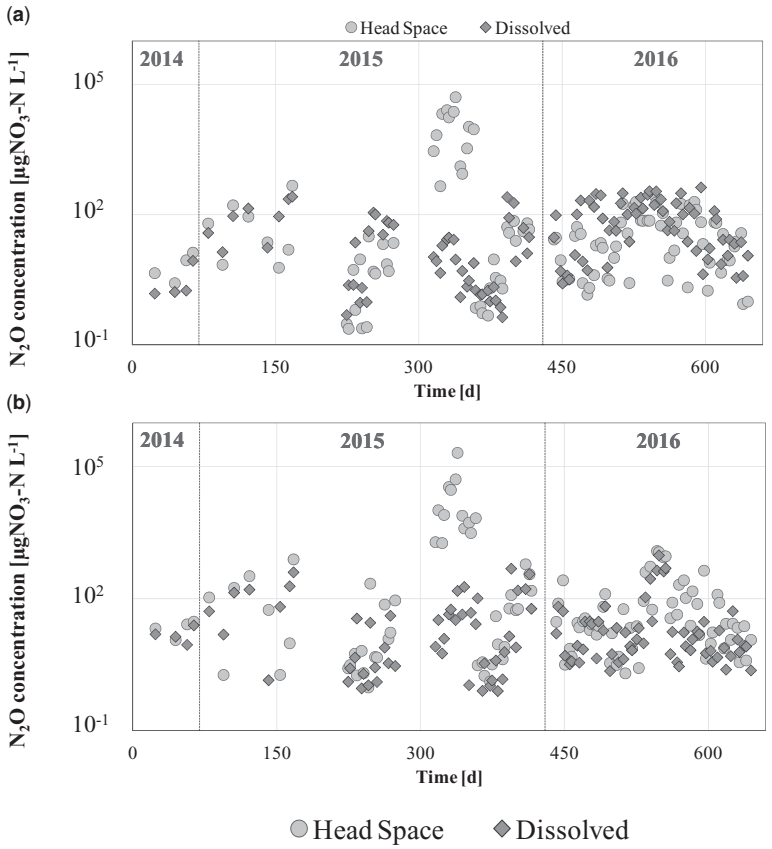

Figure 8.5 Nitrous oxide concentration measured in the head space and in the liquid bulk of aerobic (a) and anoxic (b) reactors over the experimentation (Mannina *et al.,* 2016a,b, 2017a,b,c, 2018a,b).

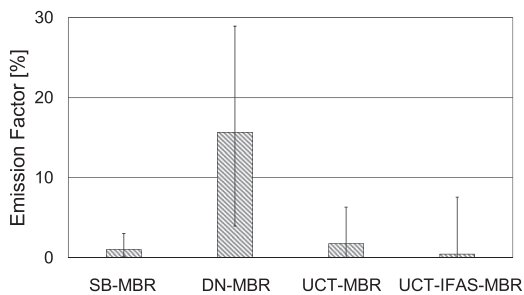

Figure 8.6 N_2O average emission factor measured for each experimental layout. The bars report minimum and maximum value for each configuration.

The data presented in Figure 8.6 demonstrate the influence by type of MBR-plant layout on the N_2O emission. The DN-MBR scheme had the highest emission factor (16% of influent nitrogen on average). It is worth noticing that the influent wastewater composition also played a significant role in the increasing of the N_2O emission. Indeed, the DN-SBR scheme treated an influent wastewater composed also of salt and diesel fuel (Mannina *et al.,* 2016a,b). The joint effect of both salt and hydrocarbon represented a disturbance factor that affected the metabolic activity of the biomass which increased the N_2O production and thus the emission. The role played by the salinity is also noticeable during the SBR-MBR configuration. The stepwise salinity increase resulted in a moderate EF, with the mean EF measured during SB-MBR period equal to 1% of influent nitrogen.

With regard to the UCT-MBR and UCT-IFAS-MBR configuration, the scarcity of carbon availability imposed by the lowest values of influent C/N ratio resulted in an increase of N_2O emission likely due to a carbon limitation for the denitrification process.

To summarize, the configuration that yielded the lowest EF was the UCT-IFAS-MBR, which featured a mean emission of 0.5% of influent nitrogen, but the operational condition of this system did influence the emission factor.

