Critical analyses of nitrous oxide emissions in a full scale activated sludge system treating low carbon-to-nitrogen ratio wastewater

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Abstract: A critical analysis of nitrous oxide emissions in a full-scale modified Ludzack Ettinger plant treating municipal wastewater with low carbon to nitrogen ratio is presented. The results of N_2O emissions were processed by coupling classical (liquid chemical/physical characterization) and new data analytics techniques (online gaseous emissions and statistical analysis). Correlation between the operational parameters of the plant and long-term online monitored nitrous oxide emissions was conducted. The analysis considered the effect of off-gas sampling methods, the variability of feeding characteristics and the main liquid process variables as the principle parameters that may affect nitrous oxide emissions. In order to detect and assess the causal relationships between online monitored system variables and nitrous oxide emissions, statistical and event-based sensitivity analysis was adopted to identify causal relationships between the variables of the system. Observations revealed that lower ratio between carbon and nitrogen (COD:N) resulted in higher N_2O emissions. The average nitrous oxide emission factors changed from 0.0089 $gN_2O/kgTN_{in}$ to 0.051 $gN_2O/kgTN_{in}$, that corresponded to denitrification limited by organic carbon availability. The nitrous oxide dynamics were not significantly influenced by dissolved oxygen variations (within the range of 1.5 – 2 mg/L). However daily peaks of nitrous oxide emissions occurred when aeration flow-rate resulting was higher and stripped more nitrous oxide from liquid.

Keywords: Nitrous oxide emissions, Full-scale monitoring, Activated sludge, Sensitivity analysis; Gas sampling assessment, Emission Factors

1. Introduction

Biological processes are significant sources of greenhouse gases (GHGs), mainly carbon dioxide (CO_2), methane (CH_4) and dinitrogen oxide (N_2O) in wastewater treatment plants (WWTPs) (Kampschreur et al., 2008). N_2O emissions are considered as the most potent (~300 more than CO_2) contributor to global warming. Numerous studies to date have focussed on real-field N_2O monitoring and the understanding of the causes on N_2O formation (IPPC, 2013). Several studies reveal that characteristics of the wastewater, operating parameters, configuration, environmental conditions and microbiological diversity of the biological processes have significant impact on N_2O generation and on operational carbon footprint of WWTPs. Critical effect was found in relation to the carbon to nitrogen ratio both in lab- or pilot- scale biofilm systems (He et al., 2017; Zhang et al, 2016), for aerobic granules and suspended activated sludge (Gao et al, 2016; Sun et al., 2014; He et al., 2017; Ge et al., 2017). Modelling studies also confirm the phenomena (Jose et al., 2016; Law et al., 2012). To the best of authors' knowledge the effect low C:N on N_2O emissions in full scale WWTPs has not been studied. Moreover, there is little evidence of extensive analytical studies in the literature regarding GHGs emissions from full scale plants. Therefore, quantifying the N_2O production and determining an effective mitigation approach to employ in existing full scale biological processes is needed.

Uncertainties and potential sources of error of the monitoring equipment (e.g. noise factors) and variability in the sampling chamber and technique can contribute to the lack of accurate and robust measurements of N_2O (Desloover et al., 2016) in full scale plants. The differences in the chamber configuration (Desloover et al., 2011; Ren et al., 2013; Rodrigues Caballero et al., 2015; Hwang et al. 2016), chamber area and material (Abooobakar et al., 2013; Sun et al., 2015) and parameters monitored in the chamber (Pan et al., 2016; Rodriguez-Caballero et al., 2014), contribute to the complexity and to large variations in measurements of the key indicators of plant performance and

emissions (Cavazzuti, M. 2013). The full understanding of the uncertainties in GHG emissions and the biological processes in full scale wastewater systems is a pertaining challenge (Massara et al., 2017 and Daelman et al., 2015).

This study addresses this gap of knowledge by analysing the results of N_2O emissions in a full-scale WWTP by performing classical (liquid chemical/physical characterization) and new data analytics techniques (online gaseous emissions and statistical analysis) to critically examine the relation between the monitored variables and N_2O gaseous emissions. The study attempts both to calibrate the optimal sampling method and to systematically relate the gaseous emissions with the main liquid variables routinely analysed. Moreover, for the first time the critical role of the C:N ratio is discussed calculating the emission factors (EF) from the full-scale mass balances. Event-based sensitivity analysis (Tavakoli et al. 2013 a, b) is applied to identify potential dependencies between the system variables monitored online and the N_2O emissions of the biological reactor.

2. Material and methods

2.1 Wastewater treatment process

The municipal wastewater treatment plant (WWTP) of Falconara Marittima (Italy) is fed by low C:N ratio wastewater. It has a design capacity of 80,000 PE and a design average influent flow of 30,000 m^3/d. Infiltration from groundwater and marine intrusions cause under-loading influent conditions during the dry weather. The real influent capacity (calculated on COD basis) is equal to 36,035±1,100 PE during the period of this study. After degritting, desanding and primary settling, the wastewater is biologically treated with activated sludge process in two identical parallel lines applying the conventional Modified Ludzack Ettinger scheme. The total volume of the biological compartments is 13,700 m^3. The aerated compartments are equipped by ceramic fine bubble diffusers; the air supply ranges between 1,870 and 9,210 m^3/h. An automatic system controls the four blowers (Robuschi mod.

RBS LP120) based on the concentration of the dissolved oxygen (DO) in the aerobic reactor (three different operating settings: 0.4, 1.0 and 3.0 mg/L). The denitrification bioreaction volume is 8,860 m^3, with surface area of 507 m^2. The nitrification bioreaction volume is 4,900 m^3 , with surface area of 560 m^2. This study analyses one of the two parallel lines of the activated sludge bioreactor. The system is continuously monitored by on-line sensors (Dissolved Oxygen – DO- ; Temperature – T-; Mixed Liquor Suspended Solid-MLSS- and Oxidation Reduction Potential - ORP) and magnetic flow meters (influent, effluent, recirculation and waste sludge). The average sludge retention time (SRT) was 10 days and the sludge recycle ratio ($Q_{sludge\ recycled}/Q_{influent}$) was 0.5. The MLVSS (Mixed Liquor Volatile Suspended Solids) concentration was 3,485±636 mg/L (ratio MLVSS/MLSS 0.61). The DO in the nitrification reactor was 4.3±0.9 mgO_2/L and the pH was buffered at 8.1±0.2 due to under-loading characteristics of the influent. The monitoring campaign was lasted 52 days (September-November) with average temperature of 17.7±1.5 °C.

