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New tool for the determination of the nitrogen accumulation rate in the washing liquid of a biotrickling filter treating ammonia emissions

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Abstract

A new tool to determine the Specific Nitrogen Accumulation Rate (SNAR expressed in $\text{g}_{\text{NH}_3} \text{h}^{-1} \text{m}^{-3}$ _{packingmaterial}) in the washing liquid of a biotrickling filter for treating ammonia (NH_3) emissions is proposed. The tool is based on the relationship which exists between the electrical conductivity (EC) of the water and the amount of nitrogen salts dissolved in the water (i.e. ammonium NH_4^+ , nitrite NO_2^- , and nitrate NO_3^-). The methodology was applied experimentally by carrying out EC measurements for 5 months in a lab-scale biotrickling filter treating gaseous ammonia emissions. In addition to the EC measurements, the temperature and pH of the liquid phase were recorded. The temperature, NH_3 and N_2O concentrations (inlet and outlet) were also measured in the gas phase. It was demonstrated that the continuous EC record over time would appear to be a valuable tool in determining the amount of nitrogen actually accumulated into the liquid phase of the biotrickling filter. Thus, the parameter SNAR could be used to characterize the ability of the biotrickling filter to remove ammonia without measurement on the gas phase. It was also shown that high values of the ionic strength of the water ($\text{EC} > 25 \text{ mS cm}^{-1}$) dramatically affects the nitrogen accumulation rate.

Keywords

Ammonia; Mass transfer; Biofiltration; Electrical Conductivity; Nitrogen accumulation rate; Livestock facilities

Highlights

A new tool to determine the ability of a biotrickling filter to remove NH_3 is proposed

The tool is based on measuring the electrical conductivity of water (EC)

The Specific Nitrogen Accumulation Rate is obtained without measure on the gas phase

High values of the ionic strength of the water dramatically affect NH_3 removal

1. Introduction

Gaseous effluents emitted by intensive piggeries are a major concern for air pollution worldwide [1]. This pollution includes fine particle matter (PM_{10} , $\text{PM}_{2.5}$), greenhouse gases (GHG; i.e. carbon dioxide CO_2 , methane CH_4 and nitrous oxide N_2O), odor and ammonia (NH_3). Ammonia is considered the main pollutant emitted by piggeries [2]. It acts as an aerosol precursor in the troposphere and leads to the acidification of soil and water [3,4] so it has to be removed. Air scrubbers, i.e. chemical scrubbers and biotrickling filters, are usually used for treating gaseous effluents [5,6]. These technologies are intended to remove particle matter, odor and ammonia but are not suitable for the treatment of greenhouse gases [4,7]. Compared to biotrickling filters, chemical scrubbers have a high ammonia removal efficiency (RE up to 99% [8]) but produce waste that has to be managed, leading to increased operating costs. Biotrickling filtration is currently considered an efficient and economical technology for treating ammonia if the design is optimized [9] and the operation well-managed. In biotrickling filters, the gaseous phase is sprayed by a liquid phase (water) that is continuously recirculating via a buffer tank. Ammonia is absorbed into the water and converted into ammonium (NH_4^+). Subsequently, ammonium is oxidized into nitrite (NO_2^-) then nitrate (NO_3^-) by complex microbial communities present in the water (ammonia-oxidizing bacteria AOB, and nitrite-oxidizing bacteria NOB, respectively [10]). This process is called nitrification (Figure 1). Ammonia removal efficiencies of up to 70% are expected, but practical RE values ranging from 10 to 99% are reported in the literature [8]. Apart from varying levels of good practice applied in the use of biotrickling filters, these discrepancies may be due to the accumulation of nitrogen salts ($\Sigma \text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-$) in the water which can affect ammonia mass transfer. The presence of salts in water can possibly increase (salting-in) or decrease (salting-out) the solubility of compounds. However, despite the large number of studies dedicated to the ammonia solubility in water according to solution composition [11], the influence of the nitrogen

salts on the ammonia mass transfer is still not well understood. Although the removal of nitrogen salts by discharging some of the water loaded and replacing it with fresh water in the buffer tank is recommended, this operation is not always carried out. The discrepancies may also be explained by the accuracy of the method used to determine the efficiency of the removal. Among the main techniques for gas concentration measurements at livestock facilities, photoacoustic detection, FTIR spectroscopy, and colorimetry are the most suitable methods for ammonia measurement [1]. Colorimetry is very suitable for occasional measurements while photoacoustic detection and FTIR are more appropriate for continuous measurements. However, regular calibrations from standard are needed. Moreover, operating the analytical apparatus *in situ* is not an unimportant consideration (due to the presence of dust, water vapor, length of pipes for gas sampling, etc.) and it is not easy to obtain reproducible results. Additionally, the non-compensated interferences between the different gases present in the air (ammonia, nitrous oxide, carbon dioxide, methane and water vapor) can contribute to considerable uncertainties in the measurement (under-estimation and over-estimation are possible [12]). Beyond the uncertainties in the measurement, animal activities also lead to continuous fluctuations of ammonia concentration over time, and consequently large ranges of efficiencies over a short period of time can be observed. The objective of this study is therefore to develop an accurate and robust new strategy for determining the amount of nitrogen actually transferred and accumulated in the liquid phase of a biotrickling filter without measurement on the gas phase. The influence of the accumulation of nitrogen salts in the water on the mass transfer is also considered. The present work demonstrates that measuring the electrical conductivity (EC) of the water in the buffer tank of a laboratory scale biotrickling filter represents progress in the determination of ammonia removal.

2. Ammonia mass transfer in biotrickling filters

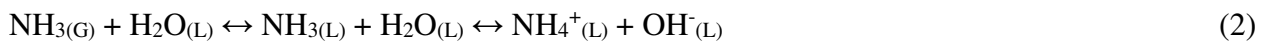
In absorption processes, the amount of ammonia transferred between the gas and liquid phases corresponds to the product between the mass transfer coefficient and the concentration driving force:

$$N = K_L a \left(\frac{C_G}{H} - C_L \right) \quad (1)$$

where C_G and C_L are the ammonia concentrations in the gas and liquid phases respectively (in g m^{-3}), and H is the Henry coefficient (dimensionless). In this study, C_L is called $\text{NH}_{3(L)}$ to avoid ambiguity. The mass transfer coefficient $K_L a$ (s^{-1}) depends mainly on the hydrodynamics of the biotrickling filter, whereas the driving force depends on the thermodynamic ammonia equilibrium

between gas and liquid. For a given biotrickling filter operating at a constant temperature and constant gas and liquid flow rates (i.e. H constant), the ammonia mass transfer is governed by the $K_L a$ since the effective area for mass transfer " a " changes due to biomass growth, and the driving force. Considering the driving force, the mass transfer is greater when the ammonia concentration in the gas is high and that in the liquid is low. Since the ammonia concentration in the air from piggeries is relatively low ($0-18 \text{ mg m}^{-3}$ [1]), it is important to keep the concentration in the liquid phase close to zero to maintain the maximum driving force, to guarantee the efficiency of the ammonia removal.

