Dynamics of GHG emissions from a typical full-scale WWTP in Italy

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Abstract:

Purpose

The current work presents the results of a long-term online N_2O monitoring campaign in an Italian wastewater treatment plant (WWTP) that applies conventional activated sludge process. The aim of this study is to examine the effect of different gaseous sampling methods on the profile of N_2O emissions in a full-scale WWTP.

Methods

The effect of operational parameters of the secondary treatment on the generation of N_2O emissions is investigated through the continuous monitoring of N_2O, NO and NO_2 emissions in the nitrification reactor. Statistical and event-driven sensitivity analysis based on cause-effect relationships was applied to evaluate potential relationships between the online monitored parameters and the N_2O emissions. Two different types of gas chambers were examined; fixed and floating.

Results

The average N_2O emission factor (EF) was 0.001% and 0.005% of TN in the influent for the fixed and floating chambers respectively. The diurnal variation of N_2O emissions varied significantly for the different gas chambers. The results indicated that the rate of N_2O emissions was partly affected by the different gas chambers; however, a COD:TN ratio lower than 4:1 systematically resulted in higher N_2O emissions. The sensitivity analysis showed that the N_2O dynamics are not significantly affected by dissolved oxygen (DO) variations (within the range of 1.5 – 2 mg/L).

Conclusions

The effect of the application of different gas chambers on the N2O profiles demonstrated the significant role of the sampling protocol within the full-scale N_2O monitoring campaigns. In the current study, N2O emissions were mainly affected by the ammonia loading rate in the reactor.

K**eywords:** Nitrous oxide emissions, Full-scale monitoring, Activated sludge, event based sensitivity analysis; gas sampling assessment

1. Introduction

Biological processes are a significant source of greenhouse gases (GHGs), mainly carbon dioxide (CO_2), methane (CH_4) and dinitrogen oxide (N_2O) in wastewater treatment plants (WWTP) [1]. Considering the global warming potential of N_2O (~300 more than CO_2), several real-field N_2O monitoring campaigns have focused on understanding the formation mechanisms of N_2O in the past years [2]. The operating parameters, the configuration, environmental conditions and the microbiological diversity of the biological processes affect significantly N_2O generation and GHGs footprint of WWTPs. However, GHG emissions' data from full-scale urban wastewater systems present different trends [3] and there are still uncertainties on the process conditions generating GHG emissions in full-scale biological processes [4]. Uncertainties and potential sources of error of the monitoring equipment and the currently applied sampling methods are main factors that can potentially hinder robust measurements [5]. There is significant variability in the chamber techniques employed for gaseous N_2O monitoring, including differences in the chamber configuration [6–9], chamber area and material [10,11] and parameters monitored in the chamber [12,13]. The uncertainties related with the different sampling strategies have not yet been assessed. The aim of this study is to examine the effect of different gaseous sampling methods on the profile of N_2O emissions in a full-scale WWTP. Event-based sensitivity analysis is applied to identify potential dependencies between the system parameters monitored online and the GHG emissions of the biological reactor.

2. Material and methods

2.1 Wastewater treatment process

The wastewater treatment plant (WWTP) of Falconara Marittima (Italy) has a design capacity of 80,000 PE and a nominal influent flow of 30,000 m3/d. After degritting, desanding and primary settling, the wastewater is biologically treated with activated sludge process in two identical parallel lines applying conventional pre-denitrification and nitrification process. The total volume of the biological compartments is 13,700 m3. The aerated compartments are equipped by ceramic fine bubble diffusers; the air supply ranges between 1,870 and 9,210 m3/h. An automatic system controls the four blowers (Robuschi mod. RBS LP120) based on the concentration of the dissolved oxygen (DO) in the nitrification reactor (three different operative set points: 0.4, 1.0 and 3.0 mg/L). One line is considered in the analysis. The denitrification reactor has a volume of 930 m3 and a surface area of 212 m2, whereas the nitrification compartment has a volume of 2,450 m3 and a surface area of 556 m2. The system is continuously monitored by probes (DO, Temperature, MLSS and ORP) and magnetic flow meters (influent, effluent, recirculation and waste sludge). The sludge retention time (SRT) is 10 days with 0.5 recirculation ratio. Additionally, the MLVSS concentration is 3,485±636 mg/L (ratio MLVSS/MLSS 0.61). The DO in the nitrification reactor is 4.3±0.9 mgO2/L and the pH is constant at 8.1±0.2. The average temperature during the monitoring campaign was 17.7±1.5 °C.

