Nitrous oxide and methane emissions from a plug-flow full-scale bioreactor and assessment of its carbon footprint

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Nitrous oxide and methane emissions from a plug-flow full-scale bioreactor and assessment of its carbon footprint


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Declarations of interests: none
Daily emissions monitored during 5 months

CH4  N2O

C- footprint

Daily emissions monitored during 5 months

CH4  N2O

C- footprint

Daily emissions monitored during 5 months

CH4  N2O

C- footprint

Daily emissions monitored during 5 months

CH4  N2O

C- footprint

Daily emissions monitored during 5 months

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ABSTRACT

Fugitive greenhouse gas (GHG) emissions in the form of nitrous oxide (N\textsubscript{2}O) and methane (CH\textsubscript{4}) have been reported from many different wastewater treatment plants. However, the majority of the current literature only reports emissions during short periods of time and only focuses on one of the two GHGs. In this study, N\textsubscript{2}O and CH\textsubscript{4} emissions from the aerated parts of a plug-flow full-scale bioreactor treating municipal wastewater were studied over five months from November through March. A multiple gas hood collection system was used to simultaneously monitor the first three aerated compartments of the plug-flow bioreactor. Results show temporal variations in N\textsubscript{2}O emissions with N\textsubscript{2}O detected during November, no emissions during December and January, and a recovery of emissions from February onwards. In addition, different spatial emissions were found across the three aerated zones, with the highest N\textsubscript{2}O emissions detected in the second aerated zone. A daily N\textsubscript{2}O emission pattern was characterised by an N\textsubscript{2}O peak correlated with the ammonium that arrived in the monitored zone. However, CH\textsubscript{4} emissions occurred during the whole monitored period and showed a spatial variability inside the plug-flow bioreactor, presenting the highest emissions in the first aerated zone and then decreasing in the two subsequent zones. In addition, the dynamic carbon footprint (C-footprint) of the bioreactor is presented in
which the contribution of the direct and indirect emissions (related to electricity consumption) is assessed. Results show that CH$_4$ emissions account for the majority of the direct emissions. Moreover, CH$_4$ and N$_2$O emissions represent approximately 60% of the total emissions (direct and indirect) originating from the bioreactors.

**Keywords:** carbon footprint; municipal wastewater treatment; emission factor; nitrous oxide; methane; multiple hood monitoring.

### 1. INTRODUCTION

Over the past few years concern regarding the quantification and investigation of greenhouse gas (GHG) emissions from full-scale biological nutrient removal processes has increased. In particular, nitrous oxide (N$_2$O) has attracted considerable interest among researchers because of its high global warming potential (GWP) (298 times higher than that of carbon dioxide, CO$_2$) (IPCC, 2014). N$_2$O emitted from wastewater treatment plants (WWTPs) is mainly produced during the biological conversion of nitrogen into nitrogen gas (N$_2$) through the nitrification and denitrification processes (Kampschreur et al., 2009). During nitrification, ammonium (NH$_4^+$) is oxidised to nitrite (NO$_2^-$) by ammonia oxidizing bacteria (AOB) and then to nitrate (NO$_3^-$) by nitrite oxidizing bacteria (NOB) under aerobic conditions. Though N$_2$O is not an intermediate of this process, it can be produced as an end product by AOB via two metabolic pathways: (i) hydroxylamine oxidation (Law et al., 2012a) and (ii) nitrifier denitrification (Wunderlin et al., 2012). The activation of these pathways by AOB is influenced by several factors such as low dissolved oxygen (DO) concentration, NO$_2^-$ accumulation, and transient conditions from low activity to high activity (Law et al., 2012a). However, during denitrification, NO$_3^-$ is reduced to nitrogen gas (N$_2$) under anoxic conditions with NO$_2^-$, nitric oxide (NO), and N$_2$O as intermediates. There are
several factors affecting the accumulation of N\textsubscript{2}O during denitrification such as the limiting organic matter present in the wastewater, and the presence of DO and free nitrous acid (FNA, the protonated species of NO\textsubscript{2}–) (Law et al., 2012a).

Although there has been considerable research regarding N\textsubscript{2}O emissions from WWTPs, results are variable and the consensus to explain the exact causes has not been found. The reasons for this are related to not only the different WWTP configurations and conditions of operation but also to the different monitoring methodologies used and the length of the monitoring campaigns. The methods to quantify GHG emissions have evolved from analysing grab samples to continuous online gas monitoring using commercially available portable gas analysers (GWRC 2011). Gas collection hoods are located on the bioreactor surface, capturing the gas emitted and allowing a more reliable quantification of the emission dynamics and their diurnal variability (Pan et al., 2016).

This quantification is particularly challenging in plug-flow bioreactors because wastewater flows through the bioreactor without horizontal mixing, originating different gradients in DO and nitrogen concentrations that can be found along the bioreactor path. Different studies have monitored N\textsubscript{2}O emissions in WWTPs. Normally, these emissions are reported as N\textsubscript{2}O emission factors, which represent the percentage of the average influent Total Kjeldahl Nitrogen (TKN) load being emitted as N\textsubscript{2}O. Results from the literature show a wide range of N\textsubscript{2}O emission factors (0.036%–6.8%) and distinctive N\textsubscript{2}O emission patterns (Aboobakar et al., 2013; Ahn et al., 2010b; Kosonen et al., 2016; Rodriguez-Caballero et al. 2014, 2015). With the aim of obtaining more reliable emission patterns, Pan et al. (2016) used multiple gas collection hoods to simultaneously measure N\textsubscript{2}O emissions along a plug-flow bioreactor. N\textsubscript{2}O fluxes showed strong spatial variations along the bioreactor path, demonstrating that it is
crucial to consider spatial variations when quantifying emissions in plug-flow bioreactors.

