

1 **Effect of process parameters and operational mode on nitrous oxide**  
2 **emissions from a nitrification reactor treating reject wastewater**

3 Maite Pijuan<sup>a\*</sup>, Josep Torà<sup>b</sup>, Adrián Rodríguez-Caballero<sup>a</sup>, Elvira César<sup>c</sup>, Julián Carrera<sup>b</sup>,  
4 Julio Pérez<sup>b</sup>.

5 <sup>a</sup> Catalan Institute for Water Research (ICRA), Scientific and Technological Park of the  
6 University of Girona, 17003, Girona (Spain).

7 <sup>b</sup> Department of Chemical Engineering, School of Engineering, Universitat Autònoma de  
8 Barcelona, Spain.

9 <sup>c</sup> Depuración de Aguas del Mediterráneo (DAM), Guglielmo Marconi, 11 piso 2º,  
10 despacho 19, Parque Tecnológico 46980 Paterna (Valencia).

11 \* Corresponding author: email: [mpijuan@icra.cat](mailto:mpijuan@icra.cat); phone: +34972183380; fax:  
12 +34972183248.

13

14 **ABSTRACT**

15 Nitrous oxide (N<sub>2</sub>O) and methane emissions were monitored in a continuous granular  
16 airlift nitrification reactor from ammonium-rich wastewater (reject wastewater). N<sub>2</sub>O  
17 emissions were found to be dependent on dissolved oxygen (DO) concentration in the  
18 range of 1 to 4.5 mg O<sub>2</sub>/L, increasing within this range when reducing the DO values. At  
19 higher DO concentrations, N<sub>2</sub>O emissions remained constant at 2.2% of the N oxidized to  
20 nitrite, suggesting two different mechanisms behind N<sub>2</sub>O production, one dependent and  
21 one independent of DO concentration. Changes on ammonium, nitrite, free ammonia and  
22 free nitrous acid concentrations did not have an effect on N<sub>2</sub>O emissions within the  
23 concentration range tested. When operating the reactor in a sequencing batch mode under  
24 high DO concentration (> 5 mg O<sub>2</sub>/L), N<sub>2</sub>O emissions increased one order of magnitude

25 reaching values of  $19.3 \pm 7.5$  % of the N oxidized. Moreover,  $\text{CH}_4$  emissions detected were  
26 due to the stripping of the soluble  $\text{CH}_4$  that remained dissolved in the reject wastewater  
27 after anaerobic digestion. Finally, an economical and carbon footprint assessment of a  
28 theoretical scaled up of the pilot plant was conducted.

29 *Keywords:* partial nitrification; reject wastewater; nitrous oxide emissions; continuous vs  
30 discontinuous operation; economical analysis.

31

## 32 **1. Introduction**

33 Specific treatments for high ammonium ( $\text{NH}_4^+$ ) streams such as reject wastewater  
34 produced in the anaerobic digester sludge dewatering process have been implemented in  
35 many wastewater treatment plants (WWTPs). Anaerobic digestion reject water is  
36 characterized by its high  $\text{NH}_4^+$  content (500-1500 mg N/L) and its treatment is normally  
37 done via partial nitrification followed by denitrification (Hellinga et al., 1998; Mulder et  
38 al., 2001) or the combination of partial nitrification with anammox (van Dongen et al.,  
39 2001) to reduce the operational costs. In the last few years, several studies have reported  
40 uncontrolled direct nitrous oxide ( $\text{N}_2\text{O}$ ) emissions during this treatment, especially in the  
41 nitrification reactor, where conversion of  $\text{NH}_4^+$  to nitrite ( $\text{NO}_2^-$ ) occurs due to the action of  
42 ammonia oxidizing bacteria (AOB) (Kampschreur et al., 2008a; de Graaff et al., 2010;  
43 Desloover et al., 2011; Law et al., 2012). In full-scale partial nitrification installations  $\text{N}_2\text{O}$   
44 values ranging from 1.7 to 6.6% of the nitrogen load have been measured, which  
45 correspond to 3.4-11.2 % of the  $\text{NH}_4^+$ -N oxidized emitted as  $\text{N}_2\text{O}$  since these systems  
46 operate with partial conversion of  $\text{NH}_4^+$  to  $\text{NO}_2^-$  (Kampschreur et al., 2008a; Desloover et  
47 al., 2011).  $\text{N}_2\text{O}$  has a warming potential 265 times higher than that of  $\text{CO}_2$  (IPCC 2013)

48 and in some cases might be responsible of the majority of the carbon footprint of the  
49 plant, especially in those systems with high conversion of  $\text{NH}_4^+$  to  $\text{NO}_2^-$ .

50 AOB are known to be net producers of  $\text{N}_2\text{O}$  which originates via two possible pathways:  
51 a) oxidation of hydroxylamine ( $\text{NH}_2\text{OH}$ ) which could be regulated by the concentration  
52 of free ammonia (Stein 2011); b) the reduction of  $\text{NO}_2^-$  to  $\text{N}_2\text{O}$  in a process known as  
53 nitrifier denitrification (Bock et al., 1995). Low dissolved oxygen (DO) concentration  
54 levels, high  $\text{NO}_2^-$  concentrations and variation in influent  $\text{NH}_4^+$  concentrations have been  
55 identified to promote  $\text{N}_2\text{O}$  formation (Kampschreur et al., 2009a). To this end, effective  
56 process control specifically devoted to keep desired set-points for the key parameters of  
57 operation in nitrification reactors (i.e. DO concentration,  $\text{NH}_4^+$  concentration, pH) should  
58 be targeted.

59 The aim of this manuscript was to identify the DO,  $\text{NH}_4^+$  and free ammonia concentration  
60 thresholds that originated the lowest  $\text{N}_2\text{O}$  emissions in a nitrification reactor. The novel  
61 control strategy applied in this reactor and described in Bartrolí et al. (2010) allowed the  
62 flexibility of operating at a desired DO set-point without compromising the effectiveness  
63 of the system. The control strategy also allowed to operate at full (100% conversion of  
64  $\text{NH}_4^+$  to  $\text{NO}_2^-$ ) or partial nitrification (50% conversion of  $\text{NH}_4^+$  to  $\text{NO}_2^-$ ) depending on the  
65 subsequent denitrification step: either heterotrophic or autotrophic (anammox),  
66 respectively. A comparison in terms of treatment performance and  $\text{N}_2\text{O}$  emissions  
67 between continuous and discontinuous operation mode for the same reactor is also  
68 presented and highlights the importance of considering greenhouse gas emissions when  
69 implementing a technology. Finally, an economic and carbon footprint analysis of

70 applying a N<sub>2</sub>O mitigation strategy was conducted for the pilot plant and extrapolated to  
71 real facilities.

72

## 73 **2. Materials and methods**

### 74 **2.1. Pilot plant**

#### 75 2.1.1. Continuous operation

76 The pilot plant consisted in a 150L granular airlift reactor with a height to diameter ratio  
77 of 8.4. It was located in a municipal WWTP in Catalonia, Spain, and it was performing  
78 full partial nitrification of reject wastewater produced in situ during the dewatering  
79 process of the anaerobic digester sludge from the WWTP. The temperature of the reactor  
80 was kept at 30°C by using an electric heating system and a temperature controller. The  
81 pH was maintained at 7.5±0.2 through the addition of solid Na<sub>2</sub>CO<sub>3</sub>. DO concentration  
82 was monitored with an online DO probe (LDO luminescence sensor, Hach-Lange,  
83 Düsseldorf, Germany) and was maintained around the desired set-point (see table 1) by  
84 changing the aeration flow-rate (from 11 to 100 L/min). The total ammonium nitrogen  
85 (TAN=NH<sub>4</sub><sup>+</sup>-N/L+NH<sub>3</sub>-N/L) concentration in the bulk liquid was monitored with an  
86 online probe (NH<sub>4</sub>D sc probe with a Cartrical cartridge, Hach Lange, Düsseldorf,  
87 Germany).