As shown in Figure 1, once absorbed in water NH_3 is ionized into ammonium ion (NH_4^+), according to the reaction and leading to an increase in the pH of the water (OH^- production):



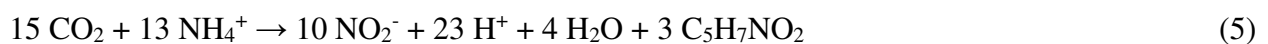
In the liquid, the ionized ammonium ion (NH_4^+) and un-ionized ammonia ($\text{NH}_{3(\text{L})}$) are in equilibrium, which is dependent on both the temperature and pH of the liquid. In aerobic conditions, microorganisms can convert an ammonium ion (NH_4^+) into different nitrogen species, mainly nitrite and nitrate ions (NO_2^- and NO_3^-). This two-step process known as nitrification requires chemolithoautotrophic bacteria with the ability to use ammonium or nitrite as the only energy source and CO_2 to satisfy the carbon requirement. In the first step, ammonia-oxidizing bacteria (AOB) such as *Nitrosomonas*, *Nitrosococcus*, *Nitrospira*, *Nitrosolobus* or *Nitrosovibrio* [13] oxidize ammonium into nitrite. Two protons H^+ are then formed, leading to a decrease in the pH of the water:



In the second step, nitrite-oxidizing bacteria (NOB) such as *Nitrobacter*, *Nitrococcus*, *Nitrospina* or *Nitrospira* oxidize the nitrite into nitrate:



Using the formula $\text{C}_5\text{H}_7\text{NO}_2$ for biomass characterization, the overall equations describing the biomass growth can be written as follows (for AOB and NOB respectively):



The activity and growth of AOB and NOB depend on temperature, pH, oxygen availability and concentration of the substrate [14]. However, growth is usually low, cell division needing several days or weeks according to the species in question [15]. The nitrification process, preferably with a pH of around 6.5-8 [16] and temperature conditions around 26-38°C [15], leads to a progressive

accumulation of ammonium, nitrite and nitrate ions in the washing liquid. Basically, an equilibrium is obtained between the cation (NH_4^+) and the anions (NO_2^- , NO_3^-), the amount of ammonium balancing the amount of nitrite and nitrate in the water [17]. Other nitrogen species such as hydroxylamine (NH_2OH), nitric oxide (NO), nitrous oxide (N_2O) and atmospheric nitrogen (N_2) can also be obtained during the nitrification process. It is possible, therefore, that some of the ammonia dissolved in the water may be released into the atmosphere in the form of N_2O . Since N_2O is a major greenhouse gas (the impact of 1 kg of N_2O is equivalent to 298 kg of CO_2 on a time horizon of 100 years in terms of global warming potential - GWP_{100} - [4]), the formation of this secondary pollutant in biotrickling filters must be avoided. In addition, the pH also influences the nitrification process by promoting the formation of $\text{HNO}_{2(\text{L})}$ for an acidic pH, and $\text{NH}_{3(\text{L})}$ for an alkaline pH.

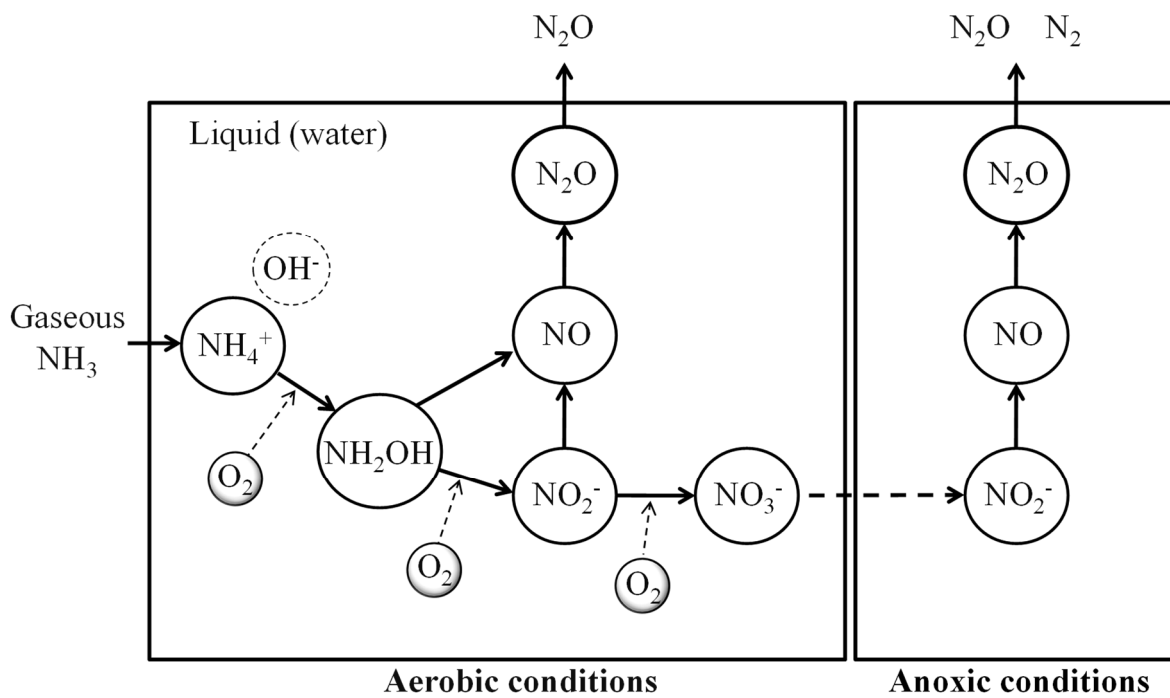


Figure 1 Schematic representation of nitrification/denitrification processes in water

According to Eq (1) the driving force depends on the concentration of ammonia in the liquid phase ($C_L=[\text{NH}_{3(\text{L})}]$). Since direct measurement of the ammonia concentration in the water is not possible, the chemical equilibrium between ammonium (NH_4^+) and ammonia ($\text{NH}_{3(\text{L})}$) in the liquid (Eq 2), which depends on the pH and the acid dissociation constant (pK_a), can be used as an indirect way of determining it. Thus, Eq (1) can be rewritten under as follows:

$$N = K_L a \left[\frac{C_G}{H} - C_{(\text{NH}_{3(\text{L})} + \text{NH}_4^+)} \left(1 - \frac{10^{-\text{pH}}}{10^{-\text{pH}} + 10^{-\text{pK}_a}} \right) \right] \quad (7)$$

According to the pH and pK_a values, the term in the right-hand parentheses ranges from 0 to 1, indicating the proportion of $NH_{3(L)}$ in the liquid phase, i.e. $NH_{3(L)}/(NH_{3(L)} + NH_4^+)$. Results are given in Figure 2 for the range of water temperatures usually encountered in industrial conditions (15 - 25°C). As observed in this figure, for pH = 6 the proportion of ammonia in the liquid tends to be 0, so the driving force should therefore always be at the maximum possible value. For higher pH values, the proportion of ammonia increases significantly to 2.7% at pH = 8 and 21.7% at pH = 9 (15°C). Consequently, as it is a proportion and as the amount of ammonium in the water may be significant due to the ammonia absorption, the concentration of ammonia in the water $[NH_{3(L)}]$ may also be significant, leading to a decrease in driving force and limitation of mass transfer, and eventually a decrease in the removal efficiency (in addition to possible biomass inhibition phenomena). The relationship between the concentrations of $NH_{3(L)}$ and NH_4^+ in the liquid phase can be deduced from Eq (5) [18]:

$$[NH_{3(L)}] = [NH_4^+] 10^{-(pK_a+pH)} \quad (8)$$

Although restricting the accumulation of ammonium in water is sometimes recommended [8], there is no data in the literature describing the direct influence of this parameter on the change in removal efficiency.