Apart from N₂O, it is also well known that WWTPs emit methane (CH₄). This GHG has a GWP 21 times higher than that of CO₂ (IPCC, 2014) and is the second most important GHG after CO₂. CH₄ can be present in the influent of a WWTP in a dissolved form after forming under the anaerobic environments present in the sewer network (Gutierrez et al., 2014). In addition, significant dissolved CH₄ concentrations are found in the reject wastewater stream originating from the anaerobic digesters which is normally recirculated to the inlet of the WWTP (Rodriguez-Caballero et al., 2014). Part of this CH₄ can be biologically oxidised in the bioreactor but some is stripped to the atmosphere in the aerated compartments. Despite this, only a few studies have quantified CH₄ emission dynamics in domestic wastewater treatment systems (Daelman et al., 2013, 2012; Rodriguez-Caballero et al., 2014).

The aim of this study was to assess the N₂O and CH₄ emission dynamics from a plug-flow full-scale bioreactor treating municipal wastewater over a period of five months. The spatial variation of these two gases across the aerated parts of the plug-flow bioreactor was also determined using a multiple hood gas collection system. To assess the carbon footprint (C-footprint) of the bioreactor a comparison between the direct and indirect emissions of the bioreactor was conducted. To the best knowledge of the authors this is the first time that a dynamic C-footprint for a full-scale bioreactor has been presented, highlighting the importance of long-term monitoring not only for N₂O but also for CH₄ to realistically assess the C-footprint of a wastewater treatment process.

2. MATERIALS AND METHODS
2.1. Description of the monitoring site

The monitoring site was the WWTP of Girona (Spain). This plant treats municipal wastewater from the main city and various nearby towns surrounding the WWTP, before the effluent is discharged into a river. The plant has the capacity of 275,000 population equivalents (PE) which corresponds to a design flow rate of 55,000 m$^3$/day with a hydraulic retention time (HRT) of 27.11 h. However, during the monitoring period the plant treated an average 42,000 m$^3$/day. The plant configuration consists of a primary treatment followed by primary settlers. Then, the wastewater is biologically treated in two parallel and identical plug-flow bioreactors using a modified Ludzack-Ettinger (MLE) configuration with biological removal of organic matter and nitrogen and chemical removal of phosphorus. The plant has the capacity to treat wastewater in three lines but at present only two lines are in operation. Both operative lines receive an equal amount of wastewater as proven by a tracer test conducted at the beginning of the monitoring campaign (data not shown).

Following biological treatment, the treated water flows to the secondary settlers and is discharged into a river meeting the legal discharge limits. The sludge is compressed in two thickeners and anaerobically digested. The reject water from both processes is released into the inlet of the plant for its treatment. A scheme of the configuration of the plant is shown in Figure 1.

Each plug-flow bioreactor has seven different connected compartments also referred to as zones: two anoxic zones at the beginning followed by three aerobic zones, another anoxic zone, and finally a final aerobic zone. There is an internal recirculation from the third aerobic zone to the second anoxic zone. Three gas hoods were placed in the first
three aerobic zones of the plug-flow bioreactor to measure the N\textsubscript{2}O and CH\textsubscript{4} emissions (Figure 2).

2.2. Gas emission measurements

Gas measurements were taken using a multiple hood gas collection system with three commercial gas collection hoods (AC'SCENT® Flux Hood). The gas hoods were not placed within the anoxic zones because there was no measurable gas flow and previous studies have shown that N\textsubscript{2}O fluxes from un-aerated zones are negligible (Law et al., 2012a; Rodriguez-Caballero et al., 2015, 2014). Monitoring was conducted over a 5-month period (November 2016 through March 2017) using the following methodology: 1) The gas collected in the hoods was flowing to a monitoring unit through a polyamide gas tubing (12 mm diameter); 2) In the monitoring unit, gas temperature, pressure and flow-rate were monitored and logged; 3) then, part of the gas was pumped to a conditioning unit to remove humidity and particles (series CSS, M&C Tech group) and from there the gas was directed to the online gas analyser (Horiba VA3000). As the analyser can only measure one gas flow at a time, software was used to control the opening and close of three solenoid valves installed after each gas flow-meter that allowed to direct the flow of the gas collected by each hood to the analyser at 20-min intervals. This software contained all the necessary codes to operate a system of sensors connected to an Arduino, and was controlled by a Raspberry Pi. The Arduino sensors were continuously reading and sending the data to the serial port (USB) of the Raspberry Pi. N\textsubscript{2}O, CH\textsubscript{4} concentration (in ppmv), temperature, flow rate, and pressure were logged at 15-s intervals. The analyser was serviced and calibrated weekly on-site, according to the manufacturer’s instructions, using the 80 ppmv N\textsubscript{2}O in N\textsubscript{2} gas standard, 160 ppmv CH\textsubscript{4} in N\textsubscript{2} gas standard, 21% oxygen (O\textsubscript{2}) in N\textsubscript{2} gas standard, and N\textsubscript{2}.

2.3. Chemical analysis
Composite samples were collected from the inlet of the plug-flow bioreactor to analyse the chemical oxygen demand (COD), biological oxygen demand (BOD), and TKN following the methods described in APHA (1995). Grab samples were also taken at 1-h intervals over 24 h using an automatic refrigerated sampler from the bioreactor inlet and the second and the third aerobic zones to analyse NO$_3^-$, NO$_2^-$, NH$_4^+$, and phosphate (PO$_4^{3-}$) via ion chromatography (ICS5000, DIONEX). Samples were collected from different parts of the plant (locations are marked in Figure 1) for the analysis of dissolved CH$_4$. They were filtered through a 0.22-µm Millipore filter and injected into a vacuumed glass tube. The tubes were stored in a fridge for 24 h to achieve the gas–liquid equilibrium. The gas phase was measured using a gas chromatograph (Thermofisher Scientific Inc., USA) equipped with a flame ionisation detector (FID). Additionally, the NH$_4^+$ concentration at the inlet of the bioreactor and in the second aerobic zone was continuously monitored by two on-line ion-selective electrodes (ammo::lyser™) coupled to a monitoring station (S::CAN Messtechnik GmbH, Austria). DO data were only available from the first and last aerobic zone and were acquired from the SCADA system of the WWTP.