88 The reactor was operated with a variation of the control strategy presented in Bartrolí et  
89 al. (2010) during the period of monitoring. The variable measured for the control loop  
90 was the TAN concentration whereas the manipulated variable was the wastewater inflow  
91 rate fed to the reactor. The feedback control loop maintaining the TAN concentration in  
92 the bulk liquid allows for a maximization of the treatment capacity at any time, because

93 the loading rate is as high as possible during the continuous operation of the reactor. The  
94 influent wastewater was added in an on/off mode controlled by the concentration of  $\text{NH}_4^+$   
95 present in the bulk liquid. When the  $\text{NH}_4^+$  concentration was lower than the set-point (40  
96 mg  $\text{NH}_4^+$ -N/L), the feeding pump was activated, until the  $\text{NH}_4^+$  concentration was again  
97 at the set-point value. With this strategy,  $\text{NH}_4^+$  concentration was always kept between  
98 the desired set-point  $\pm 5$  mg N/L and  $\text{NO}_2^-$  concentration depended on the concentration  
99 of  $\text{NH}_4^+$  in the influent, but always with an  $\text{NH}_4^+$  to  $\text{NO}_2^-$  conversion higher than 92%,  
100 except for the period where partial nitrification was applied (see figure 1). Nitrate ( $\text{NO}_3^-$ )  
101 was hardly detected in the reactor at all times, presenting concentrations around 1-2 mg  
102 N/L in the bulk liquid (see figure 1). The system was controlled and monitored through a  
103 SCADA (supervisory control and data acquisition) program. For the control system, the  
104 manipulated variable was the inflow rate of the reject water. DO concentration was  
105 manipulated by changing the air flow-rate through the opening of the pneumatic valve  
106 that could be regulated continuously (i.e. via a frequency modulated solenoid valve). The  
107 air flow-rate was kept constant during each monitoring period to decrease the impact of  
108 total aeration flow-rate on the estimation of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  emissions. The DO varied  
109 during a monitoring period within a very small range (i.e.  $\pm 0.1$  of the desired set-point).  
110 At the time of the study, the reactor had been working for more than 100 days under  
111 stable operation (see figure 1) and had a nitrogen loading rate (NLR) of 0.85 g N/Ld, a  
112 biomass concentration of 5 g MLVSS/L, and a mean granule size of 0.5 mm (Torà et al.,  
113 2013). The hydraulic retention time (HRT) was maintained within the range of 0.4-0.6 d  
114 and the sludge residence time (SRT) was kept at 50 d.

#### 115 2.1.2. Sequencing Batch Reactor operation

116 Towards the end of the study, the reactor was switched from continuous to sequencing  
117 batch reactor mode (SBR) for a period of 2 weeks. The reactor volume was decreased,  
118 resulting in 100 L after the feeding phase. The cycle time consisted in: 6 min feeding,  
119 where 50L of wastewater was fed into the reactor; an aerobic phase, with the length being  
120 controlled by the control strategy explained above and based on the TAN concentration; a  
121 settling phase which varied between 7 and 30 min depending on the cycle; and 2 min  
122 decanting phase where 50L of treated wastewater was discharged. The aeration was kept  
123 constant at 100 L/min during the reaction phase which provided a DO concentration  
124 range between 5.7 and 7.2 in all cycles tested. Solid  $\text{Na}_2\text{CO}_3$  was added when the pH  
125 reached values lower than 7.5 in the reactor bulk liquid. HRT and SRT were maintained  
126 in the same range than in the continuous operation.

## 127 **2.2. Wastewater characteristics**

128 The reject water produced in the WWTP where the pilot plant was located was stored into  
129 two tanks of 1000L at room temperature, connected alternatively to the reactor inflow  
130 pump. During the study under continuous operation the composition of the reject water  
131 was within the following concentrations: TAN  $726 \pm 50$  mg N/L, total organic carbon  
132 (TOC) 240 – 696 mg C/L, total inorganic carbon (TIC) 358 – 723 mg C/L, total nitrite  
133 nitrogen (TNN= $\text{NO}_2^-$ -N +  $\text{HNO}_2$ -N) 2 – 7 mg N/L,  $\text{NO}_3^-$  0 mg N/L, MLSS 122 – 239  
134 mg/L, MLVSS 100 – 206 mg/L; pH 8.1 – 8.8. The percentage of biodegradable organic  
135 matter in the reject water was determined as only  $5 \pm 3$  % of the total TOC following the  
136 methodology described in Suárez-Ojeda et al. (2007). Due to some changes in the  
137 operation of the WWTP anaerobic digester, the concentration of TAN decreased in the  
138 reject wastewater when the reactor operated in SBR mode resulting in  $450 \pm 78$  mg N/L.

139 **2.3. Nitrous oxide and methane monitoring**

140 Off gas was collected continuously (at 0.5L/min) from the reactor headspace which was  
141 covered with a plastic bag and connected via a gas tube to a gas conditioning unit (series  
142 CSS, M&C Tech group). The gas outlet from the conditioning unit was connected to the  
143 multicomponent online gas analyser (VA-3000, Horiba, Japan) which provided an online  
144 measurement of N<sub>2</sub>O and CH<sub>4</sub> concentrations from the gas flow. Data were logged every  
145 15 seconds for a period of 3-4 h for each of the monitoring tests.

146 **2.3.1. Monitoring during continuous operation**

147 Twenty-four monitoring tests (T1-T24) were conducted to assess the N<sub>2</sub>O and CH<sub>4</sub>  
148 emission dynamics from the reactor under different DO concentrations in the range of 1.1  
149 to 7.7 mg O<sub>2</sub>/L. The different DO concentrations are summarised in table 1 and were  
150 achieved by varying the air flow-rate from 11 to 100 L/min. The reactor operated under  
151 the conditions described for each of the tests (table 1) 24 h previous to the monitoring.

152 To explore the effect of NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, free ammonia (FA) and free nitrous acid (FNA)  
153 concentration on N<sub>2</sub>O emission, six of these tests (T11-T16) were conducted under the  
154 same DO concentration (3.2-3.3 mg/L) but with different NH<sub>4</sub><sup>+</sup> concentration and pH,  
155 providing different FA, NO<sub>2</sub><sup>-</sup> and FNA concentrations (table 2).

156 **2.3.2. Monitoring during SBR operation**

157 Five cycles (TC1-TC5) were monitored when the reactor was operated in SBR mode. The  
158 conditions of each cycle monitored are described in table 3. These conditions were  
159 applied in the SBR at least 24 h before the monitoring was conducted.

160 **2.4. Calculations**

161 The total N<sub>2</sub>O and CH<sub>4</sub> emitted were calculated using the following equations:

162 
$$N_2O \text{ emitted} = \sum (C_{N_2O-N_{gas}} \times Q_{gas} \times \Delta t) \quad (1)$$

163 
$$CH_4 \text{ emitted} = \sum (C_{CH_4_{gas}} \times Q_{gas} \times \Delta t) \quad (2)$$

164 Where

165  $C_{N_2O}$  (g N<sub>2</sub>O-N/L) = C<sub>N<sub>2</sub>O</sub> (ppmv)\*10<sup>-6</sup> \* molar gas volume<sup>-1</sup> (0.0414 mol/L at 25°C and  
166 1atm)\*28.

167  $C_{CH_4}$  (g CH<sub>4</sub>/L) = C<sub>CH<sub>4</sub></sub> (ppmv)\*10<sup>-6</sup> \* molar gas volume<sup>-1</sup> (0.0414 at 25°C and 1atm)\*16.

168 Q<sub>gas</sub>= the gas flow rate of the aeration (L/min).

169 Δt= time interval by which the off-gas N<sub>2</sub>O concentration was recorded.

170 The emission factor for N<sub>2</sub>O was calculated based on the total amount of N<sub>2</sub>O emitted in  
171 a particular time (equation 1) relative to the total NH<sub>4</sub><sup>+</sup> converted to NO<sub>2</sub><sup>-</sup> in that time (mg  
172 N<sub>2</sub>O-N/mg NH<sub>4</sub><sup>+</sup>-N). This way of calculating the emission factor is very important to  
173 compare the emission factors when the reactor is oxidizing only a certain fraction of the  
174 ammonium load (e.g. either full or partial nitrification).