2.2 Analytical methods and biomass activity tests

Mixed-liquor grab samples were collected twice per week from the nitrification and denitrification reactors whereas 24h composite samples were collected twice per week from the influent and once per week from the effluent. All the samples were analysed in terms of pH, chemical oxygen demand

(COD), total Kejdahl nitrogen (TKN), ammonia nitrogen (NH_4-N), soluble COD (sCOD), nitrate nitrogen (NO_3-N) and nitrite nitrogen (NO_2-N) according to standard methods [14]. The soluble COD was measured in the filtrate obtained after the filtration of the sample through Whatman 0.45 lm membrane filters. NO_2–N, NO_3–N were measured by ion chromatography in samples that were first filtered through 0.45 lm Whatman membranes (Dionex DX120)).

To determine the ammonia uptake rate (AUR), 1.5 L of mixed liquor was collected from the aerobic reactor and was placed in a flask under continuous aeration (DO > 4 mg/L). After 30 min, the biomass was spiked with ammonium chloride at 40 mgNH_4-N /L initial concentration and the profile of ammonium, nitrite and nitrate with time was recorded. All batch activity tests were conducted at room temperature (25 ± 2 °C) and the pH was maintained in the range of 7.4 ± 0.3. The reported activities have been normalized to the reference temperature of 20 °C using the Arrhenius temperature correction equation and to the volatile suspended solids (VSS) of the mixture. The nitrate uptake rate (NUR) tests were conducted with 1.5 L of activated sludge placed in a flask, under mild agitation. Subsequently, the biomass was spiked with fixed nitrite concentration and with an external carbon source (acetic acid) and the nitrate profiles were recorded.

2.3 N_2O monitoring strategies

N_2O emissions were monitored with the use of a MIR9000CLD analyser (Environnement Italia S.p.A.) that measures N_2O, CO_2 and CH_4 through infrared spectroscopy (IRS) and the NO and NO_2 through chemiluminescence (Eusebi et al., 2015). The analyser was calibrated once per week by standard gas cylinders. The gas flow was pumped, transported by a heating tube at 120°C, filtered for dust removal and cooled at 4°C. Two different types of gas chambers were used; fixed and floating. The main characteristics of the different gas chambers are shown in Table 1. An open tube is located on surface to avoid overpressure and allow gas suction. The outlet pipe was the same for the different gas hoods (diameter of 10 cm and length of 1 m).

Table 1: Main characteristics of the different types of gas chamber

Type	Shape	Size	Retention time (h)					
			Volume (L)	Surface (m^2)	Min	Max	Average	Std. Dev
Fixed	Cylinder	Small	80	0.157	0.086	0.100	0.095	0.005
		Medium	141	0.174	0.130	0.238	0.184	0.045
		Large	226	0.246	0.210	0.289	0.251	0.035
Floating	Truncated Cone	Small	64	0.125	0.101	0.185	0.139	0.032
		Medium	166	0.325	0.090	0.130	0.106	0.011
		Large	233	0.457	0.097	0.105	0.102	0.003

The sampling point was maintained constant during the monitoring campaign, at the head of the reactor in the nitrification basin. The fixed chambers were attached to the external wall by steel clamps, while the floating chamber was fastened by ropes. The minimum monitoring duration for each gas hood was 7 days. High-density polyethylene (HDPE) was used for the fixed gas hoods and polypropylene (PP) was used for the floating hoods. Sufficient submersion of the base of the gas chambers was applied to prevent lateral movement and introduction of external air. Cylindrical

fixed chambers were used with volumes equal to 80 L, 14 L and 226 L for the small, medium and big chambers respectively. The floating gas chambers, on the other hand, had a truncated cone structure and volumes equal to 64 L (small), 166 L (medium) and 233 L (big).