2.4. Calculations

This section presents all the calculations used in the manuscript.

2.4.1. N$_2$O and CH$_4$ emission factors

To calculate the N$_2$O and CH$_4$ emission factors, equations 1 and 2 were used (Rodriguez-Caballero et al., 2014) as follows:

\[
N_2O\text{ emitted} = \sum_i^n \left( \sum (C_{N-N_2O} \cdot Q_{\text{gas}} \cdot \Delta t)_{\text{hood } i} \right) \cdot \frac{A_{\text{zone } i}}{A_{\text{hood } i}} \quad \text{(Eq. 1)}
\]

where
\[ C_{N-N_2O} = C_{N-N_2O} \text{ (ppmv)} \cdot N_2O \text{ molar volume (0.0402 at 1 atm and 25}^\circ\text{C)} \cdot 10^{-6} \cdot 28 \left( \frac{g \ N - N2O}{L} \right) \]  

(Eq. 2)

\( Q_{gas} \) is the gas flow rate (L/min),
\( \Delta t \) is the time interval by which the off-gas N\(_2\)O was recorded,
\( A_{\text{zone}_i} \) is the area of the zone of the plug-flow bioreactor where hood \( i \) was placed, and
\( A_{\text{hood}_i} \) is the area of the hood which was 0.13 m\(^2\).

A homologous calculation was completed for the CH\(_4\) emission but the CH\(_4\) concentration (g CH\(_4\)/L) was multiplied by 16 g CH\(_4\)/mol.

The N\(_2\)O emission factor was calculated as a percentage of the average influent TKN load of the WWTP emitted as N\(_2\)O (equation 3). The same methodology was used for calculating the CH\(_4\) emission factors, in which the influent TKN was replaced by the COD load (equation 4).

\[
N_2O \text{ Emission factor} \ (\%) = \frac{N_2O \text{ emitted}}{TKN \text{ load}} \times 100 \times 2 \]  

(Eq. 3)

\[
CH_4 \text{ Emission factor} \ (\%) = \frac{CH_4 \text{ emitted}}{DOO \text{ load}} \times 100 \times 2 \]  

(Eq. 4)

where

the TKN load corresponds to the same time interval \( \Delta t \)

2.4.2. Conversion of N\(_2\)O and CH\(_4\) into CO\(_2\) equivalents

CO\(_2\) equivalents for the N\(_2\)O and CH\(_4\) emissions found in this study were calculated as follows:

\[
N_2O \text{ as CO}_2 \text{ equivalents} \ (Kg CO_2/m^3) = \frac{N_2O \text{ emitted (Kg N/d)}}{\text{Influent wastewater flow (m}^3\text{/d)}} \times 298 \times 2 \]  

(Eq. 5)

\[
CH_4 \text{ as CO}_2 \text{ equivalents} \ (Kg CO_2/m^3) = \frac{CH_4 \text{ emitted (Kg/d)}}{\text{Influent wastewater flow (m}^3\text{/d)}} \times 21 \times 2 \]  

(Eq. 6)
Equations 3, 4, 5, and 6 are multiplied by 2 because it was assumed that both operative plug-flow bioreactors present in the plant had the same emissions.

2.4.3. Statistical analysis

Pearson’s correlation coefficient ($r$) is the test statistic that measures the statistical relationship between two variables. Pearson's correlation statistical analysis was completed using equation 7 (SPSS tutorials: Pearson Correlation):

$$r = \frac{\sigma_{xy}}{\sigma_x \cdot \sigma_y} \quad \text{(Eq. 7)}$$

where

$\sigma_{x,y}$ is the covariance of variables $x$ and $y$,
$\sigma_x$ is the standard deviation of $x$,
$\sigma_y$ is the standard deviation of $y$, and
$x$ and $y$ are the variables of the statistical analysis.

The degree of correlation was the following:

- Perfect: If the value is near $\pm 1$.
- High degree: If the coefficient value is between $\pm 0.50$ and $\pm 1$.
- Moderate degree: If the value is between $\pm 0.30$ and $\pm 0.49$.
- Low degree: When the value is below $+0.29$.

In this study a p-value less than 0.05 was considered significant.

3. RESULTS

3.1. Process performance in the WWTP

The WWTP of Girona presented a $91\% \pm 6\%$, $87\% \pm 5\%$, and $98\% \pm 1\%$ COD, TKN, and P-PO$_4^3$ removal, respectively, during the monitoring period. The plug-flow bioreactors operated correctly following regular patterns. The main characteristics of the influent wastewater and treated effluent as well as some process parameters are summarised in Table 1.
3.2. Spatial and temporal $\text{N}_2\text{O}$ and $\text{CH}_4$ emission patterns

$\text{N}_2\text{O}$ and $\text{CH}_4$ emissions were monitored across the first three aerobic sections of one of the plug-flow bioreactors from November 2016 through March 2017. To ease the comparison of the data collected, it was grouped into 6 or 7-day periods and total emissions as well as emission factors were calculated for each of these periods. Figure 4 shows an example of three different periods distributed across the monitoring period. $\text{N}_2\text{O}$ emissions showed a different pattern among the three zones. $\text{N}_2\text{O}$ emissions from the first aeration zone were nearly negligible during the monitoring period. However, aerobic zones 2 and 3 presented similar emission profiles, with peaks of $\text{N}_2\text{O}$ occurring on a daily basis. In addition, different temporal emissions were found, with emissions detected in November, a decrease in emissions occurring at the beginning of December until reaching a no emission period that lasted until the end of February. Emissions started again at the end of February and continue to increase until the end of the monitoring period.

