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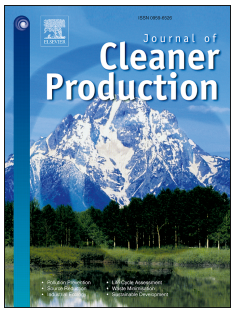

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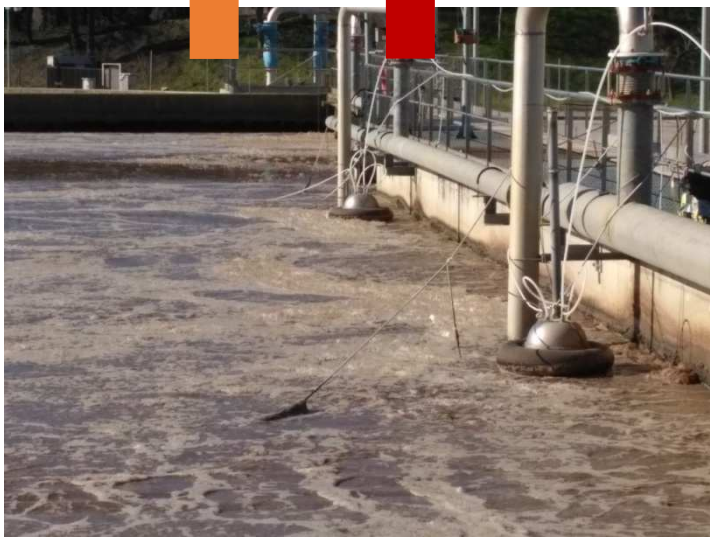
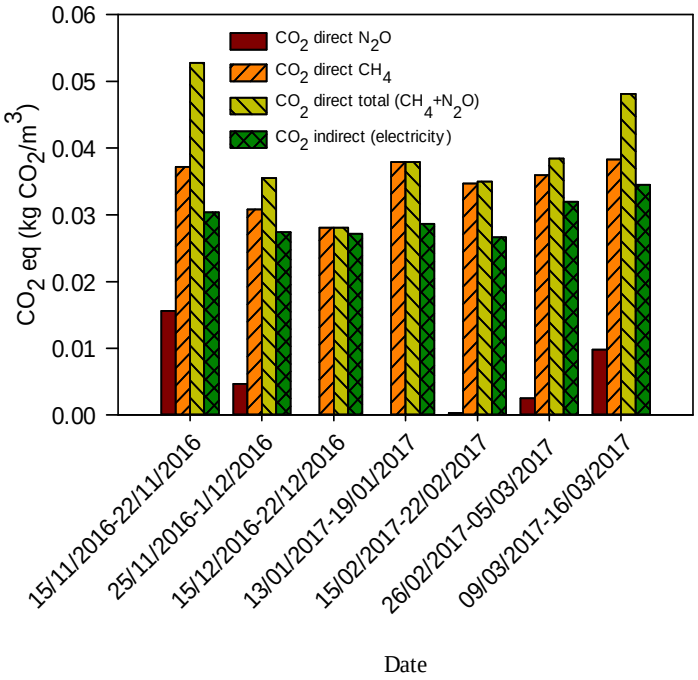
Declarations of interests: none

Daily emissions monitored during 5 months

CH_4 N_2O



C- footprint



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ABSTRACT

Fugitive greenhouse gas (GHG) emissions in the form of nitrous oxide (N_2O) and methane (CH_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_2O and CH_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_2O emissions with N_2O 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_2O emissions detected in the second aerated zone. A daily N_2O emission pattern was characterised by an N_2O peak correlated with the ammonium that arrived in the monitored zone. However, CH_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_2O 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_2O) 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_2O 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_2O 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_2O as intermediates. There are

several factors affecting the accumulation of N_2O 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_2^-) (Law et al., 2012a).

Although there has been considerable research regarding N_2O 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_2O emissions in WWTPs. Normally, these emissions are reported as N_2O emission factors, which represent the percentage of the average influent Total Kjeldahl Nitrogen (TKN) load being emitted as N_2O. Results from the literature show a wide range of N_2O emission factors (0.036%–6.8%) and distinctive N_2O 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_2O emissions along a plug-flow bioreactor. N_2O 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 N_2O, it is also well known that WWTPs emit methane (CH_4). This GHG has a GWP 21 times higher than that of CO_2 (IPCC, 2014) and is the second most important GHG after CO_2. CH_4 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 CH_4 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 CH_4 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 CH_4 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 N_2O and CH_4 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 N_2O but also for CH_4 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_2O and CH_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_2O 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_2O, CH_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_2O in N_2 gas standard, 160 ppmv CH_4 in N_2 gas standard, 21% oxygen (O_2) in N_2 gas standard, and N_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 24h the 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_2O and CH_4 emission factors