Initial calibration tests were performed by changing the position of the gas analyser and connecting it to all the types of samplers. The acquisition time lasted 1 hour for each gas sampler. Six tests were performed for each gas chamber and the testing period lasted for 1 week.

2.4 Event based data processing and sensitivity analysis

An un-biased event-based sensitivity analysis was applied in order to investigate dependencies between the GHG emissions and the parameters that are monitored online in biological process [15,16] for the periods monitored by the different gas chambers (EventiC). This technique enables the identification of patterns (strength of relations) between the monitored parameters (DO, blowers flow rate, MLSS, Q_{in}) and gas fluxes (N_2O, CH_4, NO_2, CO_2). Tangible and reasonable changes to the signals of the sensors in the system were translated into events. In order to track events in a sensor signal the standard deviation of the signal fluctuation for all the time period is calculated. Threshold for registering an event is taken if the difference between two consecutive values is ≥15% for DO and ≥5% for all the other variables monitored, of this standard deviation. The event-base sensitivity analysis enables the identification of cause-effect relationship between the causes of state change in the system and the system response and therefore provides insight on which input variables (i.e. ammonia, DO) impact a specific output (i.e. N_2O, CH_4). The un-biased sensitivity analysis detects and defines the most relevant parameters (many to one and many to many relationship) by implementing the algorithm in the data from the different gas hoods and groups the influential variables in a look-up table. A detailed description of the method can be found in the study of Danishvar et al. [17].

3. Results and discussion

3.1 Wastewater characteristics and plant performance

The main influent and effluent characteristics are shown in Table 2. The influent flow-rate is 14,210±4,652 m^3/d. The TN concentration in the influent is 28.6±10.5 mg/L typically formed by ammonium nitrogen (25.1±3.2 mg/L). Negligible nitrite and nitrate concentrations were detected in the influent. The average effluent mass loads were 2.87±2.00 and 196.50±86.05 kgN/d of NH_4-N and TN respectively, which is affected by precipitation during the monitoring campaign. The TN and COD removal efficiencies were 40±20% and 59±13% respectively (Table 2).

Table 2: Daily average influent and effluent characteristics and kinetic rates

	pH	TSS	COD	CODs	TKN	NH_4-N	NO_2-N	NO_3-N	kn	kd_{max}	Real kd
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	kgN/kgML VSS/d	%	%
Influent	8.1 (±0.2)	36.8 (±15.0)	88.7 (±33.5)	41.6 (±20.5)	28.6 (±10.5)	25.1 (±3.2)	0.3 (±0.2)	0.9 (±0.8)	0.111 (±0.024)	0.057 (±0.028)	0.017 (±0.005)
Effluent	7.9 (±0.1)	5.1 (±2.4)	35.1 (±5.5)	-	14.5 (±5.3)	0.2 (±0.2)	0.0 (±0.0)	12.0 (±4.6)	-	-	-
Efficiency (%)	-	-	59 (±13)	-	40 (±20)	99 (±1)	-	-	-	-	-

The low TN removal efficiency is potentially related with the low COD/TN ratio that affects the denitrification process. Complete NH_4-N removal was achieved. Additionally, the AUR was 0.111±0.024 kgNH_4-N /kgMLVSS/d and the average denitrification rate was 0.057±0.028 kgNO_x-N/kgMLVSS/d.

3.2 N_2O emissions during the testing period

The N_2O concentrations for the fixed and the floating gas chambers during the testing period are shown in Fig. 1. In the scatterplot, the N_2O concentrations are presented versus the Sampler Ratio (SR - L/m^3/h), which is equal to the volume of the head space of the gas chamber divided by the aeration flow rate. During the tests that apply high aeration flow-rate (L/m^3/h<0.05) in the fixed gas hoods, prolonged periods of low N_2O emissions were followed by sudden incremental peaks. This can be attributed to compression phenomena in the head space of the fixed chambers due to abrupt changes of the liquid level in the reactor. Therefore, during the monitoring period, N_2O values with SR lower than 0.05 L/m^3/h are not considered for the assessment of the N_2O emission factor. As shown in Fig. 1b, the floating chamber was not affected by the aeration flow-rate; the profile of the N_2O emissions remained constant during the testing period.