2.2 Analytical methods and biomass activity tests

Mixed-liquor grab samples were collected twice per week from the aerobic and pre-anoxic reactors, whereas 24h composite samples were taken 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 (APHA, 2005). The soluble COD was measured in the filtrate obtained after the filtration of the sample through Whatman 0.45 µm membrane filters. NO_2–N, NO_3–N were measured by ion chromatography in samples that were first filtered through 0.45 µm Whatman membranes (Dionex DX120).

Influent NH_4-N was monitored in real-time (by AISE-Ammonium Probe- Hach Lange Ltd) for a relevant week in the influent to the activated sludge reactor. Moreover, influent samples were collected every 2 hours in a day to quantify the typical hourly of the C:N ratio. The mechanisms for

86 N_2O production were not studied by additional dissolved N_2O in the liquid phase because this
87 knowledge has been provided by other bench- or pilot-scale studies (Mannina et al., 2018; Wunderlin
88 et al., 2012). However, a significant gap of knowledge concerns the full scale WWTPs especially
89 considering the real variable influent characteristics (i.e. C:N) and gaseous mass loads directly
90 emitted in the atmosphere.

91 Moreover, to monitor the stability of the respiratory activity of the microbial community, nitrification
92 and denitrification kinetics were an analysed by batch tests. To determine the ammonia utilization
93 rate AUR, 1.5 L of mixed liquor was collected from the aerobic reactor and was placed in a flask
94 under continuous aeration (DO > 4 mg/L). After 30 min, the biomass was spiked with ammonium
95 chloride at 40 mgNH_4-N/L initial concentration and the profiles of ammonium, nitrite and nitrate with
96 time were measured. All batch respirometry tests were conducted at room temperature (25 ± 2 °C)
97 and the pH was maintained at 7.4 ± 0.3. The reported activities were normalized to the reference
98 temperature of 20 °C using the Arrhenius temperature correction equation and to the volatile
99 suspended solids (VSS) of the mixture. The nitrate utilization rate (NUR) tests were conducted with
100 1.5 L of activated sludge placed in a flask, under mild agitation. Subsequently, the biomass was spiked
101 with fixed nitrate concentration and with an external carbon source (acetic acid) and the nitrate
102 profiles were measured.

103 **2.3 N_2O sampling and monitoring strategies**

104 N_2O emissions were continuously monitored with MIR9000CLD analyser (Environment Italia
105 S.p.A.). The analyser measures N_2O, CO_2 and CH_4 through infrared spectroscopy (IRS) and the NO
106 and NO_2 by chemiluminescence (Eusebi et al., 2016). Weekly calibration using standard gas cylinders
107 was performed. The gas flow was pumped, transported by a heating tube at 120°C, filtered for dust
108 removal and cooled at 4°C. More than one type of sampling chamber was tested to optimize the N_2O
109 measurement procedure. In particular, two different types of gas chambers were used: fixed and

floating. The main characteristics of the different gas chambers are shown in Table 1 and in Table 2 as 3D images, shapes, volumes and configurations. An open tube is located on the surface to 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

Table 2

The sampling point to measure the N_2O emissions was chosen in the aerobic reactor as basin where the gaseous products were mainly stripped and emitted in the atmosphere. The sampling point was placed at the head of the reactor in the aerobic basin for 46 days and at the end for 7 days. The fixed chambers were attached to the external wall by steel clamps and 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. The base of the fixed gas chambers was submersed (about 5 cm) to prevent lateral movement and introduction of external air. Cylindrical fixed chambers were used with volumes equal to 80 L, 141 L and 226 L for the small, medium and large chamber. The floating gas chambers had a truncated cone structure and volumes equal to 64 L (small), 166 L (medium) and 233 L (big) (Table 2).

At the end of the continuous monitoring phase, the emission factors were calculated as emitted N_2O mass load from the aerobic reactor and they were related to the total influent nitrogen load.

2.4 N2O emissions and gas chamber headspace: optimization of the sampling methodology

Initial calibration tests (N° 36) were performed to optimize the sampling method. The main objective of the tests was to identify the best sampling methodology in terms of different types/dimensions of the applied chambers shown in Table 1 and Table 2. The tests were carried out during the first 15 days of dry weather. The sampling point was set at the head of the reactor. The tests were performed

133 in the same relevant period (from hrs 9.30 to hrs 12:30). Each test was carried out acquiring the N_2O
134 data for 1 hour with one type of chamber. At the end of the acquisition time the connection of the
135 tube of the gases analyser was quickly moved from one chamber to another (small, medium or large,
136 both floating and fixed) and another test started. Before and after this few-minutes operating time,
137 the stable conditions in the liquid phase were monitored and verified by the analysis of the main
138 dissolved nitrogen and organic forms (NH_4-N, NO_3-N, NO_2-N, CODs). Therefore, the liquid
139 conditions during the different short tests were comparable.

140 The N_2O data was linked with two variables: 1) the air supply and 2) the Sampler Ratio (SR).

141 This second coefficient was set and calculated for each test according to equation 1:

$$S \left({}^{L}/_{m^3/h} \right) = \frac{V \quad H \quad S}{A \quad S} \qquad \text{Equation 1}$$

Where:

Volume Head Space (L) changes for each type of sampling chamber

Air Supply (m^3/h) = Inlet air flow to the aerobic reactor

142 For the same type of chamber, the SR values dynamically varied because of the change of the air
143 supply in the main biological reactor. Thus, the optimal dimension of the sampling chamber compared
144 to the inlet airflow was studied to avoid over-estimation of N_2O concentrations and/or overpressure
145 phenomena.