175 To directly compare the emission factors reported in the literature for single-stage N  
176 removal systems (nitrification and anammox in 1 single reactor) with the emissions  
177 reported in this study and in other nitrification systems (Table 5), the following procedure  
178 was applied: (i) the values reported for single-stage N-removal systems (normally given  
179 in %N<sub>2</sub>O/N-load) were used to calculate emission factor as percent of N removed; (ii) a  
180 50% of the N removed was considered to be oxidized to NO<sub>2</sub><sup>-</sup> (roughly following the  
181 anammox stoichiometry); (iii) all the N<sub>2</sub>O emissions reported in these systems were  
182 assumed to be produced during the nitrification process as anammox bacteria do not  
183 produce N<sub>2</sub>O (Kartal et al., 2010). This procedure could be summarized with the  
184 following equation:

185  $\%N_2O$  emitted (per  $NH_4^+$  oxidized to  $NO_2^-$ ) = 2\* (% $N_2O$  emitted per N removed) (3)

## 186 **2.5. Economical assessment of $N_2O$ mitigation**

187 To conduct an economic and carbon footprint analysis of implementing a  $N_2O$  mitigation  
188 strategy we considered a WWTP of ca. 140000 p.e. and dimensioned a nitrification reactor  
189 to treat the reject water coming from the dewatering process of the anaerobic digester  
190 sludge (reactor volume of ca.  $100m^3$  treating ca. 160 kg N/d). Two different scenarios  
191 were taken into consideration: (i) low DO concentration (1.5 mg  $O_2/L$ ) and (ii) high DO  
192 concentration (4.5 mg  $O_2/L$ ). Aeration flow rates were estimated for both scenarios  
193 scaling up the values required for the pilot reactor (i.e. 1400 and 2000  $m^3/d$  respectively).  
194 For convenience, aeration efficiency was assumed to be equivalent to that in the pilot  
195 reactor, and the aeration flow rates were scaled up as proportional to reactor volume. The  
196 same  $N_2O$  emission factors determined with the pilot installation for each one of the  
197 scenarios (~ 6% and 2% respectively) were assumed for the full scale installation. To  
198 estimate the energy consumption associated to aeration, a pressure difference of 1.2 bar  
199 was assumed, accounting for both the reactor height and pressure drop (i.e. effective  
200 height of water column of 12 m). The energy requirements of a displacement screw  
201 blower at each one of the air flow rates (1400 and 2000  $m^3/d$ ) were estimated as 47 and  
202 71 kWh for each scenario, respectively. To this end, the indications of the manufacturer  
203 on efficiency of the equipment related to the particular compressed flow were followed  
204 although it has to be taken into account that these efficiencies often incorporate an over  
205 estimation.

206 To estimate the carbon footprint, the following equivalences were assumed: 1 kg of  $N_2O$   
207 = 265  $CO_2$  equivalents (IPCC 2013) and 1kWh = 0.544  $CO_2$  equivalents (UKWIR 2008).

208 For the economical assessment with the carbon taxes, the two scenarios chosen (low and  
209 high carbon tax) were based on the values expected to be implemented in Europe (SBS,  
210 2012).

## 211 **2.6. Chemical and microbial analysis**

212 TAN was analyzed using a continuous flow analyzer based on potentiometric  
213 determination of ammonia. TNN and  $\text{NO}_3^-$  were measured with ionic chromatography  
214 using a DIONEX ICS-2000 Integrated Reagent-Free IC System with an auto-sampler  
215 AS40. TIC and TOC were measured with an OI Analytical TOC Analyzer (Model  
216 1020A) equipped with a non-dispersive infrared (NDIR). Mixed liquor suspended solids  
217 (MLSS), and volatile MLSS (MLVSS) were determined according to standard methods  
218 (APHA, 1995). A Malvern Mastersizer 2000 instrument was used to measure the granule  
219 size and size distribution.  $\text{N}_2\text{O}$  and  $\text{CH}_4$  analysis were performed by a commercial  
220 infrared analyzer (VA-3000, Horiba, Japan). Fluorescence in situ hybridization (FISH)  
221 was performed to quantify the amount of AOB and NOB microorganisms present in the  
222 reactor. Full details about the procedure can be found in the supplementary information  
223 section.

224

## 225 **3. Results**

### 226 **3.1. Nitrogen transformations in the granular airlift reactor**

227 At the time of the study, the granular airlift reactor had been operating in continuous  
228 mode for more than 100 days, achieving partial nitrification from reject wastewater as  
229 shown in figure 1. More details about the reactor start-up and stabilization can be found  
230 in Torà et al. (2013). At the time of the experiments, the mean size of the granular sludge

231 was 0.5 mm and the microbial composition consisted of  $70\pm 10\%$  AOB and  $<1\%$  NOB.  
232 The strong oxygen limiting conditions even at high DO concentrations were assured due  
233 to the great excess of  $\text{NH}_4^+$  in the bulk liquid (Bartrolí et al., 2010).  $\text{NO}_3^-$  was always at  
234 very low values ( $< 1.5$  mg N/L) during the period of the study. The pilot plant operated at  
235 full nitrification conditions for the majority of the monitoring period. However, the control  
236 system applied also allowed its operation under partial nitrification conditions as shown in  
237 figure 1 (days 255-280).

### 238 **3.2. Emission dynamics of $\text{N}_2\text{O}$ and $\text{CH}_4$ during continuous operation**

239 An example of the  $\text{N}_2\text{O}$  and  $\text{CH}_4$  emission dynamics from the reactor under stable  
240 operation is represented in figure 2.  $\text{N}_2\text{O}$  levels in the off-gas oscillated within 40 and 85  
241 ppmv when the reactor was operated with an aeration flow of 50 L/min, increasing the  
242 concentration a few minutes after each addition of wastewater (Figure 2). The minor  
243 oscillations produced by the on-off action of the  $\text{NH}_4^+$  concentration control loop resulted  
244 in slight  $\text{NH}_4^+$  and  $\text{NO}_2^-$  concentration disturbances which seem to have an effect on the  
245  $\text{N}_2\text{O}$  emissions (Figure 2A&B). Taking into account these emissions and the  $\text{NH}_4^+$   
246 transformed to  $\text{NO}_2^-$ , the  $\text{N}_2\text{O}$  emission factor during this particular period of monitoring  
247 was 2.4%  $\text{N}_2\text{O-N/oxidized-N}$ .

248 Regarding  $\text{CH}_4$ , the emissions detected in our system came from the stripping of the  
249 soluble  $\text{CH}_4$  that remained dissolved in the reject wastewater after anaerobic digestion  
250 and were not produced in the reactor. These emissions are clearly uncoupled from the  
251  $\text{N}_2\text{O}$  emissions (see Figure 2B), showing that the  $\text{N}_2\text{O}$  variation was due to the nitrification  
252 process, and was not linked to either stripping or other physical processes that might be  
253 occurring in the reactor.

254 **3.3. Effect of DO concentration on N<sub>2</sub>O emission**

255 The effect of different DO concentrations on N<sub>2</sub>O emissions was tested by changing the  
256 aeration flow rate in the pilot plant. To compare the emissions under different DO  
257 concentrations, the N<sub>2</sub>O emission factor was calculated as described in Materials and  
258 Methods section. Figure 3 presents the N<sub>2</sub>O emission factor dependency on DO  
259 concentration.

260 The lowest N<sub>2</sub>O emission factor was measured at DO concentrations of 4.5 mg O<sub>2</sub>/L or  
261 higher (Figure 3, region b). At this range,  $2.2 \pm 0.4$  % of the NH<sub>4</sub><sup>+</sup> nitrified was emitted as  
262 N<sub>2</sub>O and was not dependent on the DO concentration. However, when reducing the DO  
263 concentration to levels lower than 4.5 mg O<sub>2</sub>/L, the N<sub>2</sub>O emission factor increased,  
264 reaching values around 6% of the NH<sub>4</sub><sup>+</sup> nitrified being emitted as N<sub>2</sub>O (Figure 3, region  
265 a). Operating the reactor under partial or full nitrification conditions did not have an effect  
266 on N<sub>2</sub>O emissions. Emissions detected under partial nitrification conditions matched the  
267 same profile as the emissions found when operating under full nitrification within the  
268 concentration DO range of 1.6-5.3 mg O<sub>2</sub>/L (highlighted in figure 3 with empty circles  
269 and triangles).

270 Stripping conditions changed among the experiments, since changes on DO concentration  
271 in the reactor could only be achieved by changing the aeration flow rate (table 1). It can  
272 not be excluded that changes in stripping conditions might also have a direct effect on the  
273 N<sub>2</sub>O emissions detected but changes in DO concentration seem to be the main driver to  
274 changes on N<sub>2</sub>O as shown by the strong correlation depicted in figure 3 and the bigger  
275 dispersion observed when depicting the correlation between N<sub>2</sub>O emission factor and air  
276 flow rate (figure SI.1)

277 **3.4. Effect of ammonium, free ammonia, nitrite and free nitrous acid on N<sub>2</sub>O**  
278 **emission.**

279 The effect of operating the pilot plant at different NH<sub>4</sub><sup>+</sup> and FA concentrations on N<sub>2</sub>O  
280 production was tested by varying the NH<sub>4</sub><sup>+</sup> concentration set-point in the control loop and  
281 the pH (Table 2). FNA concentration was calculated considering the amount of NO<sub>2</sub><sup>-</sup>  
282 present in the reactor and the pH and was also related to N<sub>2</sub>O. Results are presented in  
283 figure 4.