In order to also describe the role played by each reactor in contributing to the total emission, a comparison of mean EF assessed for each reactor during the operation of the UCT-MBR and UCT-IFAS-MBR configurations is given in Figure 8.7.

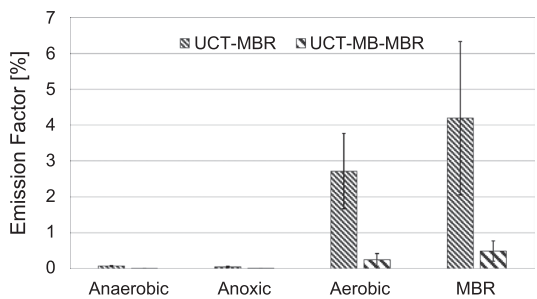

Figure 8.7 Comparison of mean EF measured in each biological reactor during the UCT-MBR and UCT-IFAS-MBR layout (Mannina *et al.,* 2017b,c, 2018a,b).

Figure 8.7 shows the strong reduction in EF that was observed in the UCT-IFAS-MBR layout. This result is likely due to an improvement in biological performance caused by the co-presence of both suspended and attached biomass. The biofilm presence improved the nitrogen removal efficiency thus leading to a lower N_2O emission.

Furthermore, it is worth noting that the highest emissions were measured in the aerated reactor in both MBR layouts, thus confirming the significant role that aeration has on N_2O emission by stripping.

In order to elucidate the influence of the operational condition as well as the layout configuration on the nitrous oxide production, a comparison of mean N_2O dissolved concentration measured in the biological reactors of the UCT-MBR and UCT-IFAS-MBR systems during the period when the influent C/N was varied, is shown in Figure 8.8.

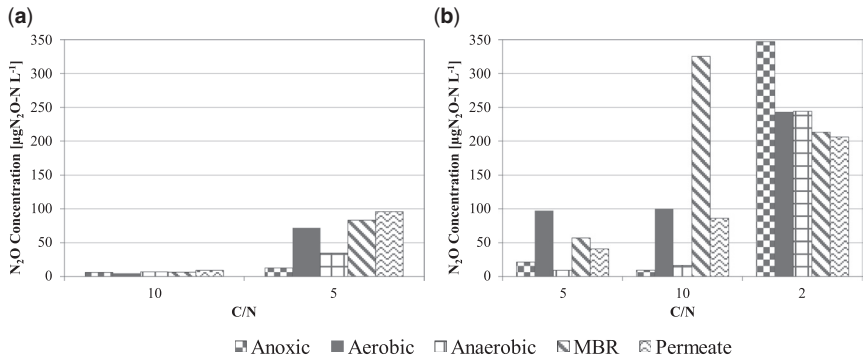

Figure 8.8 Comparison of mean N_2O dissolved concentration measured in the biological reactors in UCT-MBR (a) and UCT-IFAS-MBR (b) during the period when C/N was varied (Mannina *et al.,* 2017b,c, 2018a,b).

Figure 8.8 shows the increase in dissolved N_2O concentration with decreasing influent C/N-ratio. During the UCT-MBR experimental period (Figure 8.8a) the decrease of C/N wastewater fed to the pilot plant resulted in a drastic increase of N_2O dissolved concentration. As an example, the mean N_2O concentration measured in the permeate flow at C/N = 10 was 9.2 µg N_2O-N L^{-1}. Conversely, when the carbon availability was reduced due to the lower C/N, the mean N_2O concentration measured in the permeate flow increased to 95.9 µg N_2O-N L^{-1}, 10 times higher than in the previous period.

The results depicted in Figure 8.8b are similar; however, during the C/N = 2 period, the highest N_2O dissolved concentration was measured in the anoxic reactor. During the C/N = 10 and C/N = 5 periods, the maximum values of N_2O concentration were measured in the aerobic or in the MBR reactor. When C/N = 2 was implemented, the organic carbon deficiency for denitrification lead to a sharp increase in nitrous oxide production which reached an average concentration of 347 µg N_2O-N L^{-1}.