146 **2.5 Event based data processing and sensitivity analysis**

147 An un-biased event-based sensitivity analysis was carried out in order to investigate dependencies
148 between the N_2O emissions and the parameters that were routinely monitored in biological process
149 (APHA, 2005; Tavakoli et al., 2013) along the periods monitored by the different gas chambers
150 (EventiC; Danishvar et al, 2017). This technique enables the identification of patterns (strength of

relations) between the monitored variables (DO, blowers flow rate, MLSS, Q_{in}) and gas fluxes (N_2O). 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. Several thresholds were tested (ranging from 5% - 35% of the standard deviations of the variables) and presented the results that maximize the Event-based sensitivity analysis coefficients. The thresholds consider as events the following changes in the variables: i) DO >0.2 mg/l (>15% of the standard deviation); ii) N_2O > 0.1 kg/h (>5% of the standard deviation); iii) MLSS> 20 (>5% of the standard deviation); iv) Qin>20 m3/h (>5% of the standard deviation); v) Blowers flow-rate > 110 m^3/h (>5% of the 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). The un-biased sensitivity analysis detects and defines the most relevant variables (many to one and many to many relationships) by implementing the algorithm in the data from the different 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. (2017).

3. Results and discussion

3.1 Wastewater characteristics and plant performances

The main influent and effluent characteristics are shown in Table 3. 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, mainly as ammonium nitrogen (25.1±3.2 mg/L). The average effluent mass loads were 2.87±2.00 and 196.50±86.05 kgN/d of NH_4-N and TN. The TN and COD removal efficiencies were 40±20% and 59±13% respectively (Table 3).

Table 3

The low TN removal efficiency is related with the low biodegradable carbon to nitrogen ratio that limits the denitrification process. On the other hand, complete nitrification 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 and gas chamber headspace: optimization of the sampling methodology

The N_2O concentrations obtained during the calibration tests for the optimization of the sampling methodology are shown in Figure 1 for different air flows both for the fixed and for the floating gas chambers (Figure 1 -a Fixed and –b Floating). A linear increase of the N_2O concentrations at higher influent air flux has been found in other works (Ribeiro et al., 2017). In the current work this behaviour has been observed only for the floating chambers (Figure 1-b). Scattered distribution was found for the fixed chambers (Figure 1-a). No evident relation was found between the increment of the N_2O concentrations and the dimension (Small-Medium-Large) of the chamber used for sampling both for floating and for fixed chambers. Differently, the Sampler Ratio (SR-L/m^3/h) was calculated according to Equation 1. The results showed that the N_2O concentrations are linked with the SR value (Figure 1-c and –d) especially for the fixed chambers (Figure 1-c).

Figure 1-a-b-c-d

During the tests with high aeration flow-rate (SR <0.05 L/m^3/h) in the fixed gas hoods, incremental N_2O emissions peak were recorded. This is potentially attributed to compression phenomena in the head space of the fixed chambers and abrupt changes of the liquid level in the reactor. Therefore, during the continuous monitoring, 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. The floating chambers performed better and were not

197 influenced by the SR variations (Figure 1-d); the same floating avoids potential over pressure
198 phenomena in the head-space.

199 **3.3 N_2O emission profiles during continuous monitoring**

200 The N_2O emissions rate at the head of the reactor varied from 66.82 to 4,174.37 mg/h with average
201 load equal to 31.99±24.33 gN_2O/d during the monitoring period (Figure 2). The N2O emission profile
202 was not affected by temperature variations (18.2±0.8 °C in wastewater).

203 Figure 2

204 The variability of the daily N_2O emissions rate can be mainly attributed to the actually variable
205 influent carbon to nitrogen ratios (COD:TN: 1.3 to 5.2) that was always low. The average N_2O
206 emission rate was equal to 0.856±0.905 gN_2O/h when the COD:TN was about 3.2 (1st-20th days),
207 while it increased to 1.850±0.972 gN_2O/h at lower COD:TN ratio:1.9. The latter is in accordance to
208 the results reported in literature (Quan et al., 2012; Mannina et al., 2017). Similar limiting C:N ratios
209 resulted in N_2O increase in previous studies applying different processes (aerobic granular sludge
210 sequencing batch reactors; integrated fixed film activated sludge membrane bioreactor, respectively)
211 at pilot scale. Mannina et al. (2018) demonstrated that limiting C:N ratio of 2 gCOD/gTN resulted in
212 5 times increase of N_2O emissions from 0.12% to 5% (expressed as emitted N_2O compared with the
213 influent TN). Furthermore, in an Anammox process, C:N ratios of 3.0–0.65 were responsible for the
214 increment of N_2O production (Zhang et al., 2015).

215 Daelman et al. (Daelman et al., 2015) reported that the N_2O emissions during the continuous
216 monitoring were very low (0.174±0.90 gN_2O/h) at the end of the reactor. The geometry of the reactor
217 was considered even in this study. The aerated activated sludge basin (length 35 and width 15 m) can
218 be assimilated to n.3 completely stirred tank reactors that can lead to secondary behaviours observed
219 in plug-flow configuration (Ming, 2016).

Moreover, the N_2O emissions, the main operative variables and the daily variations were statistically analysed to better understand the role of the liquid variables. The boxplots of the hourly N_2O emissions in the nitrification reactor are shown in Figure 3. N_2O emissions' dynamics are characterized by significant daily variability in accordance with the results of previous studies (Aboobakar et al, 2013; Daelman et al., 2013; Rodriguez-Caballero et al., 2014).

Figure 3

The minimum daily N_2O fluxes are observed between 03:00 am and 10:00 am, while a subsequent peak occurs between 18:00 pm and 20:00 pm. No specific correlation between the N_2O emissions and the liquid influent flowrate was observed (Figure 3). Similar flow (about 500 m3/h) was recorded after hours 11:00 am without clear relation between the hydraulic overloading conditions and the peaks of N_2O emissions.