284 The pilot plant operated under the same DO concentration (3.2-3.3 mg O<sub>2</sub>/L) when these  
285 experiments were carried out to exclude the effect of DO on N<sub>2</sub>O emissions. The N<sub>2</sub>O  
286 emission factor remained constant at 4.4±0.3% of the NH<sub>4</sub><sup>+</sup> oxidized emitted as N<sub>2</sub>O  
287 despite of the wide range of NH<sub>4</sub><sup>+</sup>, FA, NO<sub>2</sub><sup>-</sup> and FNA concentrations tested. Therefore it  
288 can be concluded that within the concentration range tested and with a DO concentration  
289 of 3.3 mg O<sub>2</sub>/L, changes on NH<sub>4</sub><sup>+</sup>, FA, NO<sub>2</sub><sup>-</sup> and FNA did not have an effect on N<sub>2</sub>O  
290 production. Interestingly, the N<sub>2</sub>O emission factor was independent of the performance of  
291 the granular reactor for achieving full nitrification (100% conversion of NH<sub>4</sub><sup>+</sup> to NO<sub>2</sub><sup>-</sup>) or  
292 partial nitrification (50-75% conversion of NH<sub>4</sub><sup>+</sup> to NO<sub>2</sub><sup>-</sup>).

293 **3.5. Emission dynamics of N<sub>2</sub>O and CH<sub>4</sub> during SBR operation**

294 The pilot plant was shifted from continuous to SBR operation mode to study if this  
295 operation had an effect on the overall nitrogen transformations in the plant. For a period  
296 of two weeks, five different cycle studies (Table 3) were monitored and one of them is  
297 presented in figure 5.

298 During SBR operation an aeration flow rate of 100L/min was applied. DO concentration  
299 followed the same pattern in all the cycles: a slow increase during the reaction phase

300 (from 5.6 till 7.2 mg O<sub>2</sub>/L approximately), a sharp decrease as soon as aeration stopped  
301 during the settling phase (from 7.2 till 0.5 mg O<sub>2</sub>/L in the cycle with the longest settling  
302 time tested, 30 min) and a sharp increase as soon as aeration started during the feeding  
303 (reaching 5.2-5.5 mg O<sub>2</sub>/L in the first minute of aeration). pH increased at the beginning  
304 of the cycle to values close to 8 due to the alkalinity provided by the wastewater. After  
305 that, and due to the nitrification reaction, pH decreased until 7.5, when pH control started.  
306 The cycle length was controlled by the NH<sub>4</sub><sup>+</sup> set-point applied in the control loop. As  
307 soon as the concentration reached values lower than 40 mg N/L, aeration stopped and  
308 settling started. NO<sub>2</sub><sup>-</sup> concentrations in the bulk liquid were comprised between 190  
309 (beginning of the cycle) and 370 mg N/L (end of the aeration phase) at all times during  
310 SBR operation. These concentrations were lower than those measured in the bulk liquor  
311 during continuous monitoring. This was due to the lower NH<sub>4</sub><sup>+</sup> concentration present in  
312 the reject wastewater when the reactor operated in SBR mode.

313 Peaks of CH<sub>4</sub> and N<sub>2</sub>O were detected at the beginning of the cycle as soon as aeration  
314 started. The CH<sub>4</sub> peak corresponded to the stripping of the soluble CH<sub>4</sub> present in the  
315 reject wastewater. Indeed, this peak was 10 times higher than the peaks detected under  
316 continuous operation but this was because 10 times more wastewater was added as a  
317 pulse under SBR operation. No difference was found when considering the total amount  
318 of CH<sub>4</sub> emitted per wastewater treated (Figure SI.2). The N<sub>2</sub>O profile also displayed a  
319 peak at the beginning of the aeration phase reaching concentrations of 1000 ppmv during  
320 the first 10 min of the cycle. After that the N<sub>2</sub>O concentration decreased until values  
321 around 100 ppmv towards the end of the aerobic phase. This concentration from the end  
322 of aeration was very similar to the concentrations measured during the monitoring

323 conducted under continuous operation at similar operational conditions (Tests T18, T22,  
324 T24 performed at 100L/min of aeration flow rate; 4.4-6.7 mg O<sub>2</sub>/L; 7.5-8 pH). However,  
325 when considering the total N<sub>2</sub>O emitted per N oxidized, the emission factor obtained  
326 during SBR operation was 19.3 ± 7.5 %, one order of magnitude higher than the 2.2 ± 0.4  
327 % found under continuous operation at the same DO concentration range. The application  
328 of different settling times during SBR operation mode did not show an apparent  
329 correlation with the N<sub>2</sub>O emitted during the cycle (Figure SI.3).

### 330 **3.6. Economical assessment of N<sub>2</sub>O mitigation**

331 From the results presented, operating the reactor in a continuous mode at high aeration  
332 rates (DO concentration > 4.5 mg O<sub>2</sub>/L) can be postulated as an effective approach to  
333 mitigate N<sub>2</sub>O emissions. However, from the practical point of view, this can be seen as an  
334 expensive operational strategy, since it involves higher electricity consumption. In fact  
335 the main operating costs of such an installation have been related to the electricity used to  
336 aerate the reactor (Carrera et al., 2010). If lowering greenhouse gas emissions during  
337 wastewater treatment is not associated with an economical incentive it will be difficult for  
338 the industry to implement mitigation strategies that imply increasing operational costs.  
339 However, many governments are starting to implement a price tag or carbon tax on  
340 pollution to discourage industry from emitting greenhouse gases in an attempt to control  
341 global warming. In this sense, a more elaborated assessment has been performed taking  
342 into account three different scenarios: (i) without carbon tax; (ii) applying a low carbon  
343 tax; (iii) applying a high carbon tax (Table 4). To conduct such analysis the obtained N<sub>2</sub>O  
344 emission factors have been applied to a scaled up theoretical nitrification system treating  
345 the reject wastewater from a 140,000 p.e. WWTP. It has to be taken into account that

346 theoretical calculations incorporate some assumptions such as same stripping efficiency  
347 for the pilot plant as for the full-scale theoretical installation, which might differ from the  
348 reality.

349 In continuous mode, operating at a higher DO to mitigate N<sub>2</sub>O emissions resulted in a  
350 43% lower carbon footprint. Remarkably, at low DO concentration N<sub>2</sub>O emissions were  
351 estimated to account for 81% of the total carbon footprint. The analysis shows that  
352 operating with the lowest carbon emission will only be economically feasible in the high  
353 carbon tax scenario.

354 A similar analysis was conducted with the emission factors found for the SBR operation.  
355 For convenience, nitrogen loading rate and aeration needs were considered equivalent to  
356 those determined for the continuous mode of operation. The carbon footprint increased  
357 almost three times even when comparing with the low DO scenario in the continuous  
358 mode. In case of application of carbon taxes, the SBR technology would not be a good  
359 choice for the nitrification of reject wastewater in view of the costs analysis.

360

## 361 **4. Discussion**

### 362 **4.1. Possible N<sub>2</sub>O production pathways affecting N<sub>2</sub>O emissions under different DO** 363 **concentrations**

364 DO is considered an important parameter affecting N<sub>2</sub>O emissions, with lower DO  
365 concentrations increasing N<sub>2</sub>O emissions (Kampschreur et al., 2009a). However, it is still  
366 unclear if a DO concentration threshold to minimise N<sub>2</sub>O emissions can be established for  
367 nitrifying systems since different N<sub>2</sub>O emission factors have been reported at different  
368 DO concentrations (Table 5).