To calculate the N_2O and CH_4 emission factors, equations 1 and 2 were used (Rodriguez-Caballero et al., 2014) as follows:

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

where

$C_{N-N_2O} = C_{N-N_2O}$ (ppmv) · N_2O molar volume (0.0402 at 1atm and 25°C) · 10^{-6} ·

$$28 \left(g\, N - N2O / L \right) \quad \text{(Eq. 2)}$$

Q_{gas} is the gas flow rate (L/min),

Δt is the time interval by which the off-gas N_2O was recorded,

$A_{zone\ i}$ is the area of the zone of the plug-flow bioreactor where hood *i* was placed, and

$A_{hood\ i}$ 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_2O emission factor was calculated as a percentage of the average influent TKN load of the WWTP emitted as N_2O (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).

$$N_2O\ Emission\ factor\ (\%) = \frac{N_2O\ emitted}{TKN\ load} * 100 * 2 \quad \text{(Eq. 3)}$$

$$CH_4\ Emission\ factor\ (\%) = \frac{CH_4\ emitted}{DQO\ load} * 100 * 2 \quad \text{(Eq. 4)}$$

where

the TKN load corresponds to the same time interval Δt

2.4.2. Conversion of N_2O and CH_4 into CO_2 equivalents

CO_2 equivalents for the N_2O and CH_4 emissions found in this study were calculated as follows:

$$N_2O\ as\ CO_2\ equivalents\ (KgCO_2/m^3) = \frac{N_2O\ emitted\ (Kg\ N/d)}{Influent\ wastewater\ flow\ (m^3/d)} * 298 * 2$$

(Eq. 5)

$$CH_4\ as\ CO_2\ equivalents\ (KgCO_2/m^3) = \frac{CH_4\ emitted\ (Kg/d)}{Influent\ wastewater\ flow\ (\frac{m^3}{d})} * 21 * 2$$

(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):

$$r = \frac{\sigma_{x,y}}{\sigma_x \cdot \sigma_y} \qquad \text{(Eq. 7)}$$

where

$\sigma_{x,y}$ is the covariance of variables x and y,

σ_x is the standard deviation of x,

σ_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 ± 1.

High degree: If the coefficient value is between ± 0.50 and ± 1.

Moderate degree: If the value is between ± 0.30 and ± 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%±6%, 87%±5%, and 98%±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 N_2O and CH_4 emission patterns

N_2O and 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. N_2O emissions showed a different pattern among the three zones. N_2O 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 N_2O 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 N_2O 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 N_2O and CH_4 emissions (Table 2).

The only significant correlation found was between the N_2O 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_2O emissions (December and January). However, despite this correlation, it is difficult to establish a direct link between temperature and N_2O because temperature affects many other processes that can also affect N_2O emissions, such as the nitrification rate. All the other investigated parameters did not show a strong correlation with N_2O 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_2O and CH_4 emitted from each hood for seven periods between November and March. Regarding N_2O, the fact that no emissions were detected in aerobic zone 1 indicates that no significant N_2O 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_2O and CH_4 emission factors were also calculated for each period and are shown in Table 4.

The N_2O 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_2O and CH_4 emissions

There are many operational factors that can have an influence on N_2O and CH_4 emissions. In this section the main contributing factors affecting the emissions detected are discussed.

3.3.1. N_2O daily emission patterns

All the N_2O emissions found depicted a very similar daily fluctuation, with N_2O emitted in the form of a peak. When analysing more in depth the emissions from different periods, two slightly different N_2O emission patterns were detected during the monitoring period. Figure 6 presents two 6-day period profiles in which N_2O 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_2O emission profile (Pearson correlation index (r)=0.80; p=0.029). When NH_4^+ started increasing there was an immediate increase in N_2O 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_2O emissions started again in aeration zone 2 after a period without emissions (Figure 6b). The N_2O 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_2O emissions was not significant (r=0.326, p=0.475). The reason behind the differences in the N_2O 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_2O 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_2O peak emission could be related to transient conditions rather than nitrification.

To further explore the correlation of this N_2O 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.