Therefore, further analysis was undertaken by studying the hourly influent ammonia and COD concentrations. A typical example of daily variability is shown in Figure 4. Hourly variations between 17.5 and 19.4 mg/L for ammonia nitrogen and between 61.6 and 20.1 mg/L for COD were observed with peaks of COD:TN during 12:00-16:00, where the N_2O distribution showed almost minimum N_2O emissions. The latter reveals that the variation of the COD:TN ratio strongly affects the N_2O emissions during the day.

Figure 4

The cumulative emitted N_2O mass loads (LN_2O) and the influent TN (LTN) values are shown in Figure 5. The emission factors were reported for the periods characterized by COD:N lower than 4 (1st-20th days), COD:N higher than 4 (21st-45th days) and when the sampling was carried out at the end of the reactor (Figure 5). The average N_2O emission factor is 0.001 and 0.005 % of TN in the influent, respectively for the first (1st-20th days) and for the second period (21st-45th days). Lower

243 emissions are observed when the influent COD:N ratio is higher than 4. The lower was the COD:N
244 ratio the higher was the emitted N_2O: about 5 times higher compared to the periods with higher
245 COD:TN ratio (0.0505 gN_2O/kgTN, R2=0.8853).

246 Figure 5

247 The biomass-based EF was equal to 2.11±0.98 and 5.01±2.09 mgN_2O/kgMLVSS/d for the first and
248 second period with different COD:N ratios. The EF of current study is lower than the EF values
249 reported in other studies that monitor on-line gaseous emissions at full-scale. Yan et al., 2014, found
250 emission factors ranging from 0.04 to 0.1% of the TN influent for an Anaerobic-Anoxic-Oxic system.
251 Similarly, Rodriguez-Caballero et al., 2014, reported N_2O emissions equal to 0.116% of the influent
252 TN in a plug-flow reactor.

253 **3.2 Statistical and sensitivity analysis**

254 An-event based sensitivity analysis was carried out in order to identify the relationship between the
255 N2O emissions and the monitored parameters. The results are given Table 4. The gaseous emissions
256 from the nitrification reactor have been examined with reference to the variables monitored online
257 when the floating hood was applied with SR higher than 0.05 $L/m^3/h$.

258 Table 4

259 A weak relationship was identified between the N_2O emissions, the air flow-rate and the DO
260 concentration in the reactor. In line with the results of this study, Rodriguez-Caballero et al. (2014)
261 found that the N_2O dynamics were not significantly affected by DO variations (within the range of
262 1.5 – 2 mg/L) when the nitrification efficiency was constant. Moderate relationship was identified
263 between the influent flow-rate and the N_2O fluxes; the latter is supported by the daily behaviour of
264 N_2O emissions (Figure 3). Additionally, the MLSS concentration was relatively steady during the
265 monitoring campaign and therefore, it is not directly linked with the behaviour of N_2O emissions.

According to event-based sensitivity analysis, the blowers' flow-rate affects the N_2O emission fluxes. The typical N_2O emissions (g/h) profile is shown in Figure 6 with the aeration flow-rate and with the residual DO for two days of monitoring. Low concentrations of residual dissolved oxygen was not a limiting factor (Figure 6). The latter supports the obtained results during the experimental campaign considering the low impact of the DO concentrations (4.6±0.7 mg DO /l during 1st-20th days and 4.1±1.6 mgDO/l during 21st-45th days) and the constant nitrification rates (kn of 0.116±0.016 $kgNH_4$-N/kgMLVSS/d during 1st-20th days and kn of 0.118±0.031 $kgNH_4$-N/kgMLVSS/d during 21st-45th days 4.1±1.6 mg/l).

Figure 6

The dynamics of the variables are different. However, daily peaks of N_2O emissions occurred when the aeration flow-rate was higher than 3,500 m^3/h. Therefore, although higher N2O emissions were related to the low C:N ratios that limited heterotrophic denitrification, higher aeration flow rates increase N2O stripping phenomena and related N2O emissions.

4 Conclusions

A full scale activated sludge plant treating low carbon:nitrogen ratio municipal wastewater was continuously analysed for 52 days to study N2O emissions.

This long-term continuous critical monitoring led to the following conclusions related to: a) the sampling methods; b) the full scale observed effects of influent and operating variables. In particular:

a) the optimization of the sampling methods was carried out by testing different types of chambers. Uncertainties of the N_2O concentrations were observed when the Sampling Ratio between the chamber volume and the air supply was lower than 0.05 L/m^3/h. Finally, the floating chambers were more reliable compared to the fixed sampling systems.

b) the N_2O load emitted directly from the aeration basin was related to the carbon to nitrogen ratio mainly and to the variability of the influent load. Low COD:N ratio limited the denitrification and led to 5-times higher N_2O emissions. Major differences were observed around the COD:TN = 4: 0.856±0.905 gN_2O/h when COD:TN > 4 versus 1.850±0.972 gN_2O/h when COD:TN < 4. The statistical elaboration of N_2O emissions further supported those conclusions: hourly N2O peak emissions are higher when the COD:N ratio is lower. The sensitivity analysis showed that the N_2O dynamics are not significantly affected by DO variations (within the range of 1.5 – 2 mg/L). However, daily peaks of N_2O emissions are observed at higher aeration flow-rate that result in higher stripping of the produced and dissolved N_2O.

Finally, when COD:N ratio was higher than 4, the cumulative emitted N_2O mass loads (EF) varied from 0.051 $gN_2O/kgTN_{influent}$ to 0.0089 $gN2O/kgTN_{influent}$. Therefore, the equalization of the influent can be advantageous even in terms of N_2O emissions.