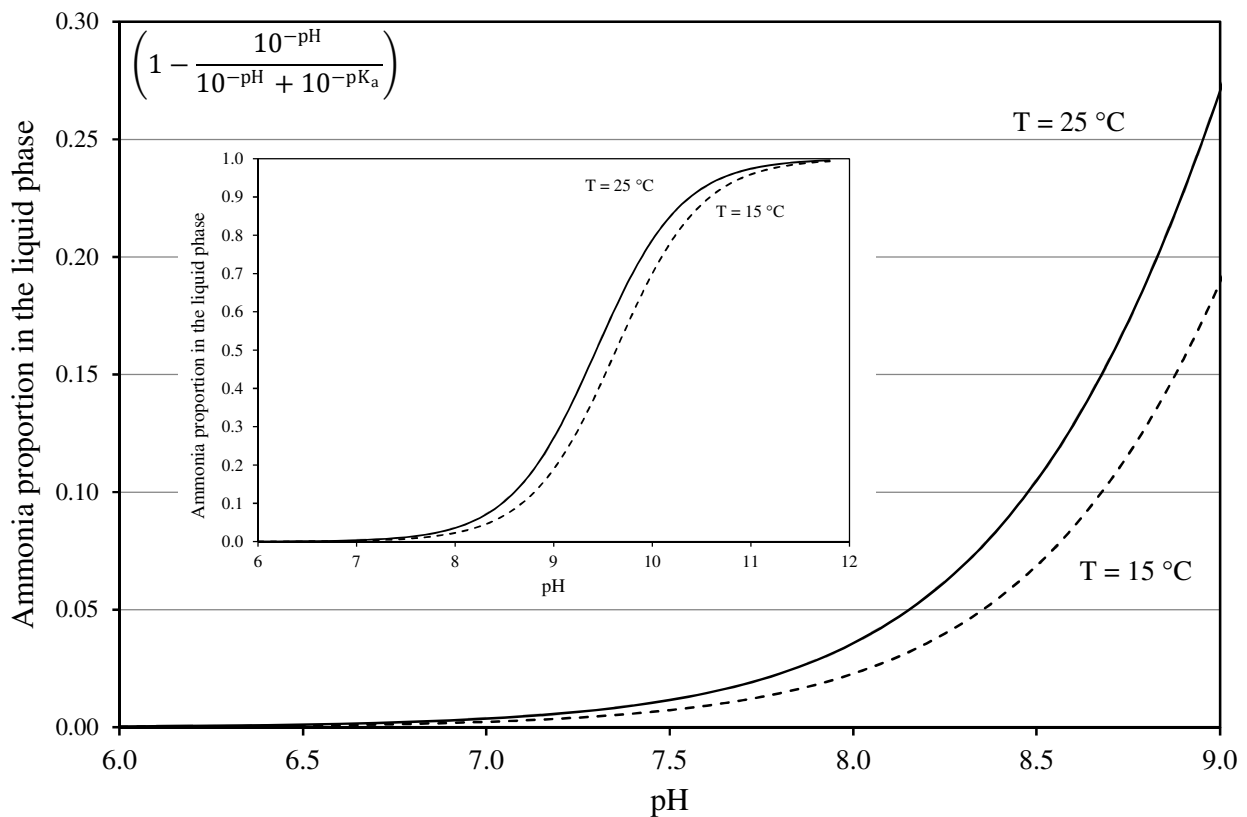


Figure 2 Ammonia/ammonium proportion in the liquid phase according to pH value ($pK_a=9.632$ at 15 °C; $pK_a=9.431$ at 25 °C; data from [18])

3. A simple method of determining the Specific Nitrogen Accumulation Rate (SNAR) in the washing liquid of biotrickling filters

Basically, the progressive accumulation of ammonium, nitrite and nitrate ions in the washing liquid, which are ultra-majority ions in the liquid, leads to an increase in the electrical conductivity (EC) of the water in the buffer tank [19]. A recent study has demonstrated that simple relationships exist between EC and the amount of nitrogen salts in water [20]:

$$[\text{NH}_4^+]_{\text{gN/L}} = 0.11 \text{ EC}_{\text{mS/cm}} \quad (\text{accuracy} \pm 15\%) \quad (9)$$

$$\Sigma ([\text{NH}_4^+] + [\text{NO}_2^-] + [\text{NO}_3^-])_{\text{gN/L}} = 0.22 \text{ EC}_{\text{mS/cm}} \quad (\text{accuracy} \pm 20\%) \quad (10)$$

As a result, for biotrickling filters with continuous conductivity measurement for water quality control, this relationship can be used to determine the nitrogen accumulation rate in the liquid phase (ϕ in gN h^{-1}):

$$\phi = V_{\text{water}} \frac{\Sigma ([\text{NH}_4^+] + [\text{NO}_2^-] + [\text{NO}_3^-])_{t_2} - \Sigma ([\text{NH}_4^+] + [\text{NO}_2^-] + [\text{NO}_3^-])_{t_1}}{\Delta t} = V_{\text{water}} \frac{0.22 (\text{EC}_{t_2} - \text{EC}_{t_1})}{\Delta t} \quad (11)$$

The relationship is valid if we assume that the amount of un-ionized ammonia $\text{NH}_{3(\text{L})}$ is small with regard to the amount of ammonium in the liquid phase, which is verified for $\text{pH} < 8$ (Figure 2).

Whatever the biotrickling filter considered (large-scale, pilot-scale or lab-scale), the volume of the packing material is usually known. Consequently, the specific nitrogen accumulation rate (SNAR) of any biotrickling filter can be calculated from EC measurement.

$$\text{SNAR} = \frac{\phi}{V_{\text{packing material}}} \quad (12)$$

The parameter SNAR could then be directly compared to the parameter “removal capacity RC” calculated from measurements carried out on the gas phase (Table 1). In practice, the SNAR has to be slightly lower than RC since a part of the ammonia transferred in the washing liquid can be reemitted into the air under another nitrogen forms. Similarly to the removal capacity RC, which is commonly used to characterize the ability of a biofiltration system (biofilter, biotrickling filter or bioscrubber) to remove a pollutant, the SNAR could be used to characterize the ability of a biotrickling filter to remove ammonia. Moreover, in the case where the ammonia loading rate (LR; Table 1) could be calculable, the ratio SNAR/LR quantifying the accumulation of ammonia in the washing liquid in regards to the amount of ammonia entering the biotrickling filter, could be used as an alternative to the determination of the ammonia removal efficiency based on gaseous measurement. Nonetheless, since $\text{SNAR} < \text{RC}$, the ratio SNAR/LR would be slightly lower than the

removal efficiency (RE = RC/LR) calculated from the mass balance on the gas phase, but it would better reflect the actual amount of nitrogen transferred and accumulated in the washing liquid.

Table 1 Operational parameters used

Loading Rate	$LR = \frac{Q_G}{V_p} C_G^{in}$	$g\ h^{-1}\ m^{-3}$
Removal Capacity	$RC = \frac{Q_G}{V_p} (C_G^{in} - C_G^{out})$	$g\ m^{-3}\ h^{-1}$
Removal Efficiency	$RE = 100 \frac{(C_G^{in} - C_G^{out})}{C_G^{in}}$	%
Empty Bed Residence Time	$EBRT = \frac{V_p}{Q_G}$	s
Gas velocity	$U = \frac{H}{EBRT}$	$m\ s^{-1}$

4. Materials and Methods

4.1. Biotrickling filters and operating conditions

Experiments were carried out continuously for 5 months (April - August 2019) at the laboratory of IMT Atlantique Nantes, France. The biotrickling filter used for ammonia (NH₃) removal is shown in Figure 3. The biotrickling filter consists of a cylindrical plastic column (0.305 m inlet diameter) filled with polypropylene WAT NET 150 NC 20/48 as packing material (WaluTech, Germany; specific surface area of 125 m² m⁻³; channel structure: crossflow; packing height H_p of 1.15 m corresponding to a packing volume V_p of 0.084 m³). Clean air flow from a centrifugal air fan (VCP HP 75 Europe Environment, France) was mixed with pure ammonia gas flow from an ammonia storage tank to feed the biotrickling filter at a designated ammonia inlet load. The gas flow rate of pure ammonia was controlled by a mass flow meter (Bronkhorst, Netherlands). For all experiments, the clean air flow rate was Q_G = 200 m³ h⁻¹ (corresponding to an Empty Bed Residence Time [EBRT] of 1.5 s and gas velocity U of 0.76 m s⁻¹; Table 1) and the pure ammonia flow rate was 71 mL min⁻¹ to maintain the inlet ammonia concentration at 25 ppm (i.e.