NH_4^+ 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 NO_3^- remained stable at very low levels until 12 am when it increased coinciding with the NH_4^+ decrease. Interestingly, N_2O sharply increased as soon as the NH_4^+ increased but this increase only lasted for 2 h, decreasing afterwards until reaching negligible emissions at approximately 6 pm. The NO_2^- concentration remained stable at very low levels (0.02–0.04 mg $N\text{-}NO_2^-/L$). 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. CH_4 daily emission patterns

The highest emissions of CH_4 were found in the first aerobic zone, decreasing as the wastewater flow moved towards the end of the plug-flow bioreactor. Because formation of CH_4 requires anaerobic conditions, it was assumed that this CH_4 was produced in previous compartments of the WWTP and was stripped in the aerated zones. To determine its origin, dissolved CH_4 samples were collected from different locations at the WWTP (locations shown in Figure 1). The highest dissolved CH_4 values were found in the reject wastewater stream originating from the anaerobic digesters (0.52 ± 0.22 mg CH_4-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 CH_4-COD /L). Before entering the plug-flow bioreactor, the dissolved CH_4 was 0.45 ± 0.05 mg CH_4-COD/L decreasing to 0.13 mg CH_4-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 N_2O, 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 CO_2 emissions from the plant. These emissions can be classified into direct emissions (N_2O and CH_4) 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 CO_2 emissions using the standard conversion factor of 0.308 kg CO_2/kWh which is the amount of CO_2 emitted during energy generation in Spain for 2016 according to the Catalan Office for Climate Change (OCCC) (Oficina Catalana del Canvi Climàtic, 2017).

Direct CO_2 emissions were calculated by multiplying the N_2O or CH_4 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 CO_2 emissions. During the whole monitoring period, direct CO_2 emissions were responsible for the majority of the

C-footprint of the bioreactor. CH_4 was the major contributor to direct emissions accounting for 45% and 57% of the total emissions. N_2O 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_2O 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_2O which could not be captured using the grab sample methodology. From these studies, an emission range for N_2O 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_2O 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_2O 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_2O 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_2O 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_2O 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_2O 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_2O emissions in the second aerobic zone, indicating that N_2O 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 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 N_2O, 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 CH_4 emission quantification from a WWTP treating municipal wastewater. They found that the main source of 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 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 CH_4. In this study, spatial variation was also observed along the plug-flow bioreactor with larger CH_4 emissions in the first aerated zone and diminishing through the second and third aeration zones. 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. N_2O emission and mitigation

N_2O 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 ºC. Several studies have shown that the NH_4^+ oxidation rate decreases by

50% when the temperature decreases to lower than 20 ºC (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_2O 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_2O 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_2O 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_2O 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_2O 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_2O and CH_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_2O 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_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_4 emissions decreased along the aeration path of the plug-flow bioreactor because of the stripping of the dissolved CH_4. However, the highest N_2O emissions were found in the second aerobic zone and started when the NH_4^+ reached the compartment.
- Two different N_2O emission patterns were found during the monitoring period. In November N_2O emissions occurred while NH_4^+ was present in the monitored zone indicating a direct link with the nitrification activity. However, in March, N_2O emissions occurred when NH_4^+ arrived at the location of the hood and decreased long before the NH_4^+ was depleted suggesting that transient conditions were responsible for these emissions.

- The CH_4 emissions accounted for the majority of the C-footprint of the plug-flow bioreactor, largely overcoming those of N_2O. These emissions were higher than the indirect emissions associated with electricity consumption.

Acknowledgements

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Table 1. Influent and effluent characteristics and process parameters of the WWTP of Girona.

Influent wastewater	
Flow (m^3/day)	42801.26 ± 1361.87
COD (mg COD/L)	411.58 ± 39.42
TKN (mg N/L)	44.05 ± 2.24

PO_4^{3-}-P (mg P/L)	5.20 ± 0.27
pH	7.71 ± 0.18
Plug- flow reactor monitored	
MLSS (mg/L)	3813.89 ± 207.1
MLVSS/MLSS (%)	75.06 ± 1.87
HRT (h)	15.88 ± 0.75
SRT (d)	19.27 ± 0.62
Treated Effluent	
COD (mg COD/L)	25.84 ± 2.21
TN (mg N/L)	8.28 ± 1.16
PO_4^{3-}-P (mg P/L)	0.13 ± 0.03

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.

	Units	**r**	***p*-value**
		N_2O	
Influent flow rate	m^3/day	0.245	0.087
Wastewater temperature	ºC	0.583	0.003
TKN load of the reactor	kg N/L	-0.166	0.499
		CH_4	
Influent flow rate	m^3/day	-0.172	0.234
Wastewater temperature	ºC	0.118	0.593
COD load of the reactor	kg COD/L	0.149	0.356

Table 3. N_2O and CH_4 production in aerobic zones 1, 2 and 3 from different periods comprised between November and March.

	kg N-N_2O produced/day			**kg CH_4 produced/day**		
Date	Aerobic zone 1	Aerobic zone 2	Aerobic zone 3	Aerobic zone 1	Aerobic zone 2	Aerobic zone 3