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List of Tables

Table 1: Characteristics of the sampling gas chambers

Type	Shape	Size					
			Surface (m^2)	Min	Max	Average	Std. Dev
Fixed	Cylinder	Small	0.157	0.086	0.100	0.095	0.005
		Medium	0.174	0.130	0.238	0.184	0.045
		Large	0.246	0.210	0.289	0.251	0.035

Floating	Truncated Cone	Small	0.125	0.101	0.185	0.139	0.032
		Medium	0.325	0.090	0.130	0.106	0.011
		Large	0.457	0.097	0.105	0.102	0.003

Table 2: 3D Images, shapes and volumes of the sampling gas chambers

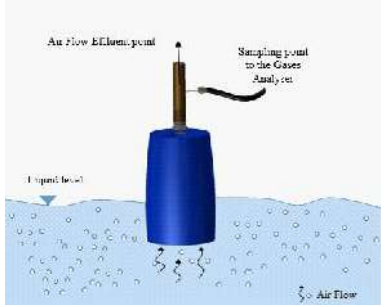
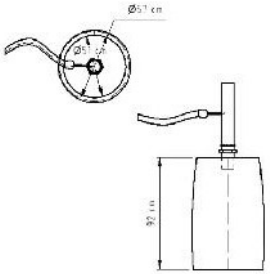
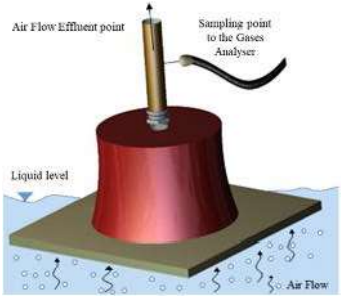
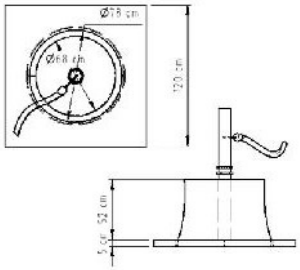
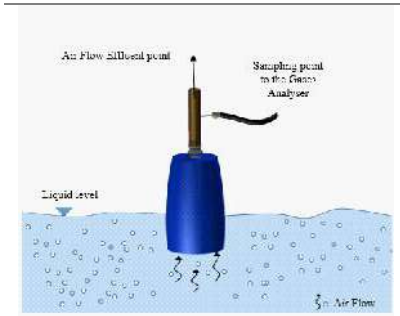
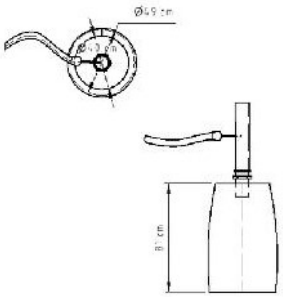
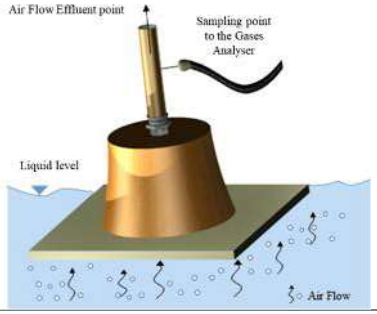
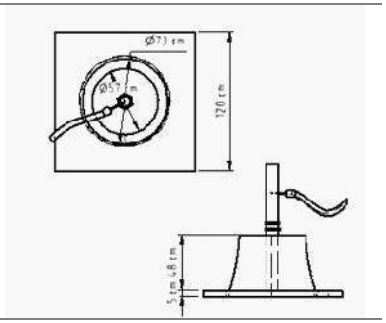
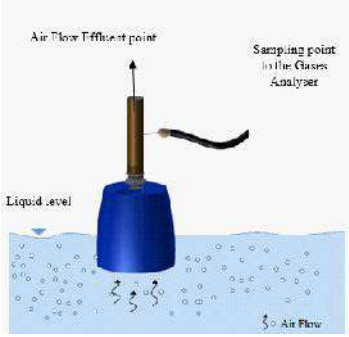
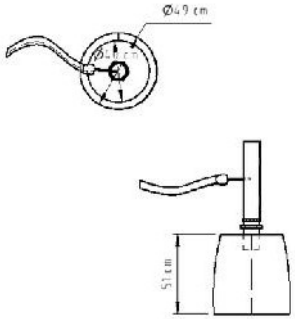
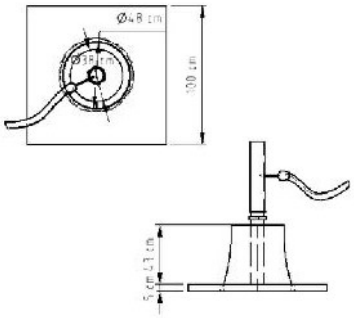
Sampler with Fixed Chamber		**Sampler with Floating Chamber**	
3D Image	Specific Dimensions	3D Image	Specific Dimensions
Large	**Useful Volume ~ 230 L**	**Large**	**Useful Volume ~ 230 L**
			
Medium	Useful Volume~150 L	Medium	Useful Volume~150 L
			
Small	Useful Volume~70 L	Small	Useful Volume~70 L
			

Table 3: Daily influent and effluent characteristics and kinetic rates (Average and Standard Deviation)

	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	$kgNH_4$-N/kgMLVSS/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)	-	-	-	-	-

Table 4: Event-based sensitivity analysis algorithm grouping the system parameters in which events have systematically coincided (dark grey: high impact, light grey: moderate impact).

	N_2O (ppm)
Qin (m^3/h)	0.52
DO (mg/L)	0.37
Blowers flow-rate (m^3/h)	0.44
MLSS	0.39