$C_G^{\text{in}} = 17.5 \text{ mg m}^{-3}$), corresponding to a loading rate (LR) of $41.7 \text{ g}_{\text{NH}_3} \text{ h}^{-1} \text{ m}^{-3}_{\text{packing material}}$ (Table 1) and an NH_3 inlet load of $69.2 \text{ g}_N \text{ day}^{-1}$. A closed water storage tank (tank volume 100 L; water volume 80 L) was used to continuously spray the packing material. Water recirculation was carried out using a centrifugal pump (SERMES Netherland) at a constant flow rate of 2.50 L min^{-1} , corresponding to a water spraying density of $2 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2}_{\text{packing material}}$. Each day, an amount of tap water was added to maintain the water level at a constant value to replace the amount of water lost through evaporation. At the beginning of the experiment, water was inoculated with 10 L of activated sludge from a wastewater treatment plant (Nantes, France). Since the objective of the study was to study the influence of the accumulation of nitrogen salts in the water, the operating procedure consisting of the discharge and replacement of salty water by fresh water was carried out as soon as the conductivity of the water reached a plateau. This procedure was repeated three times. Each time, the acclimated biomass was preserved in order to start the new cycle of measurements. During the experiments no extra carbon source was added (except Cycle 4; Table 2) and the temperature and pH of the water were not controlled.

Table 2 Operating conditions for each cycle during the experiment

Cycle 1	No nutrient added
Cycle 2	No pH control
	No temperature control
Cycle 3	Tap water added to replace evaporated water
Carbon source addition (carbohydrates including sugars)	
Cycle 4	No pH control
	No temperature control
	Tap water added to replace evaporated water

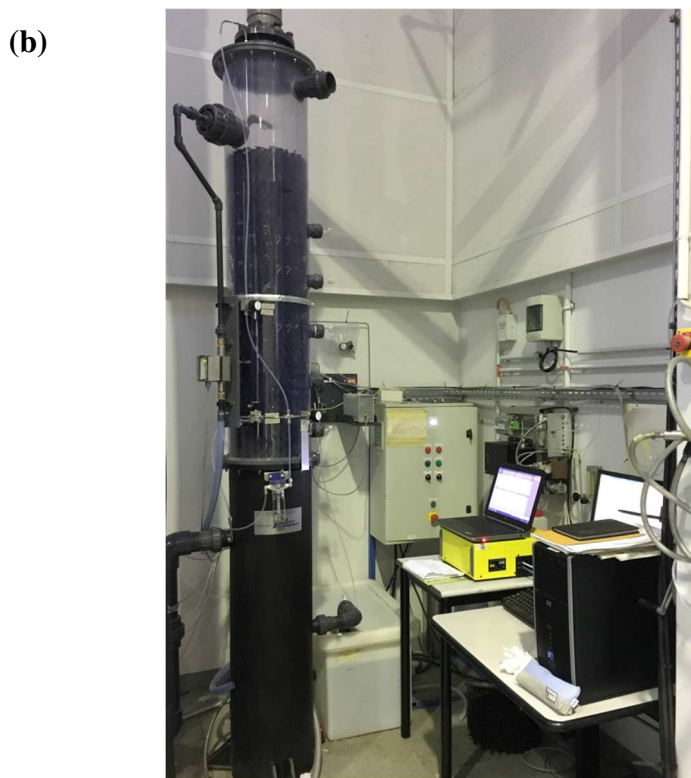
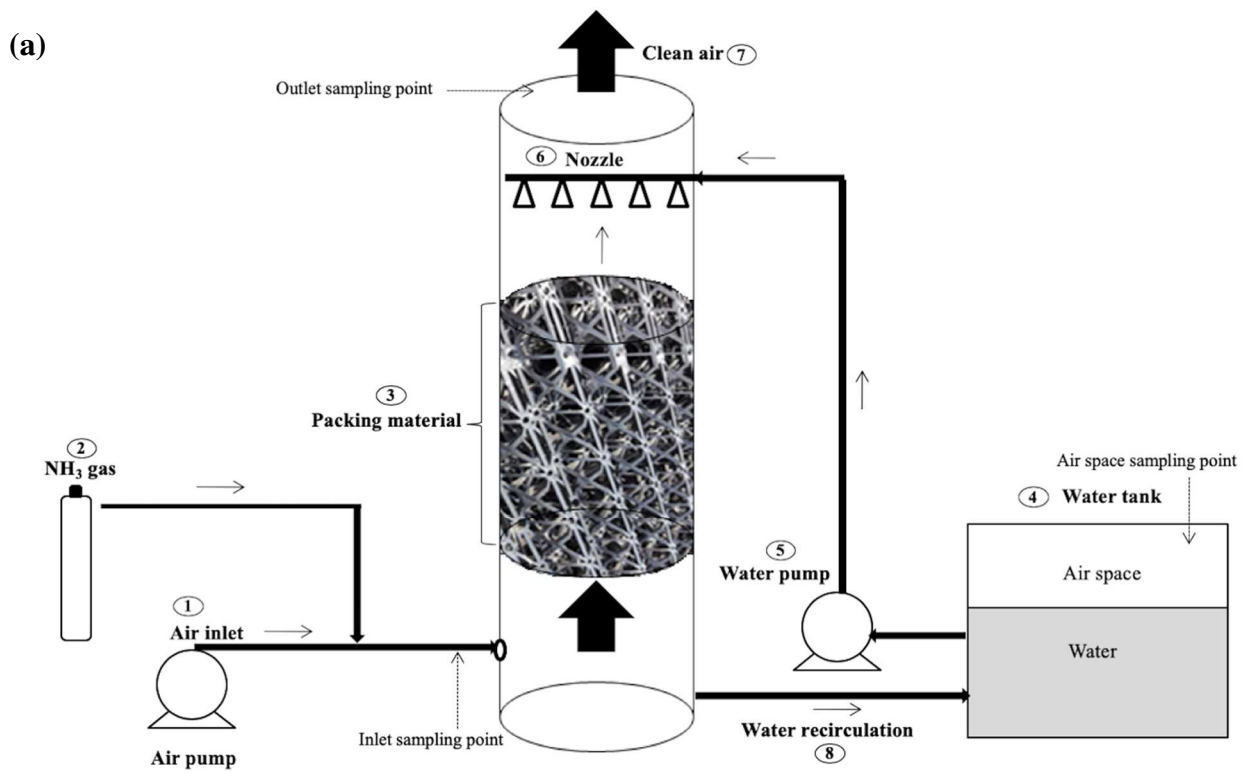


Figure 3 Schematic diagram (a) and photo (b) of the biotrickling filter used for ammonia treatment

4.2. Parameter measurement

Temperature, NH_3 and N_2O concentrations were measured in the gas phase. Three gas sampling ports were used, located at the inlet and outlet of the biotrickling filter and in the air space of the water storage tank (Figure 3). Gaseous samples were analyzed by a Fourier Transform InfraRed (FTIR) gas analyzer (GasetTM DX-4030, Environment SA) twice daily (10.00 am and 3.00 pm). The measurements were used to: (i) calculate the ammonia loading rate to be treated (LR) and the ammonia removal efficiency (RE; Table 1); (ii) determine the possible production of N_2O in the water tank; and (iii) determine the possible ammonia desorption from the water tank.

For the liquid phase, the temperature, pH and electrical conductivity (EC) were measured twice daily (10.00 am and 3.00 pm). Six replicates of the sample were analyzed. Electrical conductivity and pH were measured using a multi-channel analyzer consort C834 (Consort bvba, Turnhout, Belgium) with temperature correction. From these measurements the concentrations of NH_4^+ and $\text{NH}_{3(\text{L})}$ in the liquid phase were deduced using Eq (9) and Eq (8), respectively, and the nitrogen accumulation rate (ϕ) was calculated using Eq (11). For the range of temperatures of washing liquid recorded during the experiment, the acid dissociation constant pK_a was calculated from the relationship $\text{pK}_a = -\log_{10} (1.1639 \cdot 10^{-10} \exp(0.0463T))$ [18] (T in °C) and the ammonia Henry coefficient H was calculated from the relationship $H = 4.82439 \cdot 10^{-7} T^2 + 6.45003 \cdot 10^{-6} T + 2.12624 \cdot 10^{-4}$ [11] (T in °C). The biomass concentration in the water tank (in g L^{-1}) was also analyzed by gravimetric determination of the dry mass (10 mL samples were dried at 105°C for 72 h).