Some studies have reported a link between some of the external disturbances to which a WWTP is subjected (low carbon-to-nitrogen ratio in the influent, flow rate, incoming wastewater temperature, mixed liquor sludge retention time, etc.) and the $\text{N}_2\text{O}$ emissions detected (Mannina et al., 2017, 2018a, 2018b; Spinelli et al., 2018; Vasilaki et al., 2018). To determine if any of these parameters had an effect on the emissions detected in this study, a statistical analysis using Pearson's correlation coefficients was conducted between some measured variables and the total $\text{N}_2\text{O}$ and $\text{CH}_4$ emissions (Table 2).

The only significant correlation found was between the $\text{N}_2\text{O}$ emissions and wastewater temperature (Pearson correlation index ($r$) = 0.583; $p=0.003$). The coldest wastewater temperature (Figure S1, in Supplementary Material) occurred during the months with no
N$_2$O emissions (December and January). However, despite this correlation, it is difficult to establish a direct link between temperature and N$_2$O because temperature affects many other processes that can also affect N$_2$O emissions, such as the nitrification rate. All the other investigated parameters did not show a strong correlation with N$_2$O emissions. No significant correlations were found for either case of CH$_4$ emissions when compared to the wastewater flow rate, temperature, or COD load.

Table 3 summarises the amount of N$_2$O and CH$_4$ emitted from each hood for seven periods between November and March. Regarding N$_2$O, the fact that no emissions were detected in aerobic zone 1 indicates that no significant N$_2$O had accumulated in the previous anoxic zones. The highest emissions were found in aerobic zone 2 during the whole monitoring period (Table 3 and Table S1 in the Supplementary Material).

However, methane emissions were similar throughout the monitoring period and did not present a clear daily pattern (Figure 5 and Table 3). CH$_4$ decreased along the plug-flow bioreactor showing higher emissions in the first aerated zone than in the second and third.

The N$_2$O and CH$_4$ emission factors were also calculated for each period and are shown in Table 4.

The N$_2$O emission factor ranged from 0%–0.13% of the TKN load but presented a high fluctuation, decreasing to 0 during the months of December and January. However, the CH$_4$ emission factor was maintained relatively constant ranging between 0.28% (during the coldest months) and 0.49%.

3.3. Factors affecting N$_2$O and CH$_4$ emissions

There are many operational factors that can have an influence on N$_2$O and CH$_4$ emissions. In this section the main contributing factors affecting the emissions detected are discussed.
3.3.1. N$_2$O daily emission patterns

All the N$_2$O emissions found depicted a very similar daily fluctuation, with N$_2$O emitted in the form of a peak. When analysing more in depth the emissions from different periods, two slightly different N$_2$O emission patterns were detected during the monitoring period. Figure 6 presents two 6-day period profiles in which N$_2$O emissions are depicted together with the NH$_4^+$ concentration profile obtained from aerobic zone 2. The emission profile found during November (Figure 6a) shows a significant correlation between the NH$_4^+$ concentration profile and the N$_2$O emission profile (Pearson correlation index (r)=0.80; $p=0.029$). When NH$_4^+$ started increasing there was an immediate increase in N$_2$O in the form of a peak that decreased to undetectable levels when the NH$_4^+$ was depleted. However, this pattern changed during March, when N$_2$O emissions started again in aeration zone 2 after a period without emissions (Figure 6b). The N$_2$O peaks were lower and started with an increase in NH$_4^+$ but decreased before the NH$_4^+$ was depleted. In this case, the correlation between the NH$_4^+$ and the N$_2$O emissions was not significant (r=0.326, $p=0.475$). The reason behind the differences in the N$_2$O emission patterns from November and March are unknown. The emissions from November are correlated with the presence of NH$_4^+$ in the monitored zone, suggesting that N$_2$O is produced during nitrification of the NH$_4^+$. However, emissions from March only occur when the NH$_4^+$ enters the monitored zone, sharply decreasing long before the NH$_4^+$ is depleted. In this case, the N$_2$O peak emission could be related to transient conditions rather than nitrification.

To further explore the correlation of this N$_2$O peak with not only NH$_4^+$ but other dissolved nitrogen compounds, a 24-h grab sampling study was conducted in the aerobic zone 2 during this last period (March). Results are shown in Figure 7.
NH₄⁺ concentration started increasing at approximately 9 am until reaching a concentration of 8.5 mg N/L at approximately 3 pm. It maintained this level until it began to decreasing at 12 am reaching its lowest levels at approximately 8 am. The NO₃⁻ remained stable at very low levels until 12 am when it increased coinciding with the NH₄⁺ decrease. Interestingly, N₂O sharply increased as soon as the NH₄⁺ increased but this increase only lasted for 2 h, decreasing afterwards until reaching negligible emissions at approximately 6 pm. The NO₂⁻ concentration remained stable at very low levels (0.02–0.04 mg N-NO₂⁻/L). Similar profiles were observed in other 24-h intensive monitoring samplings in this zone and in aerobic zone 3 (Figure S2, Supplementary Material).

3.3.2. CH₄ daily emission patterns

The highest emissions of CH₄ were found in the first aerobic zone, decreasing as the wastewater flow moved towards the end of the plug-flow bioreactor. Because formation of CH₄ requires anaerobic conditions, it was assumed that this CH₄ was produced in previous compartments of the WWTP and was stripped in the aerated zones. To determine its origin, dissolved CH₄ samples were collected from different locations at the WWTP (locations shown in Figure 1). The highest dissolved CH₄ values were found in the reject wastewater stream originating from the anaerobic digesters (0.52 ± 0.22 mg CH₄-COD/L) which was pumped again to the inlet of the plant, and also in the municipal wastewater arriving to the plant from the sewer network (0.55 ± 0.19 mg CH₄-COD/L). Before entering the plug-flow bioreactor, the dissolved CH₄ was 0.45 ± 0.05 mg CH₄-COD/L decreasing to 0.13 mg CH₄-COD/L in anoxic zone 2. These values were even lower in the aerobic zones of the plug-flow bioreactor (0.04, 0.02, and below detection limit in aerobic zones 1, 2 and 3, respectively), showing the same
spatial variation pattern shown in Figure 5. As opposed to N₂O, no link was found between these emissions and any parameter measured in the bioreactor.