List of Figures

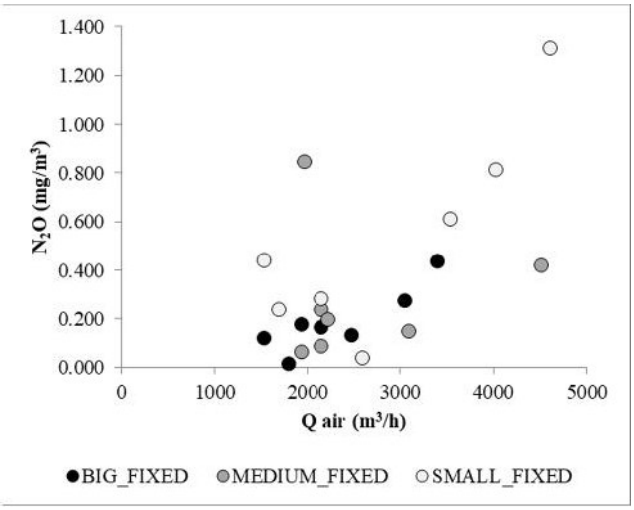


Figure 1 a- N2O-inlet air flow-Fixed gas chambers

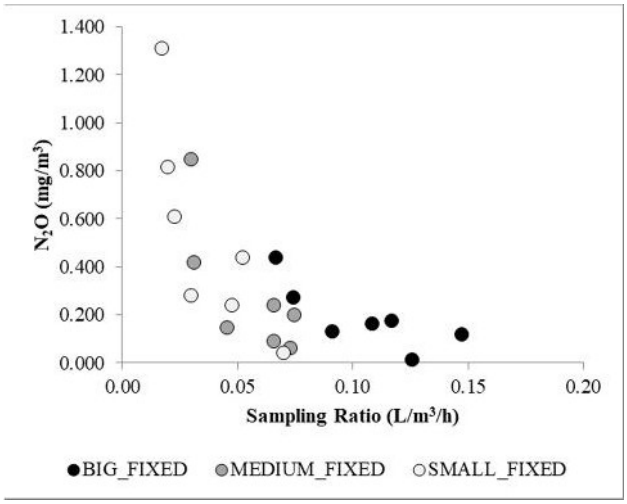


Figure 1 b- N2O-inlet air flow-Floating gas chambers

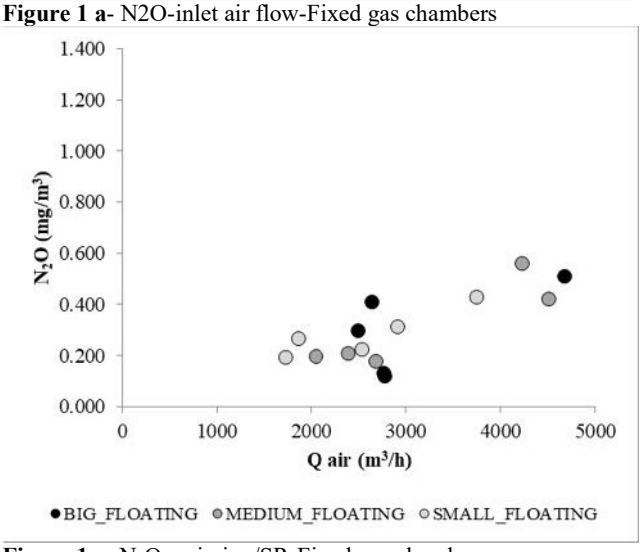


Figure 1 c- N_2O emission/SR-Fixed gas chambers

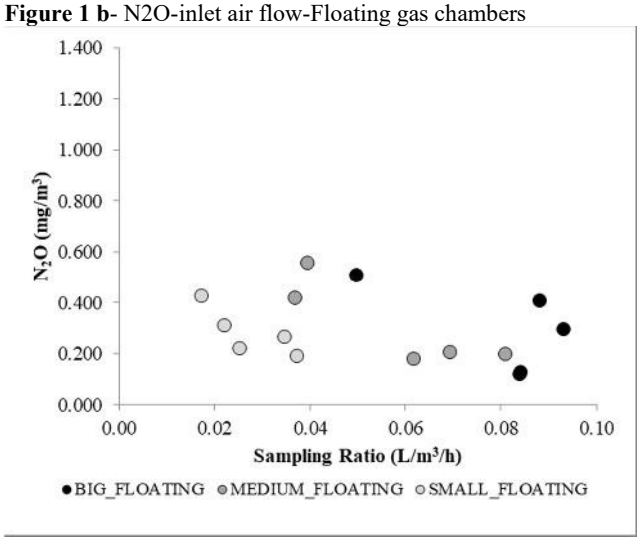


Figure 1 d- N_2O emission/SR-Floating gas chambers

Figure 1: N_2O emissions during the tests for the calibration of the sampling chambers