5. Results and discussion

The raw data recorded during the experiment on the gas and liquid phases is reported in Figure 4. Inlet ammonia concentrations C_G^{in} were $17.5 \pm 0.5 \text{ mg m}^{-3}$. As a result, the ammonia loading rate to be treated was kept constant during the experiment at $\text{LR} = 41.7 \pm 1.2 \text{ g}_{\text{NH}_3} \text{ h}^{-1} \text{ m}^{-3}_{\text{packing material}}$. The temperature of the washing liquid, which was constant during the cycle 1 (around 20°C), then ranged between 18 and 30°C during the cycle 2, between 25 and 30°C during the cycle 3, and between 20 and 25°C during the cycle 4. Such changes in temperature significantly influenced the pK_a and the ammonia Henry coefficient. As observed in Figure 4, recording the electrical conductivity of the washing liquid allows description of the ability of the biotrickling filter to transfer ammonia. For instance, the beginning of the cycle 1 was characterized by a slow increase in EC, and consequently a slow increase in the amount of nitrogen transferred in the washing liquid.

From days 25 to 52, a significant increase in EC was then observed indicating that the ammonia mass transfer dramatically improved. Concomitantly, a drop in the pH was observed confirming that the nitrification process occurred in the biotrickling filter. At the end of the cycle 1, as at the end of each cycle, the water in the tank was discharged and replaced by fresh water to decrease EC value. Similar increases in EC as in the cycle 1 were then measured in cycles 2 and 3, as well as in the cycle 4 albeit in a lesser extent, which confirmed the ability of the biotrickling filter to transfer ammonia. As a result, it can be argued that the first 25 days of the cycle 1 corresponded to the acclimation period of the biomass. Interestingly, the pH of the tap water used to feed the water tank, i.e. to fill the water tank at the beginning of each cycle and replace evaporated water each day, was alkaline (close to 9) and it can be observed that the pH value was even close to the pK_a value at the beginning of the experiment. These alkaline conditions are not favorable to ammonia mass transfer. As observed in **Figure 5**, the ammonia concentration calculated in the water ($NH_{3(L)}$) was significantly higher than the term C_G^{in}/H in the first 30 days of the experiment. As a result, the ammonia driving force was not favorable to mass transfer during the acclimation period of the biomass. Nonetheless, in spite of these negative conditions a small increase in the electrical conductivity of water combined with a decrease in pH indicates that a small proportion of the ammonia entering the system was absorbed and converted into nitrogen salts in the water. From the red line in **Figure 6**, it can be calculated that the nitrogen accumulation rate in the water was $0.64 \pm 0.13 \text{ g}_N \text{ day}^{-1}$ during this period (day 5 to 19), i.e. $SNAR = 0.39 \pm 0.08 \text{ g}_{NH_3} \text{ h}^{-1} \text{ m}^{-3}_{\text{packing material}}$. Thus, the ratio $SNAR/LR$ was $0.9 \pm 0.2\%$, indicating that only 0.9% of the ammonia entering the biotrickling filter was actually absorbed and accumulated in water (**Table 3**). It should be pointed out that this value, calculated from electrical conductivity measurements carried out in the liquid phase, is significantly different from the RE value determined from the ammonia concentrations measured in the gas phase (i.e. at the inlet and outlet of the column respectively). As observed in **Figure 4**, the RE calculated from NH_3 concentrations was around 10-18% for the first 30 days of the experiment. However, it can also be observed in **Figure 4** that the ammonia concentration in the vapor space of the water tank was significant during this period (around 5 mg m^{-3}), which can be interpreted as follows: some of the ammonia entering the biotrickling filter was transferred to the liquid phase during the contact time between phases in the packing material, then moved to the water tank and emitted into the atmosphere. But ultimately only a small fraction of the ammonia contacting the gas liquid phase was actually absorbed in the water and transformed into nitrogen salts. This finding demonstrates that monitoring the electrical conductivity of the water gives new light on the nitrogen amounts actually accumulated in the washing liquid. Thus, the change in electrical conductivity of the water from day 26 to day 50 of cycle 1 shows a regular ammonia mass transfer. During this period, the nitrogen accumulation rate in the water was $14.0 \pm 2.8 \text{ g}_N \text{ day}^{-1}$,

corresponding to a SNAR of $8.4 \pm 1.7 \text{ g}_{\text{NH}_3} \text{ h}^{-1} \text{ m}^{-3}_{\text{packing material}}$. As a result, $\text{SNAR/LR} = 20.2 \pm 4.0\%$, i.e. lower than the RE values deduced from NH_3 concentration measurements carried out in the gas phase (30-40%; Figure 4). It should be noted that possible removal by the gas flow of water droplets loaded with nitrogen salts outside the column is unlikely due to the presence of a demister. It can therefore be assumed that some of the nitrogen salts dissolved were not lost during the experiment, since water was added to the tank each day to replace water lost through evaporation. Due to the oxidation of ammonium ions in the water (Eq 3) the pH progressively decreased to 7.6, indicating that the proportion of un-ionized ammonia in the liquid (i.e. $\text{NH}_{3(\text{L})}/(\text{NH}_{3(\text{L})} + \text{NH}_4^+)$) was around 2%, corresponding to a calculated concentration $\text{NH}_{3(\text{L})} = 30 \text{ mg}_\text{N} \text{ L}^{-1}$ (Figure 5). For such conditions it can be assumed that the ammonia driving force was favorable to the mass transfer. Incidentally, the concentration in the vapor space of the water tank decreased to 3 mg m^{-3} (confirming that the RE values determined from gaseous measurements were higher than the actual value). As observed in Figure 5, due to the low ammonia concentration to be treated (C_G^{in} was fixed at 17.5 mg m^{-3} to correspond to the concentration values usually encountered in biotrickling filters for treating emissions from livestock facilities), the concentration driving force was small, the term C_G^{in}/H being in the same order of magnitude as the ammonia concentration $\text{NH}_{3(\text{L})}$ (Eq 1). Taking into account the accuracy of both parameters, it is difficult to define the favorable periods for mass transfer, i.e. $C_G^{\text{in}}/H > \text{NH}_{3(\text{L})}$. Therefore, measuring the EC provides more reliable information on mass transfer than assessing the ammonia driving force. At the end of cycle 1, the increase in electrical conductivity reached a plateau (25 mS cm^{-1} ; Figure 4) corresponding to a concentration of nitrogen salts in water of $5.3 \text{ g}_\text{N} \text{ L}^{-1}$ (i.e. $\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-$; Figure 6). As the pH conditions were therefore favorable to mass transfer and biomass activity, this plateau should be due to biomass inhibition caused by the accumulation of nitrogen salts in the water, or to the presence of other dissolved nitrogen species in the water. Biomass inhibition is due to the presence of free NH_3 (i.e. $[\text{NH}_{3(\text{L})}]$) and free HNO_2 (i.e. $[\text{HNO}_{2(\text{L})}]$) in the washing liquid. Depending on pH and temperature values, free ammonia concentrations at the end of cycle 1 ranged between 20 and $40 \text{ mg}_{\text{NH}_3} \text{ L}^{-1}$, i.e. in the range of inhibition values reported in the literature: 10-150 $\text{mg}_{\text{NH}_3} \text{ L}^{-1}$ [21]. For free HNO_2 , the correlation given in Anthonisen et al. [21] can be used to assess the concentration (free $\text{HNO}_2 = (46/14) [\text{NO}_2^-] / (\exp(-2300/T) 10^{\text{pH}})$). Since ammonium, nitrite and nitrate ions are ultra-majority ions in the washing liquid, the ionic balance implies that $[\text{NH}_4^+] = [\text{NO}_2^-] + [\text{NO}_3^-]$. The minimum free HNO_2 concentration in the washing liquid can then be calculated by assuming that $[\text{NO}_2^-] \text{ mg}_\text{N}/\text{L} = [\text{NO}_3^-] \text{ mg}_\text{N}/\text{L} = 1/2[\text{NH}_4^+] \text{ mg}_\text{N}/\text{L}$, whereas the maximum concentration is obtained by assuming that the amount of nitrate ions is very low in comparison with the amount of nitrite ions in the water (i.e. $[\text{NO}_2^-] \text{ mg}_\text{N}/\text{L} = [\text{NH}_4^+] \text{ mg}_\text{N}/\text{L}$), which is often encountered in biotrickling filters treating NH_3 emissions [17]. Thus, at the end of cycle 1, the free HNO_2 concentration in the