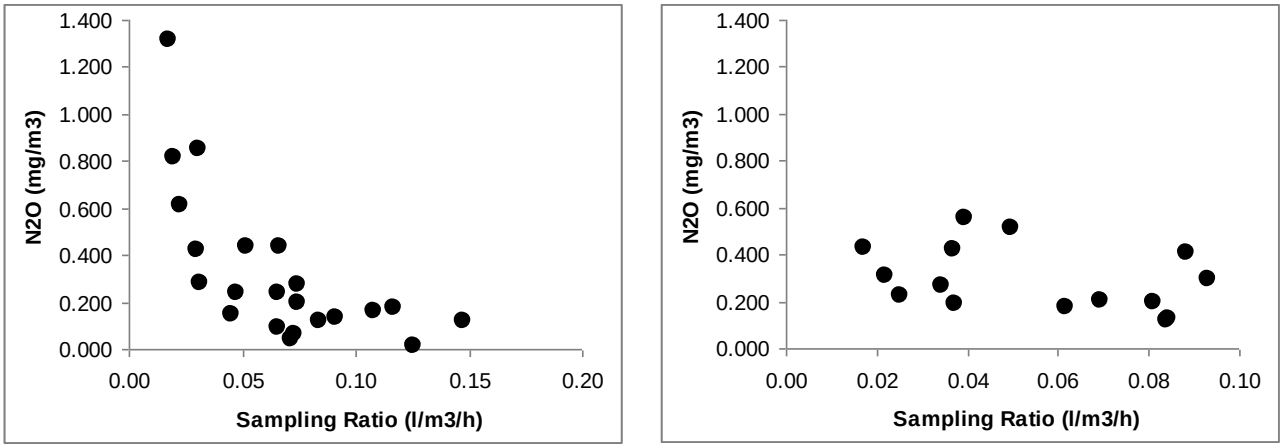


Fig. 1: (a) N_2O emission/SR-Fixed gas chambers, (b) N_2O emission/SR-Floating gas chambers

3.3 N_2O emission profiles during continuous monitoring

The net N_2O emissions rate varied significantly during the monitoring period from 66.82 to 4,174.37 mg/h with average rate equal to 31.99±24.33 gN_2O/d (Fig. 2). Even though, N_2O emissions were low during the monitoring period, the profile and range of N_2O emissions varied between the different gas chambers. The N_2O emissions rate of was partly affected by the different gas chambers; however the high variability of the daily N_2O emissions rate can be partially attributed to the variable COD:TN ratios (1.3 to 5.2) during the monitoring campaign. The average N_2O emissions rate was 0.856±0.905 gN_2O/h when the COD:TN was ~ 3.2 (1^{st}-20^{th} days). However, average emission rate increased at lower COD:TN ratio (1.9) up to 1.850±0.972 gN_2O/h in accordance with literature findings [18,19].