The mean N_2O dissolved concentrations measured in the anoxic reactor during the C/N = 10 and C/N = 5 periods were 9.5 µg N_2O-N $L^{-1}$and 21.5 µg N_2O-N L^{-1}

respectively. As the C/N ratio decreased, the nitrous oxide concentration increased. In a similar way the N_2O concentration measured in the anaerobic reactor during the C/N = 2 period increased up to 244.2 μg N_2O-N L^{-1}, more than 10 times higher than in the other periods. This behaviour is due to the deficiency of organic carbon for the denitrification, which resulted also in an increase in nitrate recycled to the anaerobic reactor. As a consequence, during the C/N = 2 period the anaerobic reactor was overloaded with nitrate thus acting as an anoxic reactor and contributing to this huge N_2O production and a failure of bio P removal (Mannina *et al.,* 2018b).

8.4.2 Indirect emissions

Aeration of MBRs can influence the amount of direct (pollutants discharged into the receiving water body and into the atmosphere) and indirect emissions. Mannina *et al.* (2016d) have recently investigated, for an MBR pilot plant, the effect of the air flow rate variation on the effluent quality index (EQI), the effluent penalty for exceeding concentration limits, and the operational cost (OC) (the exact calculation of the EQI, effluent penalty & OC can be found in Mannina & Cosenza, 2015).

Mannina *et al.* (2016d) found that by increasing the air flow rate, the EQI decreases according to an exponential pattern (with a correlation coefficient, R^2, equal to 0.61) (Figure 8.9a). The decrease of EQI with the increase of the air flow is due to the improvement of the biological processes (carbon removal and ammonia oxidation) with the increase of the dissolved oxygen inside the aerated tanks and due to the decrease of N_2O produced during the nitrification. Indeed, under oxygen limiting conditions, AOB use nitrite as the terminal electron acceptor to save oxygen for the oxygenation reaction of ammonia to hydroxylamine thus contributing to the N_2O production during nitrification (Kampschreur *et al.,* 2009). Mannina *et al.* (2016d) found also that the improvement of the biological processes at high air flow leads to a reduction of the mass of pollutants discharged to the environment with a consequent decrease of the penalty/fee to be paid (Figure 8.9b). Therefore, in terms of both EQI and effluent penalty, the highest air flow (2.3 m^3 h^{-1} in the pilot plant) represented the best operating condition. However, higher air flow increases the OC (Figure 8.9c) and the maximum OC value (3 € m^{-3}) was indeed obtained under the maximum air flow rate condition (2.3 m^3 h^{-1} in the pilot plant).

In Figure 8.10 data related to the relationship between the air flow versus, indirect (Figure 8.10a) and direct emissions (Figure 8.10b) obtained by Mannina *et al.* (2016d) are reported. The total energy required for the mechanical devices, needed to assess the indirect emission, has been quantified according to Singh and Kansal (2018).

An exponential relationship ($R^2 = 0.83$) was obtained between the air flow and the indirect (Figure 8.10a) and direct (Figure 8.10b) GHG emissions.

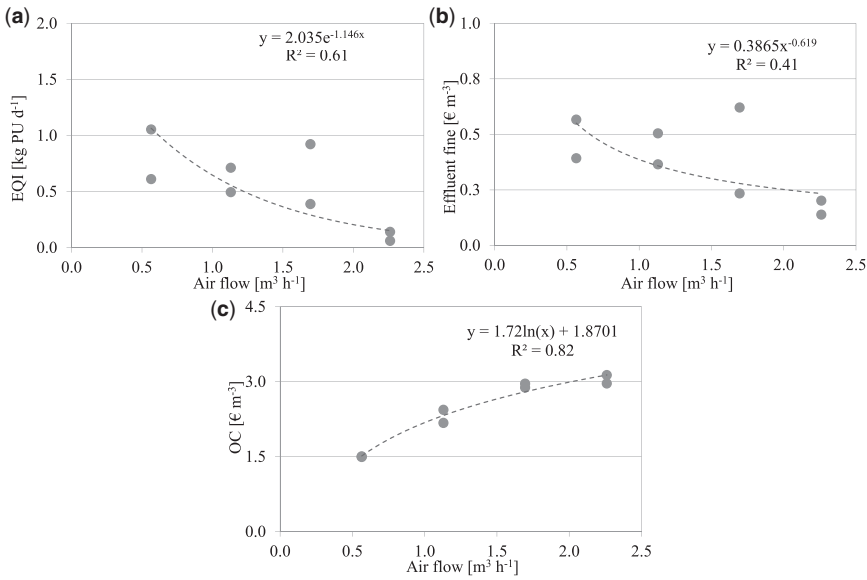

Figure 8.9 Air flow versus effluent quality index (a); effluent fine (b) and operational costs (c) (Mannina *et al.,* 2016d).