washing liquid ranged between 1 and 2 mg_{NO₂}·L⁻¹, which is in the range of inhibition values reported in the literature, i.e. between 0.22 and 2.8 mg L⁻¹ [21];. Consequently, it is probable that AOB and NOB inhibitions occurred at this level of EC values. To confirm the results obtained in cycle 1, the water in the tank was discharged and replaced by fresh water to decrease the amount of nitrogen salts (NH₄⁺, NO₂⁻ and NO₃⁻). The biomass was preserved in the water tank. The biotrickling filter was then restarted for a second cycle of measurements (the biomass concentration was 1.02 g L⁻¹).

At the beginning of cycle 2, the influent parameters were pH = 8.7 and EC = 2 mS cm⁻¹. In spite of the high initial pH value, the continuous increase in electrical conductivity indicates that a regular ammonia mass transfer occurred between the phases (SNAR deduced from EC measurement was 14.1±2.8 g_{NH₃} h⁻¹ m⁻³_{packing material} and consequently, SNAR/LR = 33.8±6.8%; **Table 3**). Concomitantly to the NH₃ transfer, the pH of the water rapidly decreased to 7.3. As a result, it can be concluded that the biomass was able to oxidize ammonium ions, confirming the benefit of renewing the washing water to avoid inhibitory effects. From day 78, the electrical conductivity of the water reached a plateau of 30 mS cm⁻¹, corresponding to a nitrogen concentration in water of 6.6 g_N L⁻¹ (**Figure 6**). Mass transfer then stopped, indicating inhibition of the biomass activity again. At the same time, the ammonia concentration in the vapor space of the water tank doubled from 3 to 6 mg_{NH₃} m⁻³ despite the pH value being around 7.0. It should be noted that there was a significant increase in the temperature of the water at the end of cycle 2. Although this temperature increase was unfavorable to ammonia absorption, it does not explain the mass transfer stopping, as demonstrated in the study of cycle 3.

After replacing the salty water with fresh water and preserving the biomass, the biotrickling filter was restarted for the third cycle of measurements. The results for cycle 3 confirmed findings of cycles 1 and 2. The nitrogen mass transfer rate was slightly lower than the value recorded during cycle 2 ($\phi = 18.1 \pm 3.6$ g_N day⁻¹ corresponding to SNAR = 10.9±2.2 g_{NH₃} h⁻¹ m⁻³_{packing material} and SNAR/LR = 26.1±5.2%), probably due to the higher temperature of the water. Nevertheless, it was verified that the ammonia accumulation rate was regular provided that EC < 25 mS cm⁻¹. Given that operating conditions were kept constant during the experiments (except the gas and water temperatures which were not controlled), it is logical that the mass transfer rate was also more or less constant with an absence of inhibition (K_{LA} and the ammonia driving force being more or less constant).

The electrical conductivity measurements recorded for cycles 1-3 show that, once started, the nitrogen accumulation rate in water remained constant until a critical EC value was reached (around

25 mS cm⁻¹). For the operating conditions applied in the present study (EBRT = 1.5 s and ammonia LR = 41.7 g m⁻³ h⁻¹), SNAR/LR ratios ranged between 20.2±4.0% and 33.8±6.8%, indicating that these operating conditions could be significantly improved to increase ammonia removal. However, the findings from cycles 1-3 also indicate that efforts made to optimize the biotrickling filter design would be useless if the electrical conductivity of water was not kept lower than the critical EC value. Above the critical value, mass transfer dramatically decreases due to possible inhibition of the biomass. Notwithstanding, as observed in **Figure 7**, calculated NH_{3(L)} concentrations were around 20 mg_N L⁻¹ or higher whatever the electrical conductivity of water, i.e. in the range of concentrations leading to inhibition of bacterial activity: 10-150 mg_{NH₃} L⁻¹ [21]. As a result, AOB inhibition should occurred even at low EC values. Note that according to Ottosen et al. [17], ammonia-oxidizing bacteria are not inhibited by NH_{3(L)}. Therefore, other reasons must be found to explain the inhibition phenomenon, especially since it has been shown that the nitrification process can occur under hypersaline conditions [22]. However, in spite of findings reported in studies on inhibition mechanisms [17,21,23–26], the causes for biomass inhibition in biotrickling filters mitigating ammonia emissions are still difficult to explain. The influence of the ionic strength of water in the Henry coefficient [27] and the pK_a [18,27] should certainly be taken into account, but this cannot explain the drop in mass transfer for EC = 25 mS cm⁻¹. Additional studies are therefore necessary to understand the significant decrease of the nitrogen accumulation rate for a given EC value.

Since the most important parameter to take into account for ammonia mass transfer in biotrickling filters is restricting the amount of nitrogen salts in the water, some of the water has to be regularly removed and replaced with fresh water to reduce the ionic strength of the water. Since the overall amount of ammonia transferred to the water is mainly converted into NH₄⁺, NO₂⁻ and NO₃⁻, i.e. neither the amount of nitrogen emitted into the atmosphere after mass transfer (in the form of NH₃, N₂O and N₂) nor the amount of nitrogen used for biomass growth being significant, it is possible to calculate the amount of fresh water needed (Q_L in m³ h⁻¹) to control the electrical conductivity at a given value:

$$Q_L = Q_G \frac{RE \ C_G^{in} \left(\frac{14}{17}\right) 10^{-6}}{0.22 \ EC} \quad (13)$$

With Q_G (the gas flow rate to be treated) in m³ h⁻¹; RE ranged between 0 and 1; C_Gⁱⁿ in mg_{NH₃} m⁻³ and EC in mS cm⁻¹. For instance, a biotrickling filter designed to treat 100,000 m³ h⁻¹ of loaded air (15 mg m⁻³) with a removal efficiency of 70% needs a water discharge of 0.197 m³ h⁻¹ (i.e. 4.72 m³

day⁻¹) for an EC value controlled at 20 mS cm⁻¹ (corresponding to $\Sigma (\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-) = 4.4 \text{ gN L}^{-1}$). In other words, an efficient biotrickling filter necessarily requires (i) the use of large amounts of water (the water lost through evaporation must also be taken into account); (ii) the addition of a secondary water treatment, which increases the operating costs and may contribute to climate change via N₂O production [28]. Note that there is a lack of data on the maximum EC value used to manage the quality of the washing liquid in biotrickling filters installed around the world (even where management via EC control is actually carried out). In 2015, van der Heyden et al. reported that in Flanders and the Netherlands the maximum allowed nitrogen content of washing liquid was set at 3.2 gN L⁻¹, corresponding to EC = 15 mS cm⁻¹ [8]. However, this indicative value, which was previously given in the 2010 version of the “VERA Test Protocol for Air Cleaning Technologies”, no longer appears in the 2018 version [29] (VERA is a multinational collaboration between Denmark, The Netherlands and Germany for testing and verifying environmental technologies in the agricultural sector). In 2017, Liu et al. indicated that half the volume of the washing liquid for bioscrubbers located in northern Germany was discharged once the EC exceeded 22 mS cm⁻¹ [30]. Fundamentally, in the absence of regulations, more data is needed on the potential control of washing liquid in biotrickling filters based on conductivity measurement.