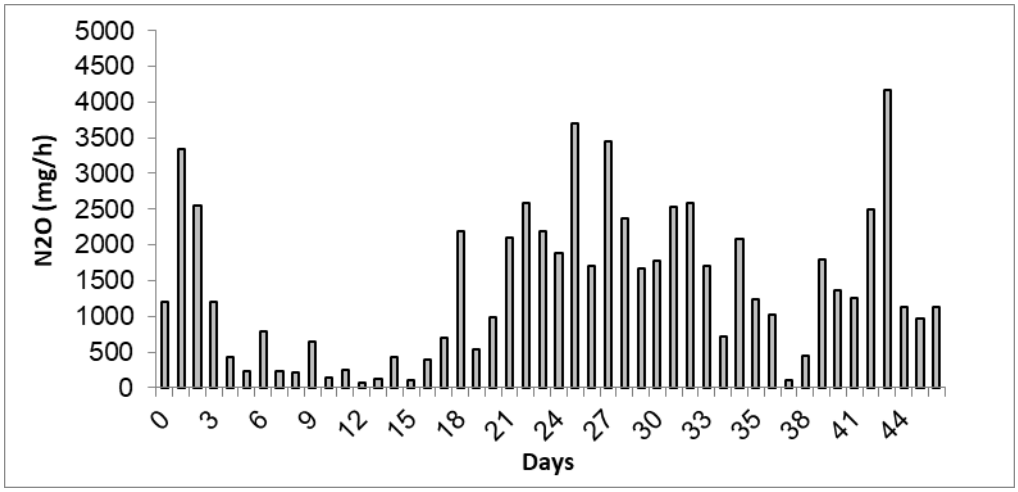
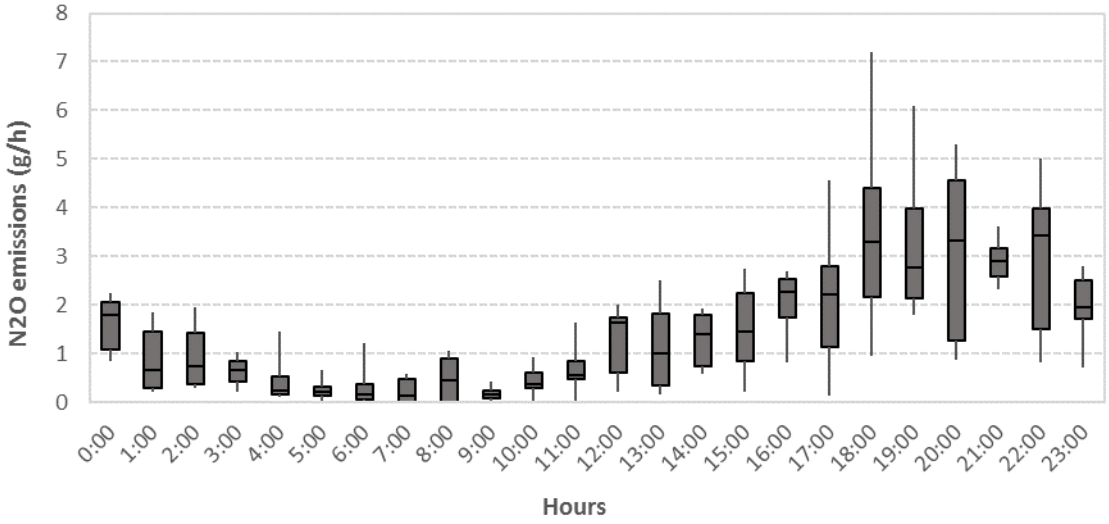


Fig. 2: N_2O emissions in nitrification reactor.

Fig. 3 shows the boxplots of the hourly N_2O emissions in the nitrification reactor when the medium floating hood was applied. for the different gas chambers, N_2O emissions' dynamics are characterized by significant diurnal variability in accordance with the results of previous studies [1,5,20]. The minimum daily N_2O emissions are observed at 03:00 am to 10:00 am, while a subsequent peak occurs from 18:00 pm to 20:00 pm. The latter follows the profile of influent flow-rate and NH_4-N loading rate. However, as it is shown if Fig. 3 (bottom), the gaseous sampling with the medium fixed gas hood did not result in a similar pattern of diurnal variability. It is unclear, though, if the different N_2O emissions' profiles are attributed to different gas chambers (floating vs chamber) or due to the nature of N_2O emissions that are highly dynamic. During the period monitored with the fixed gas hood, two prolonged periods of near-zero N_2O emissions (5/10/16-6/10/16 and 8/10/16-11/10/15) were followed by a sudden N_2O increase that lasted for 1 day. The latter can potentially affect the diurnal profile shown in Fig. 3.