369 It is accepted that two different N<sub>2</sub>O production pathways exist during nitrification: i) the  
370 nitrifier denitrification pathway and ii) the hydroxylamine oxidation pathway. Which one  
371 of these pathways is the main responsible for the N<sub>2</sub>O production in AOB is still unclear.  
372 Sutka et al. (2006) used stable nitrogen isotopes to conclude that the NH<sub>2</sub>OH oxidation  
373 pathway contributed to N<sub>2</sub>O production mainly at high DO concentrations whereas the  
374 nitrifier denitrification pathway was more active at low DO concentrations. Recently,  
375 Wunderlin et al. (2013) carried out a series of batch tests where the N<sub>2</sub>O production  
376 pathways were identified using site-specific isotope composition of N<sub>2</sub>O in real time. In  
377 their nitrification tests, there was always a combination of the two pathways that  
378 produced the N<sub>2</sub>O detected, except for the cases where only NO<sub>2</sub><sup>-</sup> was added, in which  
379 only the nitrifier denitrification pathway was active. Our results suggest the presence of at  
380 least two different predominant pathways for N<sub>2</sub>O production: one linked to the DO  
381 concentration, probably the nitrifier denitrification pathway (as can be observed in region  
382 “a” from Figure 3) and another one that would not depend on it (as can be observed in  
383 region “b” from Figure 3). The fact that N<sub>2</sub>O dependency on DO concentrations starts at a  
384 DO concentration relatively high (4 mg/L), could be due to the pilot plant operating with  
385 aerobic granular sludge. In aerobic granules, DO is consumed very fast by the  
386 microorganisms present in the outer layers of the granules (Pijuan et al., 2009), thus  
387 creating micro-aerobic or anoxic conditions in the inside of the granules which could  
388 favour the denitrification pathway in AOBs resulting in N<sub>2</sub>O formation, even at relatively  
389 high DO concentrations in the bulk liquid.

390 It can not be excluded either the possibility that a fraction of the N<sub>2</sub>O detected is  
391 produced by chemical reactions. High ammonia oxidation rates may lead to high

392 concentrations of  $\text{NH}_2\text{OH}$  which has been demonstrated to react with  $\text{NO}_2^-$  or FNA to  
393 form  $\text{N}_2\text{O}$ . As suggested by Schreiber et al. (2012) chemical  $\text{N}_2\text{O}$  production in systems  
394 dealing with high-strength N wastewater could be important. Our results show how  $\text{N}_2\text{O}$   
395 emissions can be reduced by increasing the DO concentration in the bulk liquid, but this  
396 reduction has a minimum value (the baseline in region “b”, as defined in Figure 3), that  
397 seems to be unalterable when DO concentration is further increased.

398 Interestingly our results also show that operating the reactor under different  $\text{NO}_2^-$   
399 concentrations (from 368 till 740 mg N/L) or different FNA concentrations (from 0.006  
400 till 0.065) did not affect the  $\text{N}_2\text{O}$  emissions. This could be due to the fact that the AOB of  
401 this study were adapted to high concentrations of  $\text{NO}_2^-$  (500-750 mg N/L). Previous  
402 studies have reported an increase on  $\text{N}_2\text{O}$  emissions when increasing  $\text{NO}_2^-$  concentrations  
403 in a pure culture of *Nitrosomonas europaea* (Anderson et al., 1993) and several mixed  
404 nitrifying systems (Kampchreur et al., 2008b; Tallec et al., 2006). These differences  
405 could be related to the fact that different AOB strains possess different adaptation  
406 strategies to high  $\text{NO}_2^-$  environments and therefore it is possible that the same  $\text{NO}_2^-$   
407 concentration triggers different  $\text{N}_2\text{O}$  production depending on the adaptation of AOB at  
408 that particular environment.

#### 409 **4.2. Continuous versus discontinuous operation**

410 One of the key differences between continuous and SBR operation mode is the presence  
411 of a settling phase in the last one. During settling, aeration stops, and DO sharply  
412 decreases (Figure 5), reaching DO levels  $< 1$  mg  $\text{O}_2/\text{L}$ , which could be even lower at the  
413 bottom of the reactor where all the biomass concentrates. These conditions might trigger  
414  $\text{N}_2\text{O}$  formation, which would be stripped from the bulk liquid in the subsequent aeration

415 phase, originating the high N<sub>2</sub>O peak detected. Several studies have inferred in the effect  
416 that periods of anoxia can have on N<sub>2</sub>O production from nitrifying cultures. Kampschreur  
417 et al. (2008b) reported the effect of oxygen limitation during NH<sub>4</sub><sup>+</sup> oxidation in a  
418 nitrifying lab-scale system. They observed an immediate N<sub>2</sub>O increase when air was  
419 replaced by nitrogen gas attributed to the activation of the denitrification pathway in  
420 AOBs. On the other hand, Yu et al. (2010) only observed N<sub>2</sub>O production in a pure  
421 culture of *Nitrosomonas europaea* during the recovery from a 48h period of anoxia, as  
422 soon as aeration started. Recently, Rodriguez-Caballero & Pijuan (2013) demonstrated  
423 that the majority (60-80%) of the N<sub>2</sub>O emitted from a nitrification lab-scale system treating  
424 reject wastewater originated during settling and depended on the presence of NH<sub>4</sub><sup>+</sup> and  
425 NO<sub>2</sub><sup>-</sup>.

426 Another explanation for the higher N<sub>2</sub>O production when operating in SBR mode could  
427 be the sudden variations on NH<sub>4</sub><sup>+</sup> and NO<sub>2</sub><sup>-</sup> concentrations experienced during the cycle,  
428 more pronounced than in continuous operation. Dynamic process conditions can enhance  
429 N<sub>2</sub>O production. Kampschreur et al. (2008b) studied the effect of dynamic process  
430 conditions on nitrogen oxides in a nitrifying culture. They subject the culture to a  
431 stepwise increase on NO<sub>2</sub><sup>-</sup> concentrations which gave an increase on N<sub>2</sub>O production.  
432 Recently, Law et al. (2013) reported a relationship between the specific N<sub>2</sub>O production  
433 rate and a gradual NO<sub>2</sub><sup>-</sup> accumulation in a partial nitrification culture treating synthetic  
434 reject wastewater. Interestingly, NO<sub>2</sub><sup>-</sup> had a suppressive effect on N<sub>2</sub>O production when  
435 increasing the concentration from 50 to 500 mg N/L. At higher NO<sub>2</sub><sup>-</sup> concentrations, N<sub>2</sub>O  
436 production remained constant. It is clear that more research on a fundamental level is  
437 needed to clarify these hypotheses.

438 At this stage, the use of SBR technology for nitrification of reject wastewater treatment  
439 needs further evaluation due to the higher N<sub>2</sub>O emissions it presents compared with  
440 continuous operation.

#### 441 **4.3. Impact of these results in the selection of single- or two-stage N removal**

442 Currently, the treatment of high and low-strength NH<sub>4</sub><sup>+</sup> wastewater can be carried out by  
443 single- or two-stage autotrophic N removal systems. The choice of one or another may  
444 depend on several factors such as: reactor volume, loading rate, process stability,  
445 economical issues, etc. (van Hulle et al., 2010; Jaroszynski et al., 2011). Another factor  
446 that is increasingly gaining attention is the N<sub>2</sub>O emission from these systems which could  
447 have a big impact on the overall carbon footprint of the plant. Currently, N<sub>2</sub>O emission  
448 values from single stage systems are still scarce and rather variable (see table 5). An N<sub>2</sub>O  
449 emission factor of 1.67% of the N removed was reported in a full-scale single stage  
450 nitrification-anammox reactor located in the Netherlands which corresponds to 2.5% of the  
451 N oxidized to nitrite (Table 5, Kampschreur et al., 2009b). In this reactor, nitrification and  
452 autotrophic denitrification was occurring in the same tank. Another monitoring performed  
453 recently in the same plant reported an emission factor of 2.1% of the N removed which  
454 corresponds to 4.0% of the N converted to nitrite (Castro-Barros et al., 2013).  
455 Interestingly, they detected a peak on N<sub>2</sub>O emissions when NO<sub>2</sub><sup>-</sup> accumulated in the  
456 reactor, during periods of low anammox activity, highlighting the need for efficient  
457 process control to avoid a sudden increase on N<sub>2</sub>O emissions in single stage nitrification-  
458 anammox systems.