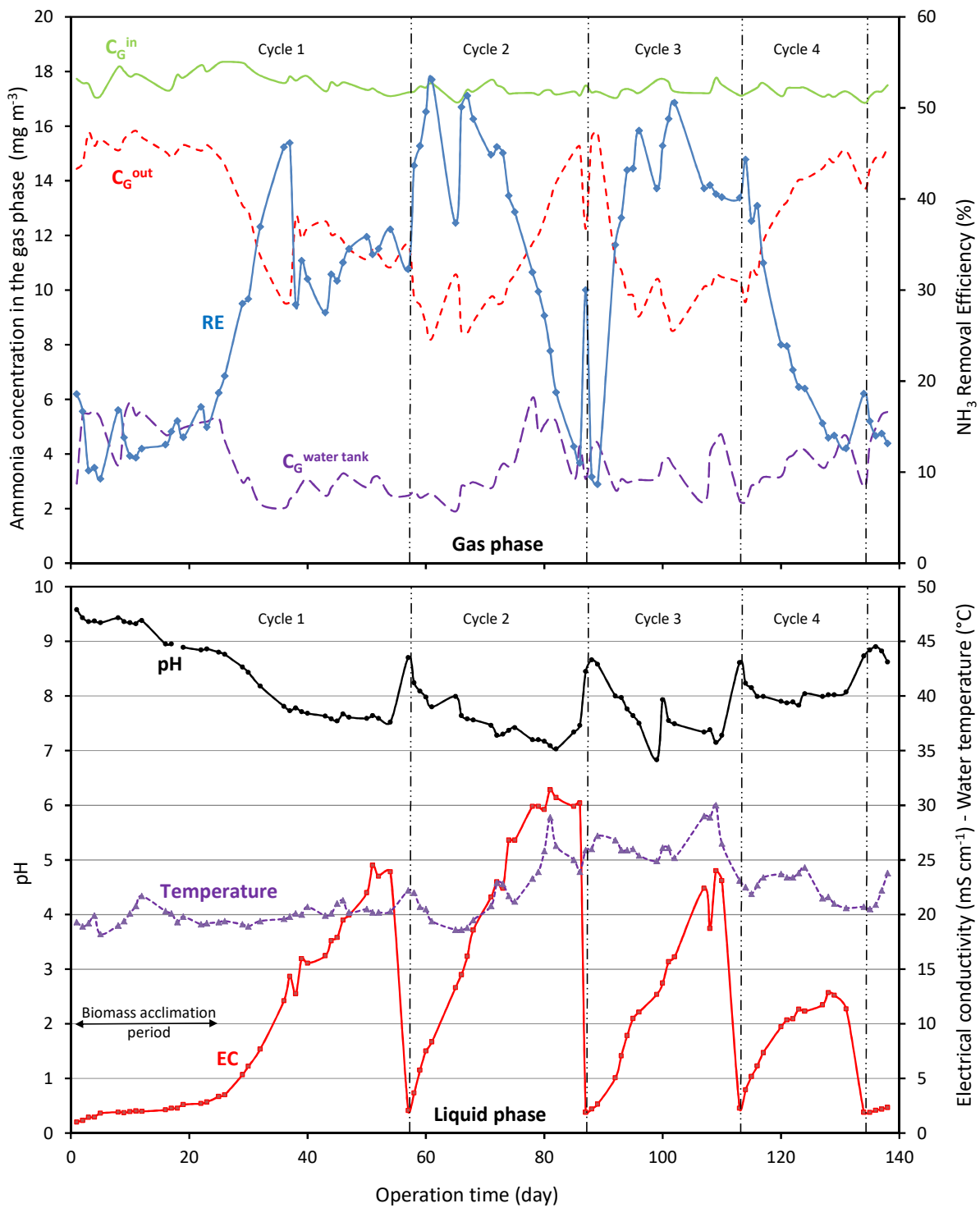


Figure 4 Raw data recorded in the gas and liquid phases during the experiments (measurements recorded daily at 3.00 pm; EBRT = 1.5 s and loading rate LR = 41.7 g m⁻³ h⁻¹)

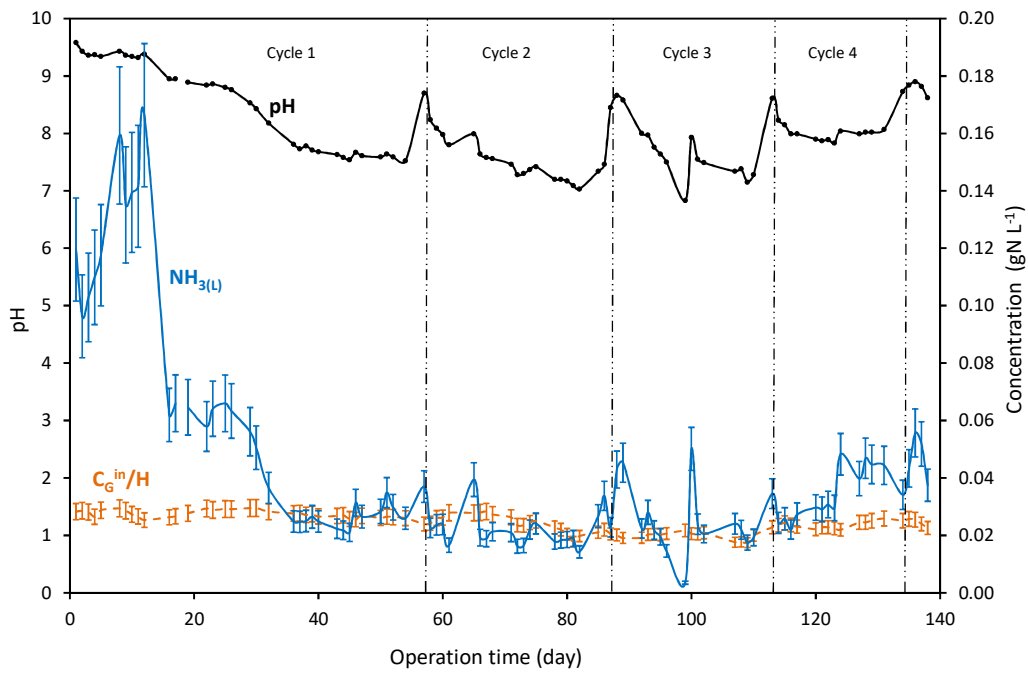


Figure 5 Calculated change in $\text{NH}_{3(\text{L})}$ and C_G^{in}/H values used in Eq (1). $\text{NH}_{3(\text{L})}$ is calculated from NH_4^+ values determined from Eq (7) (accuracy $\pm 15\%$). C_G^{in}/H takes into account the influence of temperature on the ammonia Henry coefficient H (error bars correspond to an arbitrarily estimated accuracy of $\pm 10\%$).