3.4. Carbon footprint of the plug-flow bioreactors

The C-footprint of a WWTP can be calculated considering the CO₂ emissions from the plant. These emissions can be classified into direct emissions (N₂O and CH₄) and indirect emissions (from the electricity consumption of the plant). In this study, a dynamic C-footprint of the plug-flow bioreactors was calculated considering the variations in direct emissions and in electricity consumption during the monitoring period.

The electricity consumption of the two plug-flow bioreactors operating in the plant was provided on a daily basis by the plant operators. The consumption for the seven periods presented in this study was calculated and was relatively constant (Figure 8a). The electricity consumed was transformed to indirect CO₂ emissions using the standard conversion factor of 0.308 kg CO₂/kWh which is the amount of CO₂ emitted during energy generation in Spain for 2016 according to the Catalan Office for Climate Change (OCCC) (Oficina Catalana del Canvi Climàtic, 2017).

Direct CO₂ emissions were calculated by multiplying the N₂O or CH₄ emissions by their GWP and then dividing by the wastewater treated (Equations 5 and 6 in the Materials and Methods).

To calculate the total direct emissions, it was assumed that the emissions of the studied treatment line were identical to those emitted by the other line. This assumption is justified by the fact that both bioreactors were treating the same amount of wastewater and had the same operational conditions.

Figure 8b shows a comparison of the direct and indirect CO₂ emissions. During the whole monitoring period, direct CO₂ emissions were responsible for the majority of the
C-footprint of the bioreactor. CH\textsubscript{4} was the major contributor to direct emissions accounting for 45\% and 57\% of the total emissions. N\textsubscript{2}O accounted for 15\% of the total emissions during November and March but was nearly negligible during the other months.

4. DISCUSSION

4.1. Methodology for quantifying GHG direct emissions

Many monitoring campaigns to quantify N\textsubscript{2}O emissions have been conducted during the last decade, initially focused mainly on obtaining emission factors and later trying to determine the factors affecting these emissions (Ahn et al., 2010b; Butler et al., 2009; Kampschreur et al., 2008; Rodriguez-Caballero et al., 2015). In some of the initial studies, a grab sample approach was used (Czepiel et al., 1995; Foley et al., 2010; Ye et al., 2014) but online monitoring has showed large variations in N\textsubscript{2}O which could not be captured using the grab sample methodology. From these studies, an emission range for N\textsubscript{2}O has been identified, which for most of the municipal WWTPs remains between 0 and 2.5\% of the incoming N-load. Despite this progress, it remains difficult to assess what causes the detected variations in N\textsubscript{2}O and it is very challenging to extrapolate the findings from one plant to another, making the design and implementation of mitigation strategies case specific. Table 5 summarises some of the full-scale monitoring campaigns conducted worldwide for full-scale municipal WWTPs of different configurations. Only studies using online monitoring have been considered.

Most of the monitoring campaigns conducted to date only describe emissions over a relatively short period of time ranging from 1 to 2 days to 2 months. One of the few long term studies conducted by Daelman et al. (2015) in a WWTP from the Netherlands over 16 months showed significant differences in N\textsubscript{2}O emissions throughout the year obtaining the highest emissions during April-May while barely any emission was
detected during November-December. The results presented in this manuscript also show high temporal variations among the five months monitored, highlighting the importance of long-term monitoring campaigns to reliably identify the N$_2$O emission patterns from one plant. Given this, the implementation of long-term monitoring campaigns at full-scale can be more challenging and definitely more costly than short-term campaigns. The data presented, however, shows high repeatability in the daily profiles for a short period of time (2 to 3 weeks). Therefore, long-term monitoring could be simplified by monitoring 1 week per month which would provide sufficient data to accurately estimate temporal variations.

The monitoring methodology can also influence the emission data obtained. The majority of studies use one floating hood placed in the surface of the bioreactor connected to an online analyser to quantify emissions (Table 5). However, gradients in nitrogen species concentrations, DO, solid concentrations, etc. can be found in many bioreactor configurations such as plug-flow systems, which are widely used for municipal wastewater treatment. In these systems, strong spatial variations in N$_2$O emissions have been reported which are difficult to accurately quantify. To improve this monitoring approach, Pan et al. (2016) developed a multiple gas collection hood system to simultaneously measure N$_2$O emissions along the length of a step-feed plug-flow bioreactor. Three different locations along the plug-flow were simultaneously studied and the highest N$_2$O emissions were recorded 50 m from the beginning of the aeration zone in the first step feed and at the beginning of the aerated zone in the second step feed. Using a similar multiple hood approach, this study found the highest N$_2$O emissions in the second aerobic zone, indicating that N$_2$O was produced in this compartment during nitrification and not in the anoxic zone. Once again, these reports show differential emission hotspots for plug-flow systems, stressing the need for
simultaneously monitoring multiple sites to identify where the majority of the emissions are occurring.