459 On the other hand, emissions from partial nitrification systems from lab and full-scale  
460 reactors have been also reported in the literature (Table 5). In these cases, emissions vary

461 from 0.8 to 11.2 % of the N oxidized being emitted as N<sub>2</sub>O. Our findings indicate that  
462 changes in the NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, FNA or FA concentrations have no impact on N<sub>2</sub>O emissions  
463 during nitrification within the common operational ranges. Therefore, emissions detected in  
464 two stage nitrification-anammox systems are expected to be similar to those found in one-  
465 stage nitrification-anammox reactors for the treatment of reject wastewater. A possible  
466 advantage for the two-stage systems is that changes in the concentration of soluble N  
467 compounds would not have a big effect on the N<sub>2</sub>O emissions probably due to the  
468 adaptation of the biomass at these N concentrations while the current data seems to  
469 suggest that small accumulation of NO<sub>2</sub><sup>-</sup> in single nitrification-anammox reactors would lead  
470 to an increased emission factor (Kampschreur et al., 2009b). More full-scale N<sub>2</sub>O  
471 monitoring campaigns are needed for systems treating high strength N wastewater to  
472 clarify the treatment technology that provides lower emissions.

473 Single-stage N-removal systems operating at low temperatures and at low nitrogen  
474 loading rates have been demonstrated as feasible, but several challenges may well  
475 difficult the final implementation. These challenges include mainly the outcompetition of  
476 anammox by NOB and conventional heterotrophic denitrifiers (Winkler et al., 2012).  
477 These limitations would not be present in a two-stage N-removal system, and the  
478 operation of such a system in continuous mode using a nitrification step similar to the one  
479 presented here, will only increase slightly the N<sub>2</sub>O emissions if adequate DO  
480 concentration is maintained in the bulk liquid. This strategy may be an alternative to be  
481 considered since nitrification has been successfully tested at low temperatures (Jemaat et  
482 al., 2013).

483

484 **5. Conclusions**

485 Nitrous oxide emissions were monitored in a nitrification airlift reactor treating reject  
486 wastewater. The main findings of this study are listed as follow:

- 487 • DO concentration can be used as a control parameter to minimise N<sub>2</sub>O emissions.  
488 Increasing the DO to 4.5 mg O<sub>2</sub>/L resulted in a decrease on N<sub>2</sub>O emissions from 6  
489 to 2.2%. However, a further increase on DO did not result in an additional  
490 reduction, suggesting the involvement of two different mechanisms responsible  
491 for N<sub>2</sub>O production.
- 492 • Continuous operation is preferred to SBR for partial nitrification systems. SBR  
493 operation resulted in a substantial increase on N<sub>2</sub>O emissions when compared to  
494 those obtained in continuous mode.
- 495 • N<sub>2</sub>O emissions would dominate the total carbon footprint in a hypothetical scale-  
496 up of the reactor studied. Operating at minimal N<sub>2</sub>O emission would only be  
497 economically feasible if a carbon tax on emissions is implemented.

498

499 **Acknowledgements**

500 Funding: AGAUR and ACCIÓ (Secretaria d'Universitats i Recerca del Departament  
501 d'Economia i Coneixement de la Generalitat de Catalunya), 2010VALOR0096,  
502 Ministerio de Economía y Competitividad (projects CTM 2011-27163 and CTQ2011-  
503 24745/PPQ) and the European Commission FP7-PEOPLE-2011-CIG 303946. Company  
504 involved for the in situ location of the set-up: Depuración de aguas del Mediterráneo,  
505 DAM. The authors thank Eduard Moliné (DAM) for helpful discussions during the

506 course of the research. M. Pijuan also acknowledges the Ramon y Cajal research  
507 fellowship (RYC-2009-04959) provided by the Spanish Government.

508

509 **Supporting information available**

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635 **LIST OF FIGURES**

636 **Figure 1.** Nitrogen transformations in the granular airlift reactor before and during the  
637 GHG monitoring period. ●  $\text{NH}_4^+$  in the reactor; □  $\text{NO}_2^-$  in the reactor; ▽  $\text{NO}_3^-$  in the  
638 reactor; ▲  $\text{NH}_4^+$  in the wastewater.

639 **Figure 2. A-** On-line  $\text{N}_2\text{O}$  and  $\text{CH}_4$  emissions from the reactor during continuous  
640 operation at DO 4.7 mg  $\text{O}_2/\text{L}$  and pH 7.5.  $\text{N}_2\text{O}$  (Black line);  $\text{CH}_4$  (grey line); influent flow  
641 (thin black line); aeration flow (dashed line);  $\text{NH}_4^+$  (●);  $\text{NO}_3^-$  (▽);  $\text{NO}_2^-$  (□). **B-** Zoom in  
642 from figure A (135-185 min).

643 **Figure 3.** Correlation between the  $\text{N}_2\text{O}$  emission factor and the DO concentration in the  
644 reactor: ● Operation under full nitrification conditions (>90%  $\text{NH}_4^+$  oxidation to  $\text{NO}_2^-$ ); ○  
645 Operation under partial nitrification conditions (70%-75%  $\text{NH}_4^+$  oxidation to  $\text{NO}_2^-$ ); Δ  
646 Operation under partial nitrification conditions (50%-55%  $\text{NH}_4^+$  oxidation to  $\text{NO}_2^-$ ).

647 **Figure 4.** Correlation between the  $\text{N}_2\text{O}$  emission factor and ammonium /nitrite (A), free  
648 ammonia (B) and free nitrous acid (C) concentrations. ●- Ammonium, FA & FNA; □-  
649 Nitrite.

650 **Figure 5.** Cycle study profile of the pilot plant operating in SBR mode with a settling  
651 time of 7 min and an aeration flow of 100 L/min. A- pH (grey line), DO (black line),  
652 ammonium (discontinuous line) and nitrite (□) concentrations; B-  $\text{N}_2\text{O}$  (black line) and  
653  $\text{CH}_4$  (grey line) emission profiles; aeration flow (discontinuous line).

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658 **TABLES**

659 **Table 1.** Experimental tests conducted under continuous operation at different dissolved  
 660 oxygen concentrations.

	<b>T1</b>	<b>T2</b>	<b>T3</b>	<b>T4</b>	<b>T5</b>	<b>T6</b>	<b>T7</b>	<b>T8</b>	<b>T9</b>	<b>T10</b>	<b>T11</b>	<b>T12</b>
DO (mg O <sub>2</sub> /L)	1.1	1.2	1.5	1.6	1.6	1.7	2.0	2.4	2.5	2.6	3.2	3.2
Air flow (L/min)	13	11	14	37	11	11	13	50	11	24	13	18
pH	7.5	7.6	7.7	7.7	7.6	8.1	7.6	7.5	7.6	7.6	7.6	7.7
	<b>T13</b>	<b>T14</b>	<b>T15</b>	<b>T16</b>	<b>T17</b>	<b>T18</b>	<b>T19</b>	<b>T20</b>	<b>T21</b>	<b>T22</b>	<b>T23</b>	<b>T24</b>
DO (mg O <sub>2</sub> /L)	3.2	3.2	3.3	3.3	4.1	4.4	4.6	4.7	4.8	5.3	6.7	7.5
Air flow (L/min)	16	15	100	27	50	100	50	50	65	100	100	50
pH	8.1	7.6	8	7.7	8.4	7.7	7.6	7.5	7.6	8.0	7.5	7.2

661

662 **Table 2.** Experimental tests conducted under continuous operation at different NH<sub>4</sub><sup>+</sup>, FA  
 663 and FNA concentrations.

	<b>T11</b>	<b>T12</b>	<b>T13</b>	<b>T14</b>	<b>T15</b>	<b>T16</b>
NH <sub>4</sub> <sup>+</sup> (mg N/L)	37.5	158	319	5.3	192	58.6
NO <sub>2</sub> <sup>-</sup> (mg/L)	629.1	519.4	368.4	663.5	554.9	740.0
FA (mg N/L)	1.2	2.0	29.4	0.2	14.3	2.3
FNA (mg N/L)	0.031	0.065	0.006	0.033	0.011	0.029
pH	7.6	7.2	8.1	7.6	8	7.7
DO (mg O <sub>2</sub> /L)	3.2	3.2	3.2	3.2	3.3	3.3

664 FA and FNA concentrations were calculated according to Anthonissen et al. (1976).

665

666

667 **Table 3.** Experimental tests conducted under SBR operation.