15/11/2016-22/11/2016	0.02 ± 0.02	0.96 ± 0.35	0.11 ± 0.04	21.88 ± 8.78	15.05 ± 3.96	1.48 ± 0.30
25/11/2016-1/12/2016	0.02 ± 0.02	0.30 ± 0.11	0.01 ± 0.01	22.76 ± 3.62	7.56 ± 0.59	2.02 ± 0.20
15/12/2016-22/12/2016	0.00 ± 0.00	0.00 ± 0.00	0.00 ±0.00	21.54 ± 2.71	6.95 ± 1.34	1.93 ± 0.42
13/01/2017-19/01/2017	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	27.76 ± 2.71	5.97 ± 1.80	1.94 ± 0.45
15/02/2017-22/02/2017	0.00 ± 0.00	0.00 ± 0.00	0.02 ± 0.03	25.63 ± 5.77	7.16 ± 4.39	3.03 ± 1.68
26/02/2017-05/03/2017	0.00 ± 0.00	0.11 ± 0.08	0.06 ± 0.04	19.32 ± 5.87	11.49 ± 1.46	3.69 ± 0.72
09/03/2017-16/03/2017	0.00 ± 0.00	0.36 ± 0.12	0.26 ± 0.12	32.92 ± 6.46	6.65 ± 3.00	3.42 ± 0.54

Table 4. N_2O and CH_4 emission factors from different periods comprised between November and March.

Date	**N_2O emission factor (%)**	**CH_4 emission factor (%)**
15/11/2016-22/11/2016	0.13%±0.04%	0.46%±0.12%
25/11/2016-01/12/2016	0.03%±0.01%	0.38%±0.04%
15/12/2016-22/12/2016	0.00%±0.00%	0.28%±0.03%
13/01/2017-19/01/2017	0.00%±0.00%	0.36%±0.03%
15/02/2017-22/02/2017	0.00%±0.00%	0.43%±0.09%
26/02/2017-05/03/2017	0.02%±0.01%	0.46%±0.08%
09/03/2017-16/03/2017	0.08%±0.02%	0.49%±0.08%

Table 5. Summary of several monitoring campaigns conducted in municipal WWTPs.

Process	Emission factors		Monitoring Methodology	Length of the study	Contribution to total C-footprint	Reference
	N_2O	CH_4				
Banderpho BNR	0.16%±0.1%	N.Q.	1 floating gas hood	24 h (winter)	N.Q.	(Ahn et al., 2010a)
Plug-flow	0.4%±0.14%	N.Q.	1 floating gas hood	24 h (winter)	N.Q.	(Ahn et al., 2010a)
Step-feed	0.18%±0.18%	N.Q.	1 floating gas hood	24 h (winter)	N.Q.	(Ahn et al., 2010a)
Carrussel+plug-flow (both covered)	N.Q.	1.13%	off-gas from reactors sent to continuous analyser	11 moths	64% from CH_4	(Daelman et al., 2012)
Carrussel+plug-flow (both covered)	2.8%	N.Q.	off-gas from reactors sent to continuous analyser	16 months	N.Q.	(Daelman et al., 2015)
Plug-flow	0.036%	N.Q.	1 floating gas hood	2 months (August-Oct)	N.Q.	(Aboobakar et al., 2013)
Plug-flow	0.116%	0.016%	1 floating gas hood	10 weeks (June-Oct)	N.Q.	(Rodriguez-Caballero et al.,

						2014)
Oxidation ditch with surface aerators	0.52%±0.16%	N.Q.	online monitoring, offline sampling, mathematical modelling and oxygen balance	1 month (Oct-Nov)	N.Q.	(Ye et al., 2014)
SBR	6.8%	0.02	1 floating gas hood	1 month (Feb-March)	60% from N_2O	(Rodriguez-Caballero et al., 2015)
Step-feed Plug-flow	1.9%±0.25%	N.Q.	3 floating gas hoods	7 weeks	N.Q.	(Pan et al., 2016)
A2O	1.29%±1.07%	N.Q.	2 floating gas hoods	12 months	N.Q.	(Wang et al., 2016b)
Aerated filter	0.017%-1.261%	N.Q.	2 floating gas hoods	12 months	N.Q.	(Wang et al., 2016a)
Nitrifying biofilter	2.26%±0.46%	N.Q.	1 floating gas hood	1 week summer	N.Q.	(Bollon et al.,

				2 weeks winter		2016)
Plug-flow	0%-0.13%	0.28% - 0.49%	3 floating gas hoods	5 months (Nov-March)	45%-57% from CH_4	This study