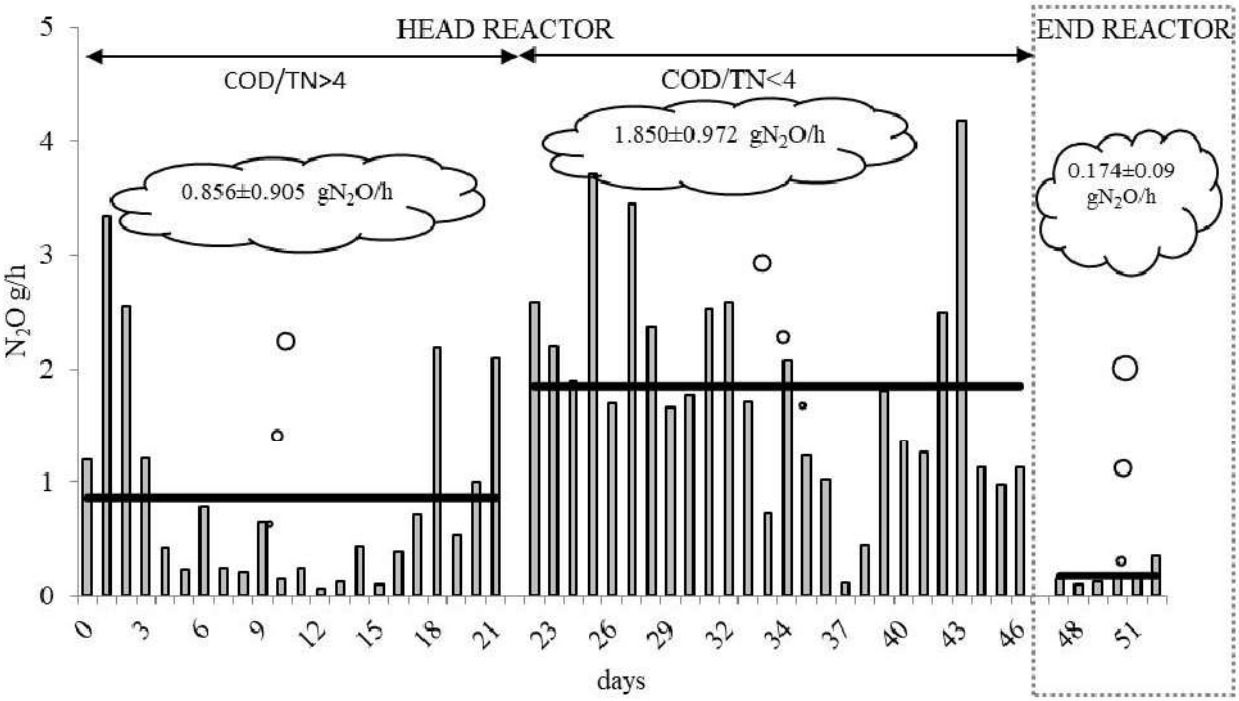


Figure 2: N_2O emissions in nitrification reactor

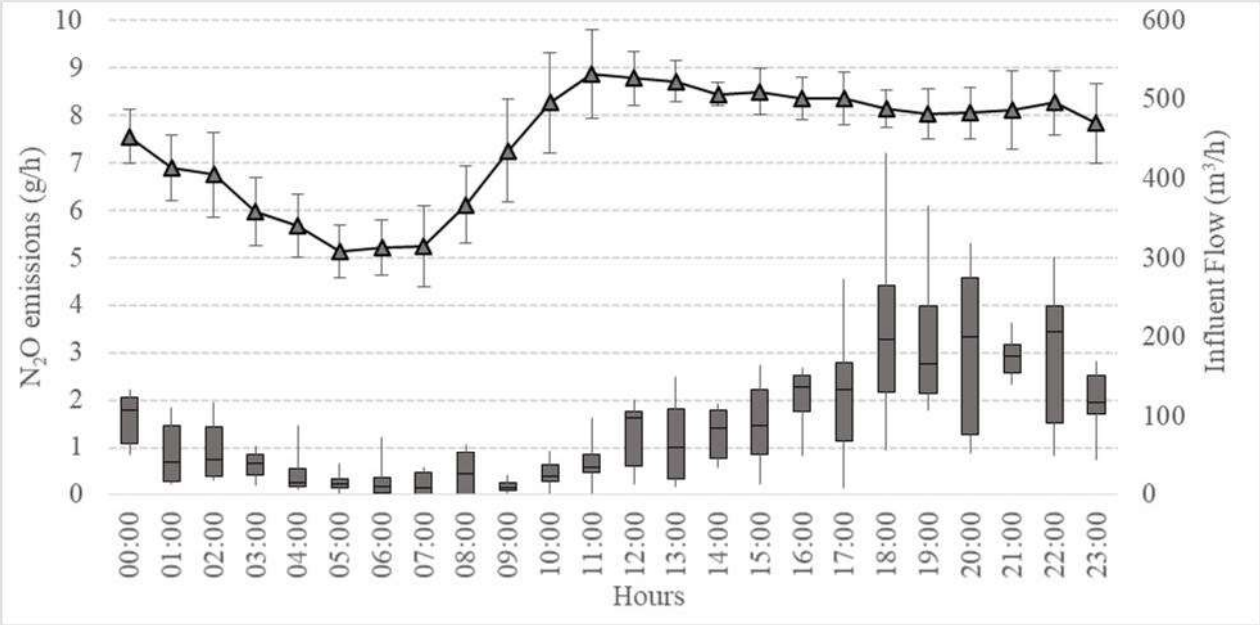


Figure 3: Boxplots of the daily variability of N_2O emissions and Influent Flow (grey boxes: interquartile range, whiskers: lines extending from the 5th to 95th percentile, median: line across the box; grey triangles: average liquid influent flow rate)

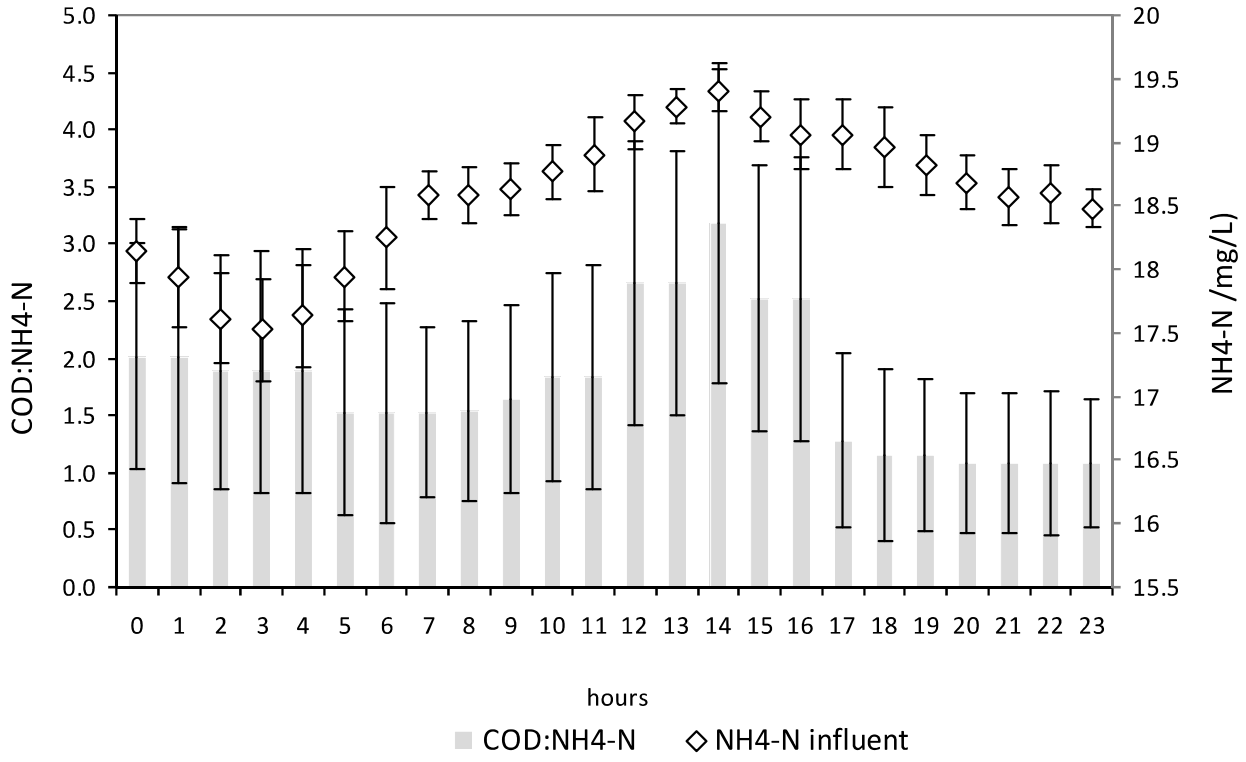


Figure 4: Typical daily variability of COD/NH_4-N and NH_4:N concentrations in the influent liquid flow