Much less information is available on \( \text{CH}_4 \) emissions from wastewater treatment despite its potential contribution to the C-footprint of the plant, and these can be much higher than those related to \( \text{N}_2\text{O} \), in particular in those plants in which sludge anaerobic digestion is in place. In 2012, Daelman and co-workers published the most comprehensive study of \( \text{CH}_4 \) emission quantification from a WWTP treating municipal wastewater. They found that the main source of \( \text{CH}_4 \) was the anaerobic digester. In their study, diurnal variability was reportedly linked to the diurnal pattern of the influent flow. However, no spatial variability was found because the bioreactors were covered. Rodriguez-Caballero et al. (2014) also monitored \( \text{CH}_4 \) emissions from a plug-flow bioreactor from a WWTP equipped with an anaerobic digester over 10 weeks. They found strong spatial variability, with the first aerobic zone emitting the majority of the \( \text{CH}_4 \). In this study, spatial variation was also observed along the plug-flow bioreactor with larger \( \text{CH}_4 \) emissions in the first aerated zone and diminishing through the second and third aeration zones. \( \text{CH}_4 \) arrived dissolved with the inlet wastewater and reject wastewater originating from the anaerobic digestion process.

4.2. Factors affecting GHG emission and possible mitigation strategies

This section discusses the main contributing factors to the GHG emissions detected and suggests possible operational strategies to minimise them.

4.2.1. \( \text{N}_2\text{O} \) emission and mitigation

\( \text{N}_2\text{O} \) emissions were only observed during November and March and were not detected during the coldest months of the monitoring period (December through February). A possible explanation for this could be the temperature of the wastewater that reached lower than 18 °C. Several studies have shown that the \( \text{NH}_4^+ \) oxidation rate decreases by
50% when the temperature decreases to lower than 20 °C (Weon et al., 2004; Bao et al., 2018). In addition, Law et al. (2012b) demonstrated an exponential relationship between the NH$_4^+$ oxidation rate and N$_2$O emissions in a highly enriched AOB population. Thus, it is possible that the NH$_4^+$ oxidation rate decreased during the coldest months, slowing down the nitrification process and avoiding emissions. Unfortunately, this cannot be validated because no nitrification kinetics were studied in the plant and the same high level of NH$_4^+$ removal was achieved by the WWTP during the entire monitoring period. When emissions occurred, two different N$_2$O profiles were observed (Figure 6). Emissions detected during November occurred while NH$_4^+$ was present, indicating that they were related to the nitrification process. However, emissions detected during March only occurred when NH$_4^+$ arrived at the location of the hood and decreased long before the NH$_4^+$ was depleted. These emissions might be linked to transient conditions as suggested by Yu et al. (2010), who found that N$_2$O production by AOB could be stimulated when there was a sudden shift from a low-activity period (for example, without NH$_4^+$) to a high-activity period (with NH$_4^+$). The difference in the N$_2$O emission patterns detected between November and March could be attributed to a change in the DO control applied in the WWTP that was implemented during January. During November, the DO concentration in the first aerobic zone was approximately 2.5 and during March this was controlled at approximately 1.5. A higher DO concentration favours higher NH$_4^+$ oxidation rates which can incur higher N$_2$O emissions during nitrification. Limiting the DO to a certain extent could minimise the emissions but attention should be paid to ensure complete nitrification and avoiding NO$_2^-$ accumulation.

4.2.2. CH$_4$ emission and mitigation
Results from this study indicate that CH$_4$ was not produced in the plug-flow bioreactor but was already present in the incoming wastewater. This is not surprising because production of CH$_4$ via biological processes requires strict anaerobic conditions that were not found in the plug-flow system. Dissolved CH$_4$ was detected in the municipal wastewater entering the plant and also in the reject wastewater stream originating from the anaerobic digesters, which was recirculated back to the inlet of the wastewater treatment processes because of the high NH$_4^+$ levels present in this stream.

The presence of dissolved CH$_4$ in wastewater was first reported in 2008 by Guisasola and co-authors (Guisasola et al., 2008). Further research has shown that archaeal communities can develop in mature sewer network biofilms and benefit from the anaerobic conditions present in some parts of these systems to transform COD into CH$_4$ (Auguet et al., 2015a). Fortunately, the production of this CH$_4$ can be prevented by the addition of different products such as NO$_3^-$, NO$_2^-$ or O$_2$, which are normally used to also control sulphide emissions from sewer networks (Jiang et al. 2010; Auguet et al. 2015). Therefore, a reduction in CH$_4$ present in the incoming wastewater is possible.

However, it is not possible to avoid the presence of dissolved CH$_4$ in the reject wastewater stream because it mainly originates in the anaerobic digester, where CH$_4$ production is enhanced and wastewater saturation cannot be avoided. Removal of dissolved methane is possible by applying several technologies such as membrane separation but their economic viability has not been fully demonstrated (Liu et al., 2014).

Overall, knowing how and where emissions occur allows design of effective mitigation strategies to control these emissions, promoting a sustainable wastewater management. This is important in the context of reducing current and future global warming which will only be achieved if all the industry sectors take responsibility for their GHG
emissions. However, if there is not an economic or legal incentive, the implementation of these strategies will be limited if they are not associated with other benefits.

5. CONCLUSIONS

This study provides a comprehensive set of N\textsubscript{2}O and CH\textsubscript{4} emission data from a five months continuous monitoring campaign conducted using a multiple hood system in a plug-flow bioreactor treating municipal wastewater from a full-scale WWTP. Also, mitigation actions are proposed to help wastewater authorities achieving more sustainable operation in their WWTPs while ensuring good effluent quality. The main conclusions are summarised as follows:

- The N\textsubscript{2}O emissions showed strong temporal variations, with no emissions detected during December and January, probably due to a decrease in the wastewater temperature that decreased the nitrification rate. However, CH\textsubscript{4} emissions were relatively constant during the monitoring period.

- Spatial variations were found for both gases across the aerated zones of the plug-flow bioreactor. CH\textsubscript{4} emissions decreased along the aeration path of the plug-flow bioreactor because of the stripping of the dissolved CH\textsubscript{4}. However, the highest N\textsubscript{2}O emissions were found in the second aerobic zone and started when the NH\textsubscript{4}\textsuperscript{+} reached the compartment.