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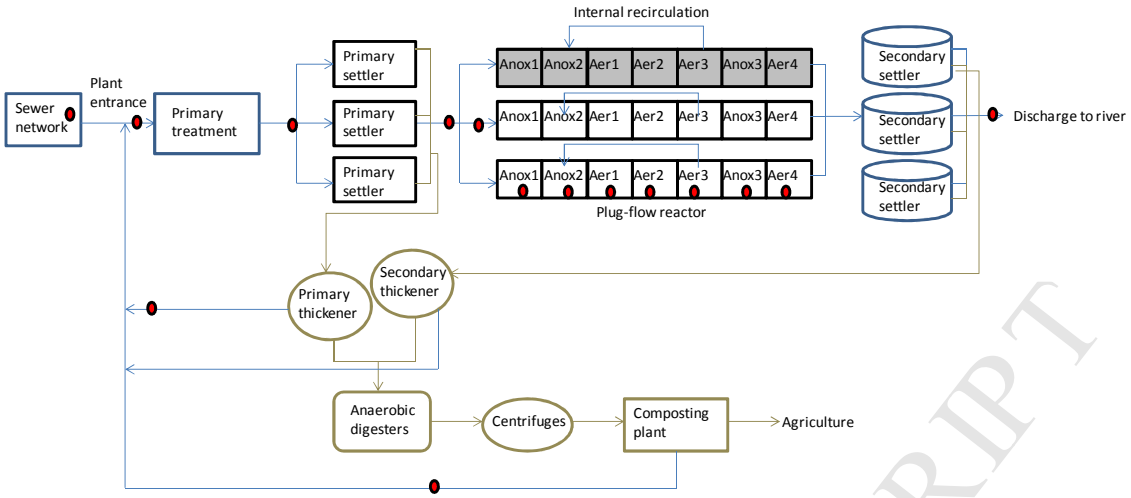

Figure 1. Scheme of the configuration of the WWTP of Girona (the plug-flow reactor line that is not operative is marked in grey; the red dots represent the locations where samples for dissolved CH_4 analyses were collected in the plug-flow reactor that was monitored).

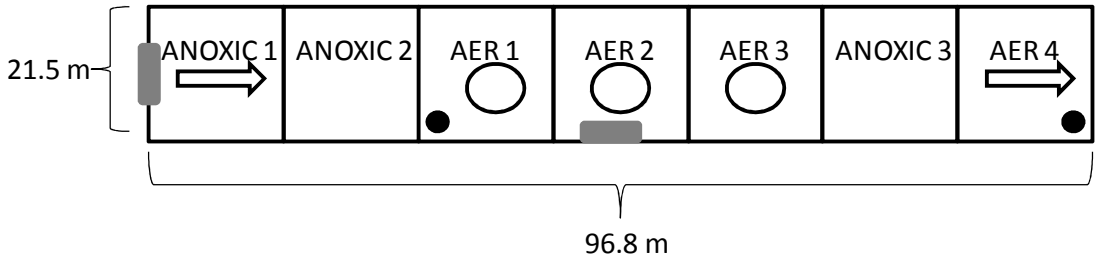

Figure 2. Plug-flow bioreactor configuration and study zones. The black dots represent the plant DO sensors in aeration zones 1 and 4. The grey rectangles represent the online ammonia sensors at the inlet of the plug-flow reactor and in aeration zone 2. The white dots represent the location where the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

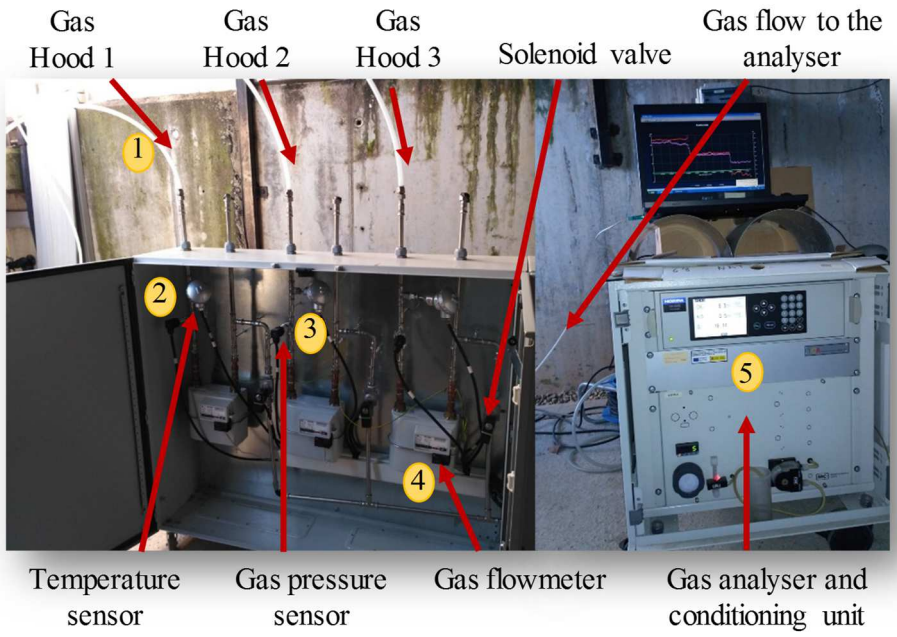

Figure 3. Multiple hood gas collection system. The gas arrives from the hoods via gas tubing (1) and passes through temperature (2) and pressure (3) sensors and a gas flowmeter (4) before arriving to the online gas analyser (5). An Arduino system controls the opening of the electro valves allowing the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