	<b>TC1</b>	<b>TC2</b>	<b>TC3</b>	<b>TC4</b>	<b>TC5</b>
DO (mg O <sub>2</sub> /L)	5.7-7.2	6.7-7.0	6.15-6.40	5.6-7.2	5.6-6.6
Air flow (L/min)	100	100	100	100	100
pH	8.4-7.4	8.4-7.6	8.5-7.6	8.2-7.4	8.4-7.4
Settling time (min)	7	15	15	23	30

668

669 **Table 4.** Annual carbon footprint and cost analysis calculated with and without carbon  
 670 taxes, considering two different DO scenarios in an installation treating the reject water  
 671 of a WWTP of 140,000 p.e. Low DO: 1.5 mg O<sub>2</sub>/L; high DO: 4.5 mg O<sub>2</sub>/L

<b>Data</b>	<b>Low DO (Continuous)</b>	<b>High DO</b>		<b>Units</b>
		<b>Continuous</b>	<b>SBR</b>	
Annual energy requirements for aeration	408,303	625,421		kWh year <sup>-1</sup>
Annual N <sub>2</sub> O emissions	3.5	1.2	11.1	Tn N <sub>2</sub> O year <sup>-1</sup>
Equivalent CO <sub>2</sub> emissions for aeration	222	340		Tn CO <sub>2</sub> eq year <sup>-1</sup>
Annual N <sub>2</sub> O emissions (CO <sub>2</sub> eq.)	927	310	2941	Tn CO <sub>2</sub> eq year <sup>-1</sup>
<b>Annual carbon footprint</b>	<b>1,149</b>	<b>650</b>	<b>3282</b>	<b>Tn CO<sub>2</sub> eq year<sup>-1</sup></b>
Annual cost associated to energy requirements for aeration	34.7	53.2		k€ year <sup>-1</sup>
Annual cost associated to CO <sub>2</sub> emissions (Low carbon tax <sup>a</sup> )	4.6	2.6	13.1	k€ year <sup>-1</sup>
Annual cost associated to CO <sub>2</sub> emissions (High carbon tax <sup>b</sup> )	34.5	19.5	98.5	k€ year <sup>-1</sup>
<b>Total annual costs (without carbon tax)</b>	<b>34.7</b>	<b>53.2</b>		<b>k€ year<sup>-1</sup></b>
<b>Total annual costs (low carbon tax)</b>	<b>39.3</b>	<b>55.8</b>	<b>66.3</b>	<b>k€ year<sup>-1</sup></b>
<b>Total annual costs (high carbon tax)</b>	<b>69.2</b>	<b>72.7</b>	<b>151.6</b>	<b>k€ year<sup>-1</sup></b>

672 Factors used for calculations: 0.085 euro / kWh; 0.544 kg CO<sub>2</sub> eq / kWh; 265 kg CO<sub>2</sub> eq / kg  
 673 N<sub>2</sub>O. <sup>a</sup>Low carbon tax: 0.004 euro / kg CO<sub>2</sub>; <sup>b</sup>High carbon tax: 0.03 euro / kg CO<sub>2</sub>. For details of  
 674 each scenario, associated calculations and references see section 2.5 of the Materials & Methods.

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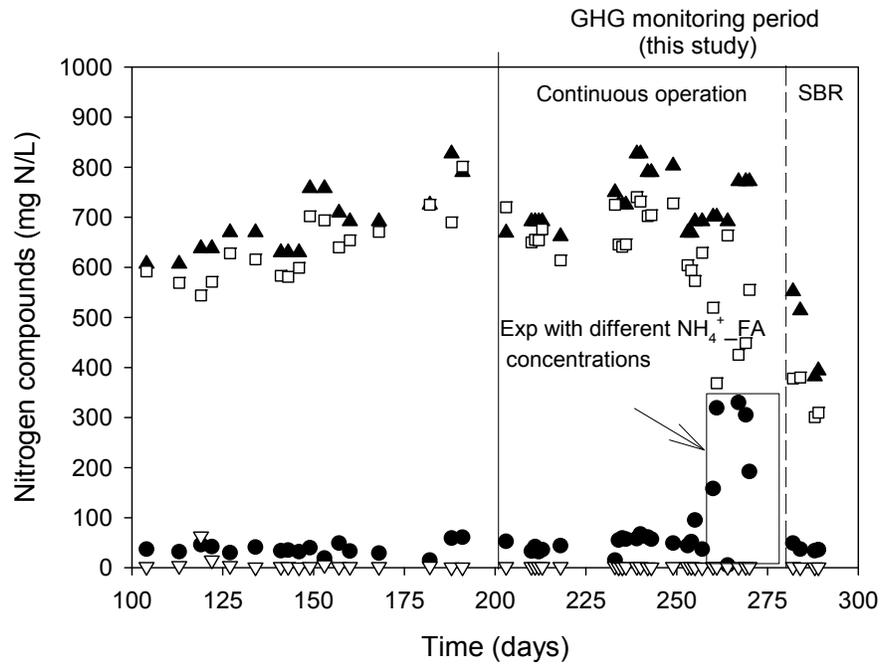
676 **Table 5.** Emission factors reported in the literature and in this study for the treatment of  
 677 high strength nitrogen wastewater.

Wastewater (reference)	Process type	DO concentration (mg O <sub>2</sub> /L)	Emission factor (%N-N <sub>2</sub> O/N-oxidized)
Anaerobically digested industrial WW (Desloover 2011)	Partial nitrification+anammox (2-stage). Full-scale. (Floccular sludge)	0.4-1.0	8.1-11.2* <sup>a</sup> *emissions from nitrification reactor
Concentrated black water (de Graaff 2010)	Partial nitrification in continuous reactor. Lab-scale. (Floccular sludge)	4.1-4.2	3.2 <sup>a</sup>
Reject WW (Joss 2009)	Partial nitrification+anammox (1-stage). SBR full-scale. (type of sludge not described)	<0.5	0.8 <sup>a</sup>
Reject WW (Kampschreur 2008a)	Partial nitrification + anammox (2-stage). Full-scale. (Floccular sludge)	2.5	3.4* *emissions from nitrification reactor
Reject WW (Kampschreur 2009b)	Partial nitrification+ anammox (1-stage). Full-scale. (Granular sludge)	5	2.5 <sup>a,b</sup>
Reject WW (Castro-Barros 2013)	Partial nitrification+anammox (1-stage). Full-scale. (Granular sludge)	N.R.	4.0 <sup>a,b</sup>
Reject WW (Law 2011)	Partial nitrification Lab-scale SBR. (Floccular sludge)	0.5-0.8	1.0
Reject WW (Rodriguez-Caballero 2013)	Partial nitrification Lab-scale SBR. (Floccular sludge)	0.8-1.5	0.8
Reject WW (this study)	Full or Partial Nitrification Pilot-scale granular airlift. (Granular sludge)	4.5-7.5	2.2
Reject WW (this study)	Full or Partial nitrification Pilot-scale granular airlift. (Granular sludge)	1.1-4.5	6.1-2.2

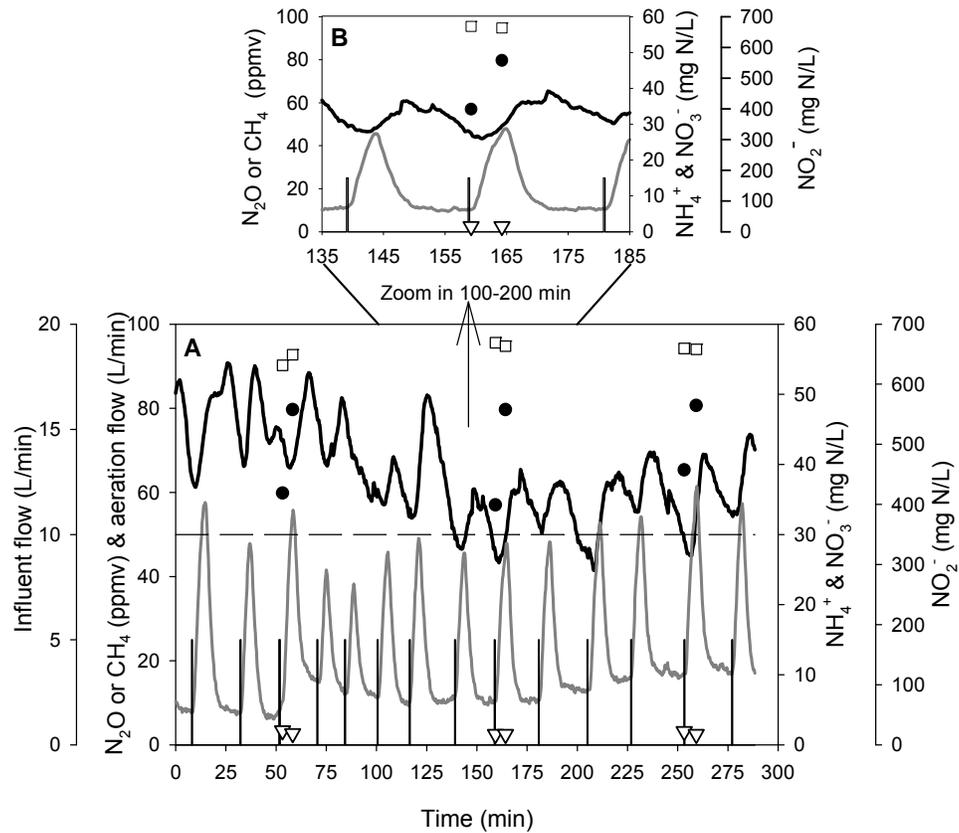
678 N.R. Not reported; <sup>a</sup> values calculated taken into account the %N<sub>2</sub>O/N load and the NH<sub>4</sub><sup>+</sup>  
 679 converted to nitrite reported. In the case of one-stage systems a 50% conversion of the  
 680 ammonium removed to nitrite has been assumed as reported in materials and methods section  
 681 (equation 3). <sup>b</sup> Values reported for the same reactor under at two different monitoring campaigns.