- Two different N\textsubscript{2}O emission patterns were found during the monitoring period. In November N\textsubscript{2}O emissions occurred while NH\textsubscript{4}\textsuperscript{+} was present in the monitored zone indicating a direct link with the nitrification activity. However, in March, N\textsubscript{2}O emissions occurred when NH\textsubscript{4}\textsuperscript{+} arrived at the location of the hood and decreased long before the NH\textsubscript{4}\textsuperscript{+} was depleted suggesting that transient conditions were responsible for these emissions.
- The CH\textsubscript{4} emissions accounted for the majority of the C-footprint of the plug-flow bioreactor, largely overcoming those of N\textsubscript{2}O. These emissions were higher than the indirect emissions associated with electricity consumption.

Acknowledgements

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<table>
<thead>
<tr>
<th><strong>Influent wastewater</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow (m\textsuperscript{3}/day)</td>
<td>42801.26 ± 1361.87</td>
</tr>
<tr>
<td>COD (mg COD/L)</td>
<td>411.58 ± 39.42</td>
</tr>
<tr>
<td>TKN (mg N/L)</td>
<td>44.05 ± 2.24</td>
</tr>
</tbody>
</table>
$PO_4^{3-}$-P (mg P/L) 5.20 ± 0.27
pH 7.71 ± 0.18

**Plug-flow reactor monitored**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MLSS (mg/L)</td>
<td>3813.89 ± 207.1</td>
</tr>
<tr>
<td>MLVSS/MLSS (%)</td>
<td>75.06 ± 1.87</td>
</tr>
<tr>
<td>HRT (h)</td>
<td>15.88 ± 0.75</td>
</tr>
<tr>
<td>SRT (d)</td>
<td>19.27 ± 0.62</td>
</tr>
</tbody>
</table>

**Treated Effluent**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg COD/L)</td>
<td>25.84 ± 2.21</td>
</tr>
<tr>
<td>TN (mg N/L)</td>
<td>8.28 ± 1.16</td>
</tr>
<tr>
<td>$PO_4^{3-}$-P (mg P/L)</td>
<td>0.13 ± 0.03</td>
</tr>
</tbody>
</table>

Data provided by plant operators. Data corresponds to an average of 151 values obtained from samples distributed across the experimental period.

**Table 2.** Pearson's correlation coefficient $r$ and $p$-value between the plug-flow $N_2O$ and $CH_4$ emission's factor and different variables.

<table>
<thead>
<tr>
<th></th>
<th>Units</th>
<th>$r$</th>
<th>$p$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2O$</td>
<td>Influent flow rate</td>
<td>m$^3$/day</td>
<td>0.245</td>
</tr>
<tr>
<td></td>
<td>Wastewater temperature</td>
<td>ºC</td>
<td>0.583</td>
</tr>
<tr>
<td></td>
<td>TKN load of the reactor</td>
<td>kg N/L</td>
<td>-0.166</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>Influent flow rate</td>
<td>m$^3$/day</td>
<td>-0.172</td>
</tr>
<tr>
<td></td>
<td>Wastewater temperature</td>
<td>ºC</td>
<td>0.118</td>
</tr>
<tr>
<td></td>
<td>COD load of the reactor</td>
<td>kg COD/L</td>
<td>0.149</td>
</tr>
</tbody>
</table>

**Table 3.** $N_2O$ and $CH_4$ production in aerobic zones 1, 2 and 3 from different periods comprised between November and March.
Table 4. N₂O and CH₄ emission factors from different periods comprised between November and March.

<table>
<thead>
<tr>
<th>Date</th>
<th>N₂O emission factor (%)</th>
<th>CH₄ emission factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15/11/2016-22/11/2016</td>
<td>0.13 ± 0.04</td>
<td>0.46 ± 0.12</td>
</tr>
<tr>
<td>25/11/2016-01/12/2016</td>
<td>0.03 ± 0.01</td>
<td>0.38 ± 0.04</td>
</tr>
<tr>
<td>15/12/2016-22/12/2016</td>
<td>0.00 ± 0.00</td>
<td>0.28 ± 0.03</td>
</tr>
<tr>
<td>13/01/2017-19/01/2017</td>
<td>0.00 ± 0.00</td>
<td>0.36 ± 0.03</td>
</tr>
<tr>
<td>15/02/2017-22/02/2017</td>
<td>0.00 ± 0.00</td>
<td>0.43 ± 0.09</td>
</tr>
<tr>
<td>26/02/2017-05/03/2017</td>
<td>0.02 ± 0.01</td>
<td>0.46 ± 0.08</td>
</tr>
<tr>
<td>09/03/2017-16/03/2017</td>
<td>0.08 ± 0.02</td>
<td>0.49 ± 0.08</td>
</tr>
</tbody>
</table>
Table 5. Summary of several monitoring campaigns conducted in municipal WWTPs.