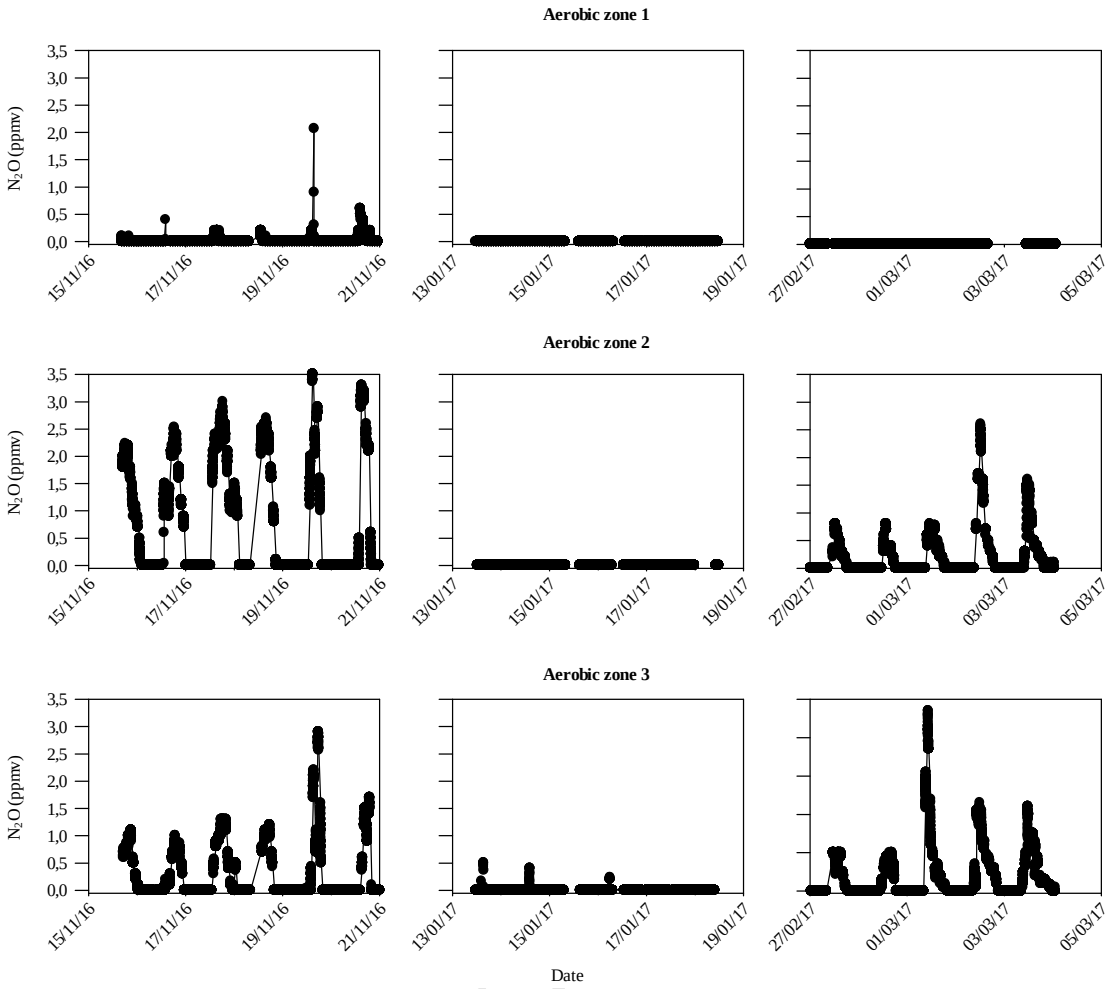

Figure 4. N_2O emissions from aerobic zones 1, 2, and 3 of the plug-flow bioreactor in November (left), January (centre), and March (right).