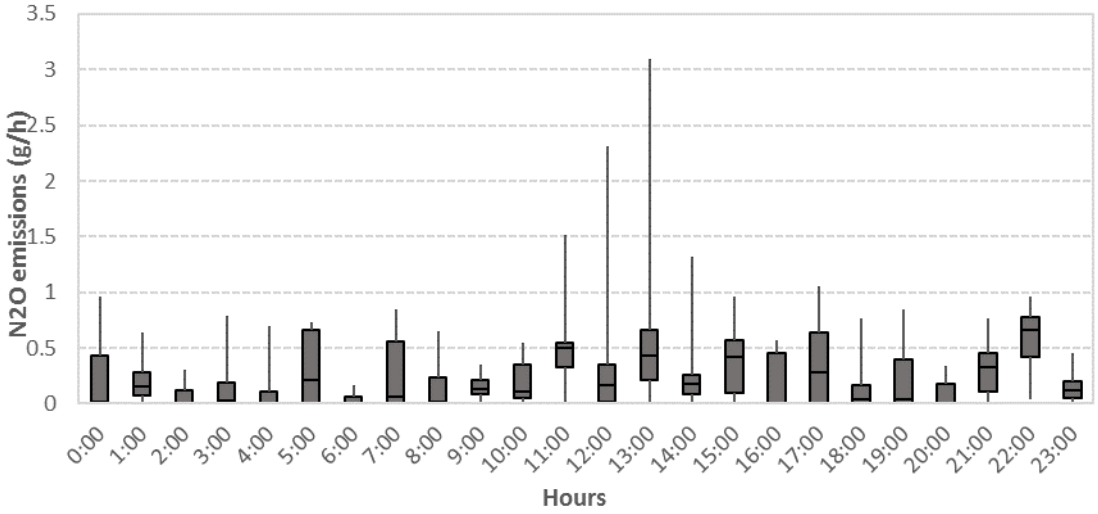


Fig. 3: Boxplots of the diurnal variability of N_2O emissions in with the floating hood (top) and the fixed hood (bottom). (grey boxes: interquartile range, whiskers: lines extending from the 5th to 95th percentile, median: line across the box)

The average N_2O emission factor (EF) is 0.001 and 0.005% of TN in the influent, for the first (1st-20th days) and the second period (21st-45th days) respectively. The EF in the current study is lower that the respective ones reported in literature dealing with on-line gaseous emissions monitoring at full-scale. Yan et al. [21], found emission factors ranging from 0.04 to 0.1% of the TN influent for an Anaerobic-Anoxic-Oxic system. Similarly, Rodriguez-Caballero et al. [13], reported N_2O emissions equal to 0.116% of the influent TN in a plug-flow reactor. The cumulative N_2O mass loads emitted (LN_2O) and TN influent (LTN) are shown in Fig. 4. Lower emissions are observed when the influent COD/TN ratio is higher than 4. The decrease of the COD:TN ratio results in an increase of the N_2O emitted (~5 times) compared to the periods with higher COD:TN ratio (0.0505 $gN_2O/kgTN$, R2=0.8853). The biomass-based EF was equal to 2.11±0.98 and 5.01±2.09 $mgN_2O/kgMLVSS/d$, for the first and second period with different COD:TN ratios, respectively.

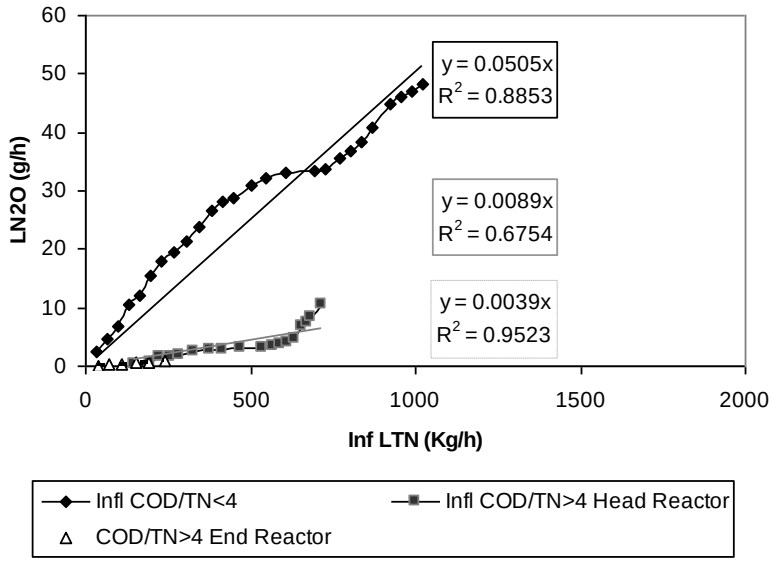


Fig. 4: Cumulative mass load of N_2O emitted and TN influent.