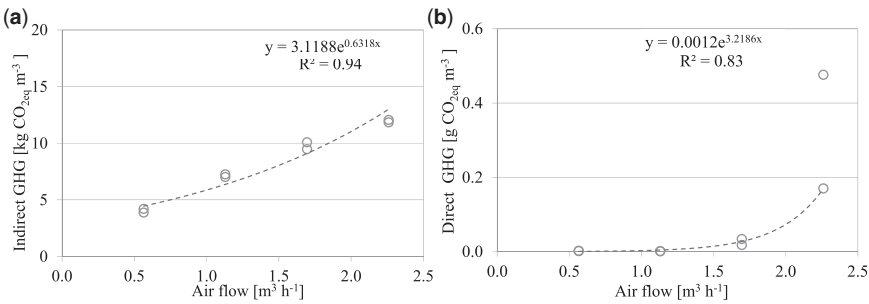

Figure 8.10 Relationship between the air flow and indirect GHG emissions (a); correlation between the air flow rate and direct GHG emissions (b).

In terms of GHG emissions (both direct and indirect) the lowest air flow (0.6 $m^3 h^{-1}$ in the pilot plant) seems to be more appropriate than the others. However, this result is in conflict with the previous results (i.e. that EQI and effluent penalty have the maximum value under the lowest air flow rate value). This indicates interlinkages between different phenomena involved. Indeed, a "multiple trade-off" has to be performed for identification of the best air flow in order to mitigate GHG emissions and reduce the EQI and OC values.

Singh and Kansal (2018) found that the energy consumption of full-scale MBRs is around 0.42 kWh m^{-3}. This value is about 40% more than that of CAS. The amount of the total GHG emitted from an MBR was found by Singh and Kansal (2018) to be equal to 0.853 $kgCO_2$ eq. m^{-3} (0.564 $kgCO_2$ eq. m^{-3} due to the transport and 0.288 $kgCO_2$ eq. m^{-3} due to the treatment).

8.5 CONCLUSIONS

Wastewater treatment plants represent a significant source of greenhouse gas and this aspect will contribute in the future to reconsideration of the targets that wastewater treatment plants must fulfil. Indeed, besides pollutant removal and operational costs reduction, targets for future WWTPs must include the reduction of greenhouse gas emissions to the environment. In this light, WWTPs will become a sort of "box" from which further knowledge should be acquired, investigating specific topics neglected so far.

The understanding of processes that enhance GHG emission as well as the knowledge of operational variables and conditions that favour their production, represent new and important knowledge acquired by the scientific community over recent years. Indeed, many efforts have been recently devoted to experimental and monitoring activities with the aim to: i. assess the main mechanisms of GHG formation, ii. evaluate the operational conditions that favour their production.

In this context, some issues related to GHG production/emission are still poorly understood and deserve further investigation. For instance, despite the fact that many studies reveal that N_2O formation mostly derives from AOB activity, the conditions that trigger its formation are still not clear. Data obtained by authors highlighted a huge variability of N_2O concentration, demonstrating the influence of plant configuration and operational conditions. In particular, low influent C/N concentration ratios increased the N_2O production significantly.

There is also the need to reconsider the management of WWTPs, by considering GHG emissions. Indeed, if the aim is only limited to respect the imposed effluent quality, at the same time minimizing the operational costs, the GHG emissions might be significant.

As an example, the decrease of the dissolved oxygen set-point inside the nitrification reactor could promote the increase of N_2O production due to incomplete nitrification, despite the reduction of the operational costs.

In light of this, a plant wide mathematical modelling could represent a useful tool for the comparison of different scenarios (in terms of either design or management) for the evaluation of the best system performance, referring to both quality of the liquid effluent, reduction of gaseous emissions and operational costs reduction.

Nevertheless, the complexity of many existing models makes them of little use, except for research purposes. The high number of model parameters coupled to algorithm complexity usually require long computational times that are in contrast with the need of fast response for plant operators.

In view of this, the aim of the scientific community should be the build-up of simplified mathematical tools, derived by complex dynamic mathematical models, to be used as decision support systems able to simulate the quality of gaseous and liquid emissions from WWTPs and to provide useful indications for the optimization of the system management.

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