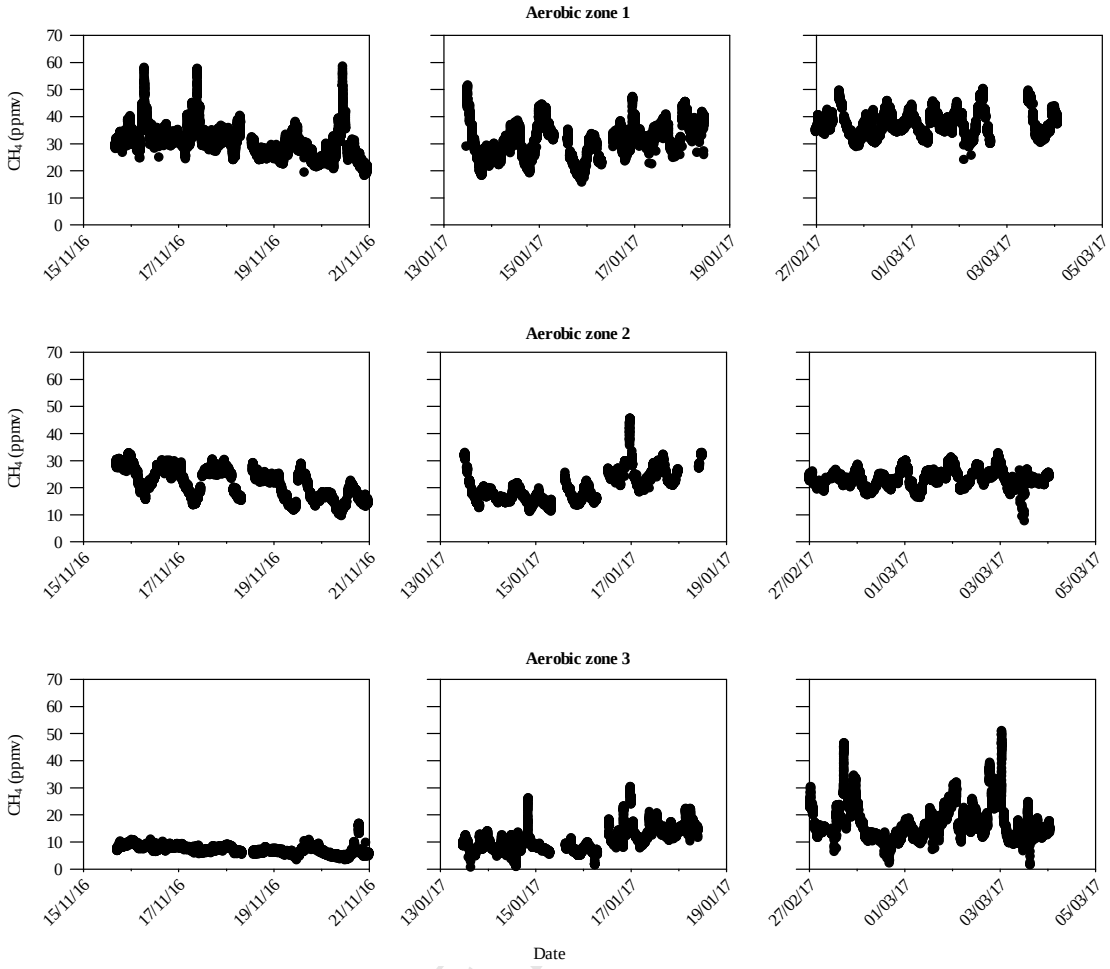

Figure 5. CH_4 emissions from aerobic zones 1, 2, and 3 of the plug-flow bioreactor during November (left), January (centre), and March (right).

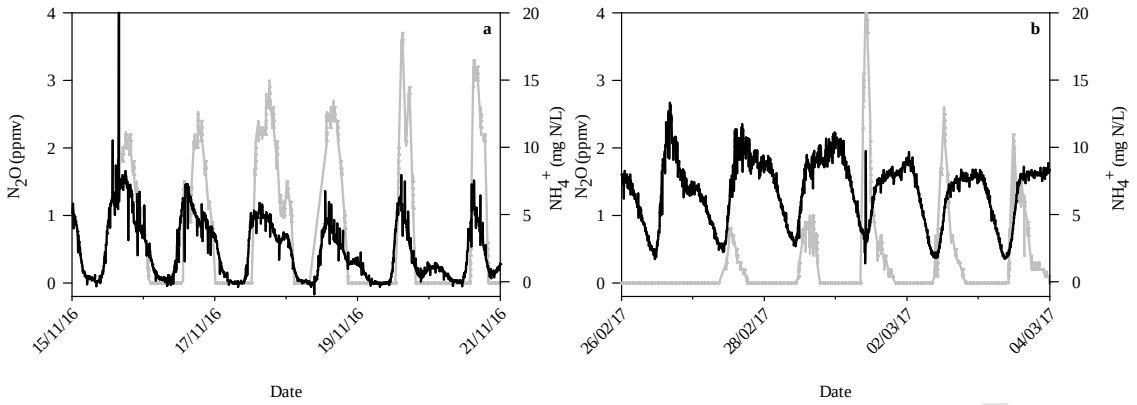

Figure 6. Typical ammonium (─) and N_2O patterns (─) in aerobic zone 2 of the plug-flow bioreactor found during the monitoring period of November (a) and the monitoring period of March (b).