3.4 Statistical and sensitivity analysis floating hood

The results from the event-based sensitivity analysis are summarized in Table 3. The dependencies of the gaseous emissions from the nitrification reactor with the parameters monitored online in the system have been examined for the period that was monitored with the floating hood. A weak relationship was identified between the N_2O emissions and the air flow-rate and the DO concentration in the reactor. In line with the results of the current work, Rodriguez-Caballero et al. [13] found that the N_2O dynamics are not significantly affected by DO variations (within the range of 1.5 – 2 mg/L) or aeration flow rate (within the range of 1500 – 4600 m3/h), since the nitrification efficiency was constant. Moderate relationship was identified between the CH_4 emissions and the air flow rate. Significant interrelations were observed between CO_2 emissions and MLSS (Table 3). According to event-based sensitivity analysis, significant changes in the MLSS concentration between two timesteps coincides with changes in the CO_2 emissions. Fig. 5 illustrates a typical CH_4 emission (ppm) profile as a function of the aeration flow-rate for two days of system's monitoring. The CH_4 emission dynamics follow a similar pattern with the aeration flow in accordance with the findings of the event clustering sensitivity analysis.

Table 3: Event-based sensitivity analysis algorithm that groups system parameters that result in systematically observed events (dark grey: high impact, light grey: moderate impact).

	N_2O (ppm)	CH_4 (ppm)	NO (ppm)	CO_2 (%)
Qin (m3/h)	0.52	0.48	0.5	0.47
DO (mg/L)	0.37	0.54	0.55	0.60
Blowers flow-rate (m3/h)	0.44	0.53	0.56	0.62
MLSS	0.39	0.55	0.54	0.75

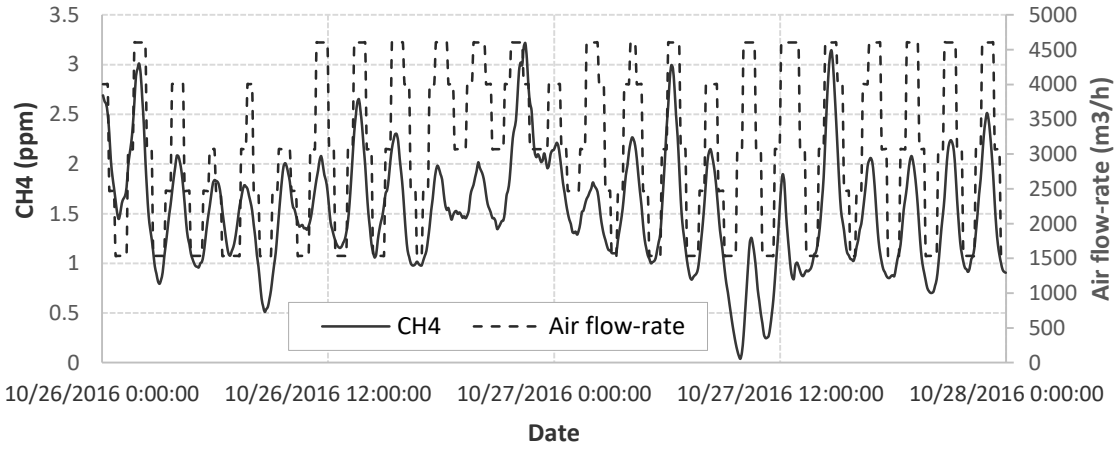


Fig. 5: Profile of CH_4 emissions and air flow-rate data in the nitrification reactor (Air flow-rate: dashed line, CH4: solid line).

4 Conclusions

The N_2O emissions profile was recorded for 52 days in a full scale conventional activated sludge process. The N_2O EF was 0.001% of the influent TN for the first period monitored with fixed gas chambers and 0.005% of the influent TN for the periods monitored with the floating gas chambers.

The results showed that lack of standardized methods for GHGs emissions sampling and monitoring results in uncertainties in the determination of the EF. Moreover, COD:TN ratio lower than 4:1 resulted in increase of N_2O emissions by a factor of 5. The sensitivity analysis demonstrated that emission fluxes were mainly affected by the variation of influent flow-rate in the reactor and therefore the ammonia loading rate.

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