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Figure1

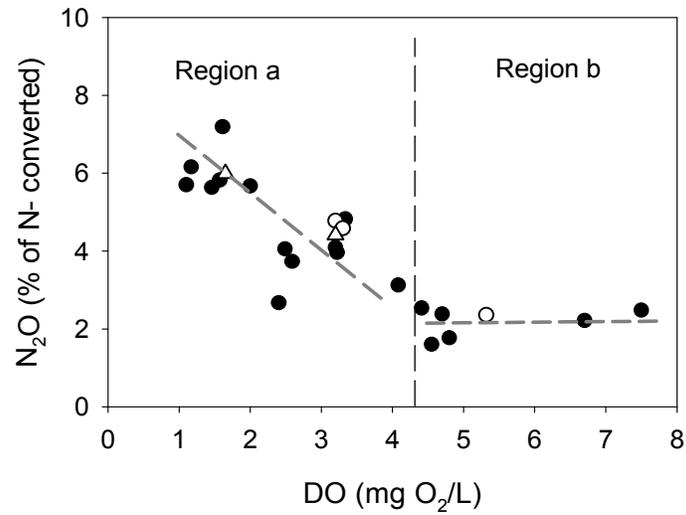


**Figure 1.** Nitrogen transformations in the granular airlift reactor before and during the GHG monitoring period. ● NH<sub>4</sub><sup>+</sup> in the reactor; □ NO<sub>2</sub><sup>-</sup> in the reactor; ▽ NO<sub>3</sub><sup>-</sup> in the reactor; ▲ NH<sub>4</sub><sup>+</sup> in the wastewater.



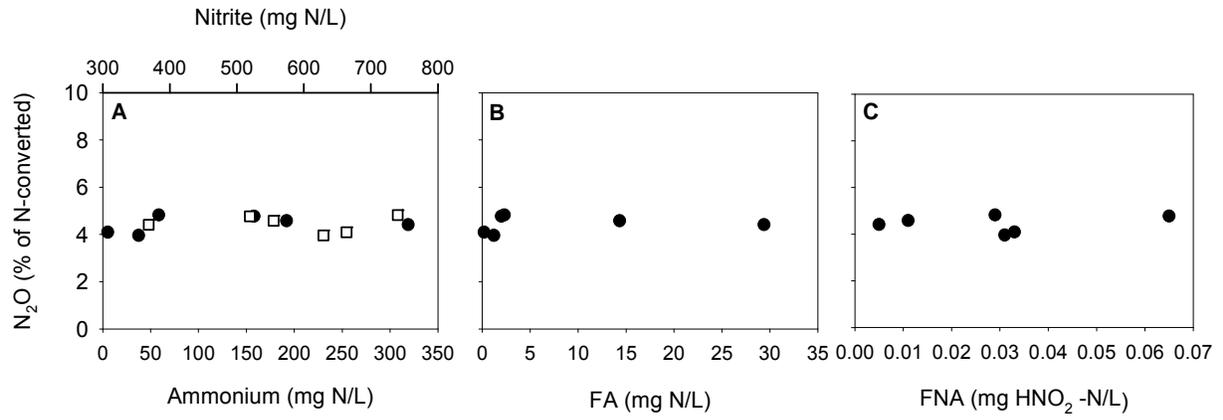
**Figure 2.** A- On-line N<sub>2</sub>O and CH<sub>4</sub> emissions from the reactor during continuous operation at DO 4.7 mg O<sub>2</sub>/L and pH 7.5. N<sub>2</sub>O (Black line); CH<sub>4</sub> (grey line); influent flow (thin black line); aeration flow (dashed line); NH<sub>4</sub><sup>+</sup> (●); NO<sub>3</sub><sup>-</sup> (▽); NO<sub>2</sub><sup>-</sup> (□). B- Zoom in from figure A (135-185 min).

Figure3

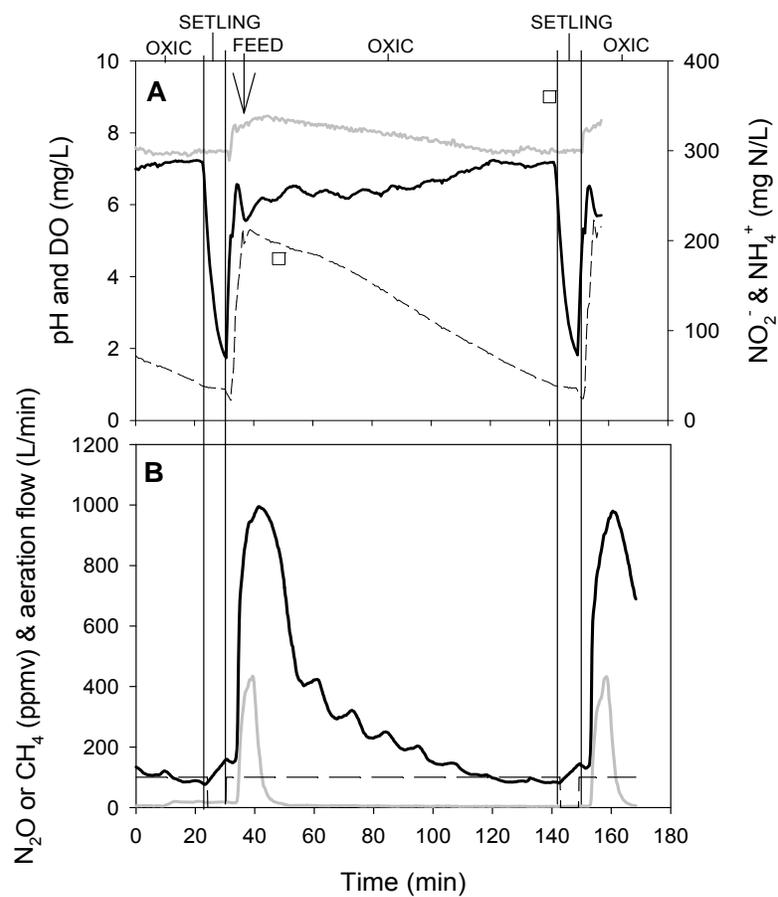


**Figure 3.** Correlation between the N<sub>2</sub>O emission factor and the DO concentration in the reactor: ● Operation under full nitrification conditions (>90% NH<sub>4</sub><sup>+</sup> oxidation to NO<sub>2</sub><sup>-</sup>); ○ Operation under partial nitrification conditions (70%-75% NH<sub>4</sub><sup>+</sup> oxidation to NO<sub>2</sub><sup>-</sup>); △ Operation under partial nitrification conditions (50%-55% NH<sub>4</sub><sup>+</sup> oxidation to NO<sub>2</sub><sup>-</sup>).

Figure 4



**Figure 4.** Correlation between the  $N_2O$  emission factor and ammonium /nitrite (A), free ammonia (B) and free nitrous acid (C) concentrations. ●- Ammonium, FA & FNA; □- Nitrite.



**Figure 5.** Cycle study profile of the pilot plant operating in SBR mode with a settling time of 7 min and an aeration flow of 100 L/min. A- pH (grey line), DO (black line), ammonium (discontinuous line) and nitrite ( $\square$ ) concentrations; B-  $\text{N}_2\text{O}$  (black line) and  $\text{CH}_4$  (grey line) emission profiles; aeration flow (discontinuous line).

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DOI 10.1016/j.watres.2013.11.009