<table>
<thead>
<tr>
<th>Process</th>
<th>Emission factors</th>
<th>Monitoring Methodology</th>
<th>Length of the study</th>
<th>Contribution to total C-footprint</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banderpho BNR</td>
<td>0.16%±0.1% N₂O</td>
<td>1 floating gas hood</td>
<td>24 h (winter)</td>
<td>N.Q.</td>
<td>(Ahn et al., 2010a)</td>
</tr>
<tr>
<td></td>
<td>N.Q. CH₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plug-flow</td>
<td>0.4%±0.14% N₂O</td>
<td>1 floating gas hood</td>
<td>24 h (winter)</td>
<td>N.Q.</td>
<td>(Ahn et al., 2010a)</td>
</tr>
<tr>
<td></td>
<td>N.Q. CH₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Step-feed</td>
<td>0.18%±0.18% N₂O</td>
<td>1 floating gas hood</td>
<td>24 h (winter)</td>
<td>N.Q.</td>
<td>(Ahn et al., 2010a)</td>
</tr>
<tr>
<td></td>
<td>N.Q. CH₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carrussel+plug-flow (both covered)</td>
<td>N.Q. CH₄</td>
<td>1.13% off-gas from reactors sent to continuous analyser</td>
<td>11 months</td>
<td>64% from CH₄</td>
<td>(Daelman et al., 2012)</td>
</tr>
<tr>
<td></td>
<td>N.Q. CH₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carrussel+plug-flow (both covered)</td>
<td>N.Q. CH₄</td>
<td>2.8% off-gas from reactors sent to continuous analyser</td>
<td>16 months</td>
<td>N.Q.</td>
<td>(Daelman et al., 2015)</td>
</tr>
<tr>
<td></td>
<td>N.Q. CH₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plug-flow</td>
<td>0.036% N₂O</td>
<td>1 floating gas hood</td>
<td>2 months (August-Oct)</td>
<td>N.Q.</td>
<td>(Aboobakar et al., 2013)</td>
</tr>
<tr>
<td></td>
<td>N.Q. CH₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plug-flow</td>
<td>0.116% N₂O</td>
<td>1 floating gas hood</td>
<td>10 weeks (June-Oct)</td>
<td>N.Q.</td>
<td>(Rodriguez-Caballero et al., 2015)</td>
</tr>
<tr>
<td></td>
<td>0.016% CH₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process Type</td>
<td>Mass Balance Loss (%)</td>
<td>Monitoring Method</td>
<td>Duration</td>
<td>Nitrogen Source</td>
<td>Reference</td>
</tr>
<tr>
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<tr>
<td>Oxidation ditch with surface aerators</td>
<td>0.52%±0.16%</td>
<td>online monitoring, offline sampling, mathematical modelling and oxygen balance</td>
<td>1 month (Oct-Nov)</td>
<td>N.Q.</td>
<td>(Ye et al., 2014)</td>
</tr>
<tr>
<td>SBR</td>
<td>6.8%</td>
<td>1 floating gas hood</td>
<td>1 month (Feb-March)</td>
<td>60% from N\textsubscript{2}O</td>
<td>(Rodriguez-Caballero et al., 2015)</td>
</tr>
<tr>
<td>Step-feed Plug-flow</td>
<td>1.9%±0.25%</td>
<td>3 floating gas hoods</td>
<td>7 weeks</td>
<td>N.Q.</td>
<td>(Pan et al., 2016)</td>
</tr>
<tr>
<td>A2O</td>
<td>1.29%±1.07%</td>
<td>2 floating gas hoods</td>
<td>12 months</td>
<td>N.Q.</td>
<td>(Wang et al., 2016b)</td>
</tr>
<tr>
<td>Aerated filter</td>
<td>0.017%-1.261%</td>
<td>2 floating gas hoods</td>
<td>12 months</td>
<td>N.Q.</td>
<td>(Wang et al., 2016a)</td>
</tr>
<tr>
<td>Nitrifying biofilter</td>
<td>2.26%±0.46%</td>
<td>1 floating gas hood</td>
<td>1 week summer</td>
<td>N.Q.</td>
<td>(Bollon et al., 2014)</td>
</tr>
<tr>
<td>Plug-flow</td>
<td>0%-0.13%</td>
<td>0.28% - 0.49%</td>
<td>3 floating gas hoods</td>
<td>5 months (Nov-March)</td>
<td>45%-57% from CH₄</td>
</tr>
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<td>----------------------</td>
<td>----------------------</td>
<td>----------------</td>
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<tr>
<td>2 weeks winter</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2016)</td>
<td></td>
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</tbody>
</table>
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Figure 1. Scheme of the configuration of the WWTP of Girona (the plug-flow reactor line that is not operative is marked in grey; the red dots represent the locations where samples for dissolved CH₄ analyses were collected in the plug-flow reactor that was monitored).

Figure 2. Plug-flow bioreactor configuration and study zones. The black dots represent the plant DO sensors in aeration zones 1 and 4. The grey rectangles represent the online ammonia sensors at the inlet of the plug-flow reactor and in aeration zone 2. The white dots represent the location where the gas hoods were placed. The arrows represent the direction of the wastewater flow.

Figure 3. Multiple hood gas collection system. The gas arrives from the hoods via gas tubing (1) and passes through temperature (2) and pressure (3) sensors and a gas flowmeter (4) before arriving to the online gas analyser (5). An Arduino system controls the opening of the electro valves allowing the gas flux to pass into the analyser.

Figure 4. N₂O emissions from aerobic zones 1, 2, and 3 of the plug-flow bioreactor in November (left), January (centre), and March (right).

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Figure 7. Daily N₂O (—), NH₄⁺ (●), NO₂⁻ (▲), and NO₃⁻ (○) concentration profiles measured in aerobic zone 2 on the 7th and 8th of March.

Figure 8. Electricity consumption (a) and direct and indirect CO₂ emissions (b) from the plug-flow bioreactor of the WWTP during the monitoring period.
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Figure 7. Daily $\text{N}_2\text{O}$ (---), $\text{NH}_4^+$ (●), $\text{NO}_2^-$ (▲), and $\text{NO}_3^-$ (○) concentration profiles measured in aerobic zone 2 on the 7th and 8th of March.
Figure 8. Electricity consumption (a) and direct and indirect CO₂ emissions (b) from the plug-flow bioreactor of the WWTP during the monitoring period.
Highlights

- Temporal and spatial GHG emissions monitored in a plug-flow full-scale bioreactor
- N\textsubscript{2}O emissions present temporal and spatial variability with periods of no emission
- N\textsubscript{2}O emissions were linked to the arrival of ammonium in the monitored zone
- Constant temporal CH\textsubscript{4} emissions were detected, showing only spatial variability
- CH\textsubscript{4} was the main contributor to the C-footprint, overcoming indirect emissions