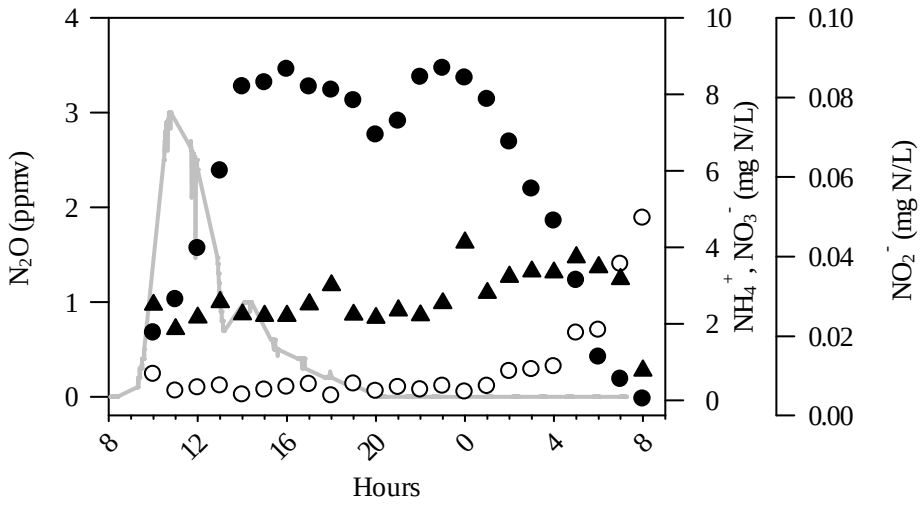

Figure 7. Daily N_2O (**—**), NH_4^+ (●), NO_2^- (▲), and NO_3^- (○) concentration profiles measured in aerobic zone 2 on the 7th and 8th of March.

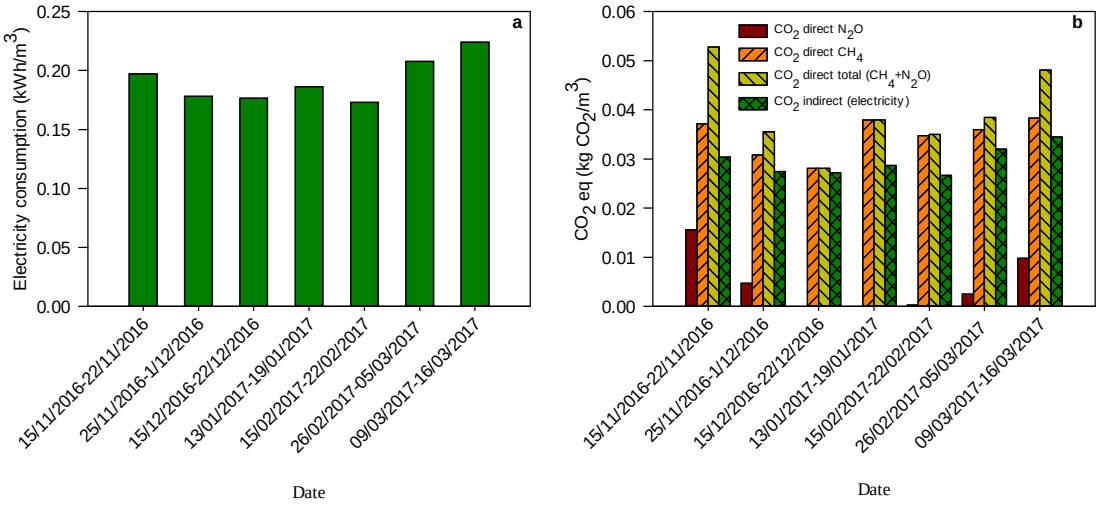

Figure 8. Electricity consumption (a) and direct and indirect CO_2 emissions (b) from the plug-flow bioreactor of the WWTP during the monitoring period.

Highlights

- Temporal and spatial GHG emissions monitored in a plug-flow full-scale bioreactor
- N_2O emissions present temporal and spatial variability with periods of no emission
- N_2O emissions were linked to the arrival of ammonium in the monitored zone
- Constant temporal CH_4 emissions were detected, showing only spatial variability
- CH_4 was the main contributor to the C-footprint, overcoming indirect emissions