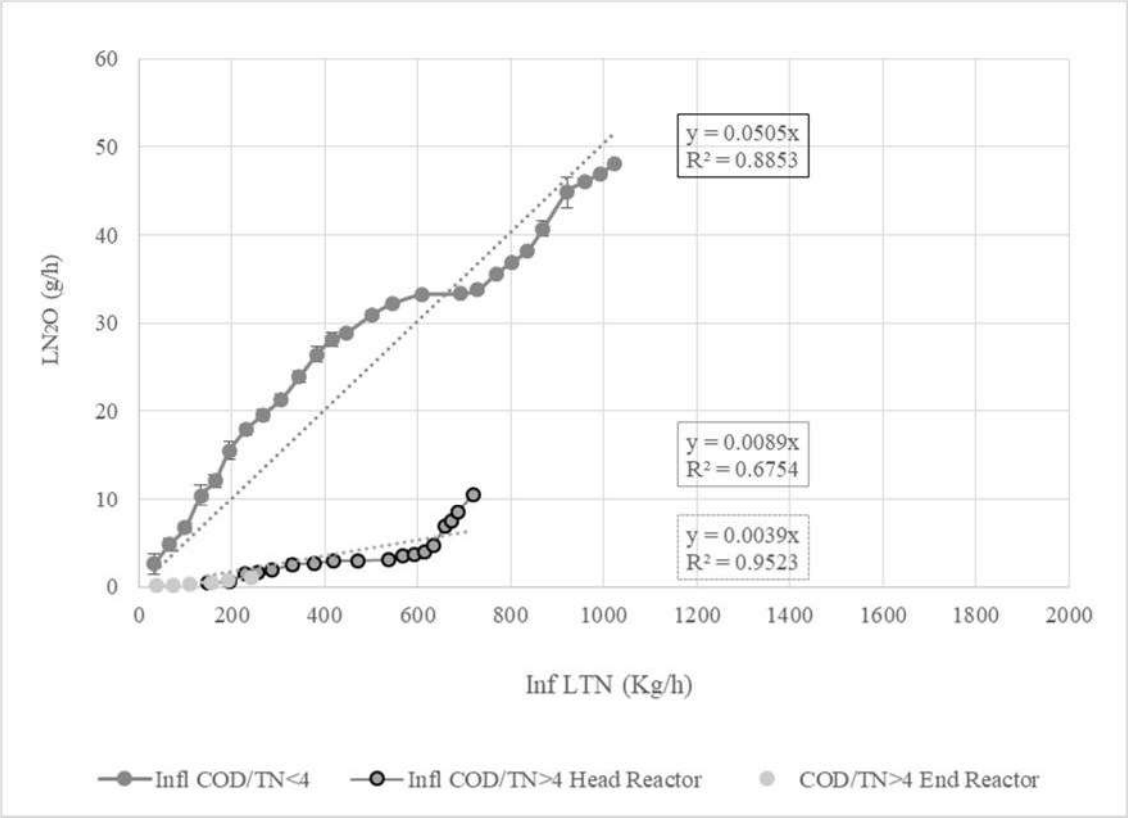


Figure 5: Cumulative mass load of N_2O emitted and TN influent (Averages and Standard Deviations).

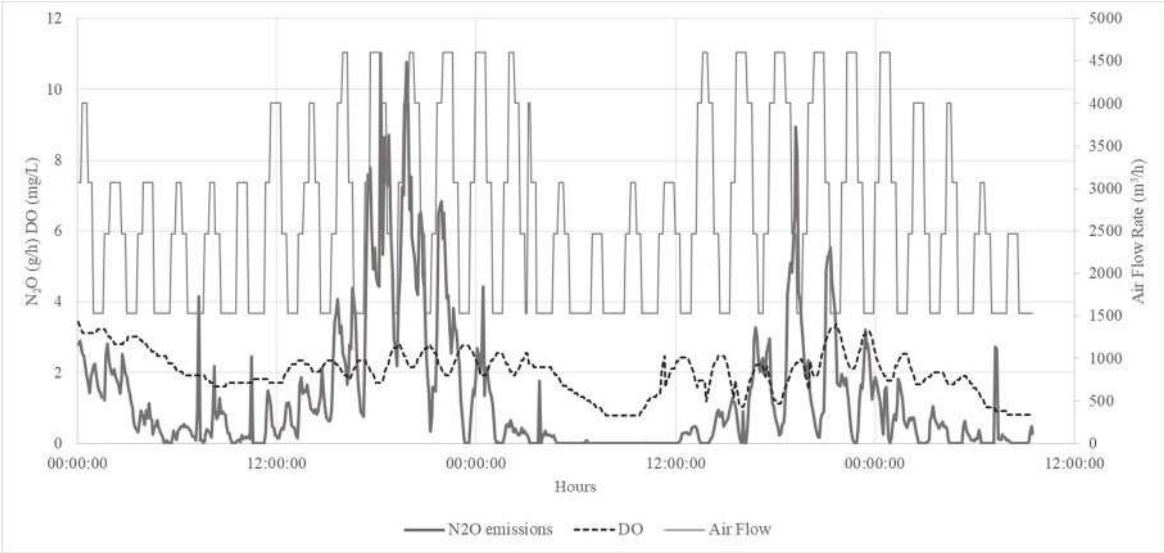


Figure 6: Profile of the N_2O emissions, air flow-rate and DO data for the nitrification reactor