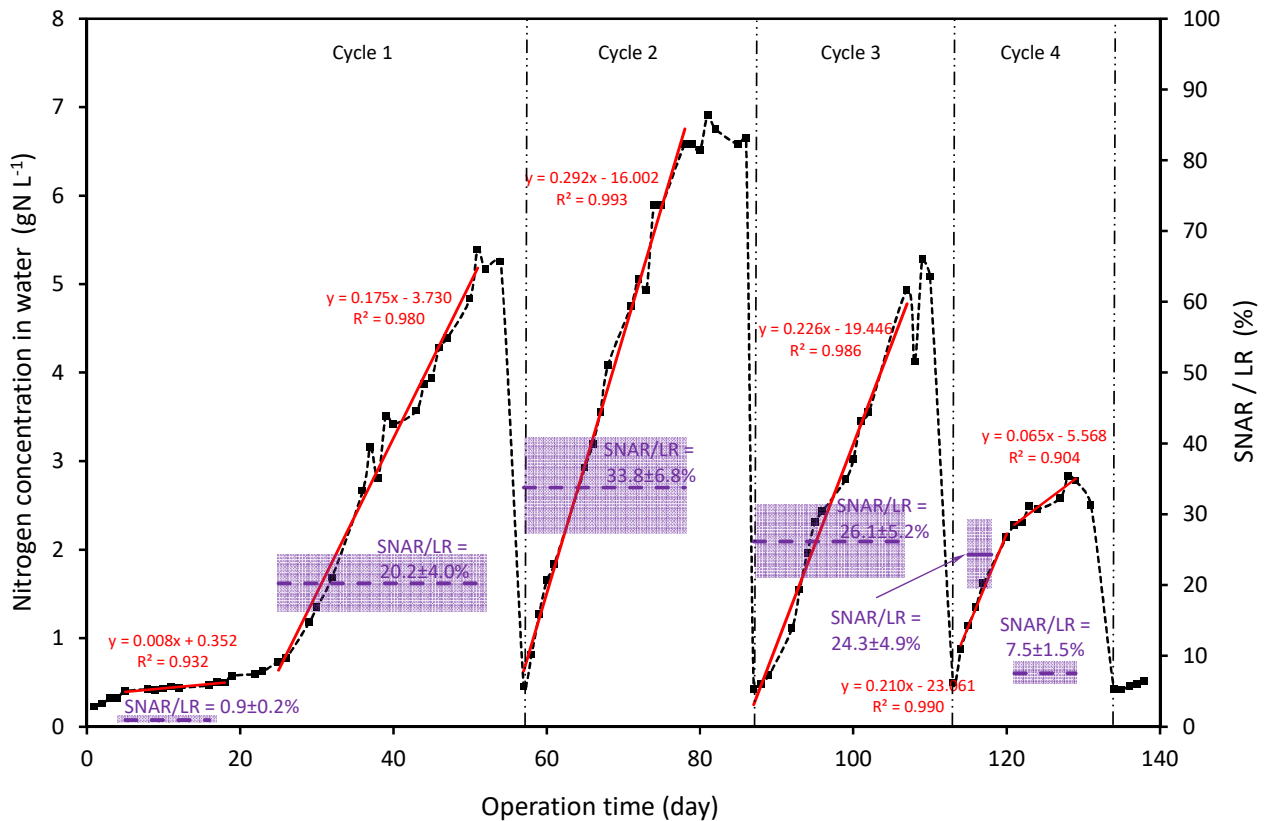


Figure 6 Change in the concentration of nitrogen species in the water (dashed curve deduced from the red curve in Figure 4 using Eq 10). Determination of the nitrogen mass transfer rate (red lines; values in $\text{g}_\text{N} \text{L}^{-1} \text{day}^{-1}$) used for the calculation of the SNAR (specific nitrogen accumulation rate) and the ratio SNAR/LR (Table 3).

Table 3 Determination of the nitrogen accumulation rate (Eq 11) and the specific nitrogen accumulation rate SNAR (Eq 12) from the electrical conductivity of water ($Q_G = 200 \text{ m}^3 \text{ h}^{-1}$; $C_G^{\text{in}} = 17.5 \text{ mg m}^{-3}$; NH_3 inlet load = 69.2 gN day^{-1} ; $\text{LR} = 41.7 \text{ gNH}_3 \text{ h}^{-1} \text{ m}^{-3} \text{ packing material}$; $V_{\text{water}} = 80 \text{ L}$)

	Slope determined from Figure 6 ($\text{gN L}^{-1} \text{ day}^{-1}$)	Nitrogen accumulation rate (ϕ in gN day^{-1})	SNAR ($\text{gNH}_3 \text{ h}^{-1} \text{ m}^{-3} \text{ packing material}$)	SNAR/LR (%)
Cycle 1	0.008	0.64 ± 0.13	0.39 ± 0.08	0.9 ± 0.2
	0.175	14.0 ± 2.8	8.4 ± 1.7	20.2 ± 4.0
Cycle 2	0.292	23.4 ± 4.7	14.1 ± 2.8	33.8 ± 6.8
Cycle 3	0.226	18.1 ± 3.6	10.9 ± 2.2	26.1 ± 5.2
Cycle 4	0.210	16.8 ± 3.4	10.1 ± 2.0	24.3 ± 4.9
	0.065	5.2 ± 1.0	3.13 ± 0.63	7.5 ± 1.5

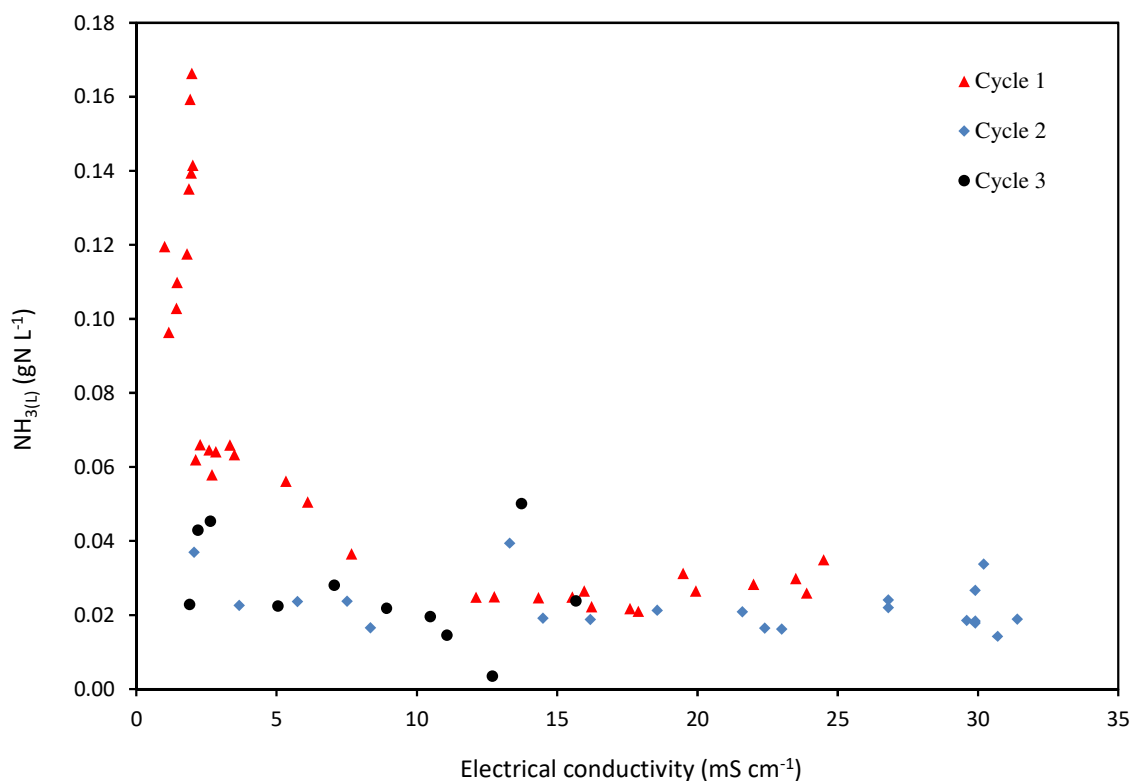


Figure 7 Ammonia concentration in the liquid phase (calculated using Eq (8) and Eq (9)) vs electrical conductivity of water

From cycles 1-3, the influence of high values of the ionic strength of water on mass transfer was demonstrated. It was also shown that efficient management of biotrickling filters requires large

amounts of fresh water. Basically, agricultural activities such as livestock rearing use the available ground water as fresh water, which could be a long-term issue [31]. The ability to use other types of water (of varying quality and composition) is therefore conceivable. In addition, the transfer of particle matter containing organic carbon can occur between gas and liquid in livestock facilities. Since water quality can affect mass transfer between phases, the objective of the fourth cycle of measurements was therefore to test the influence of a small addition of carbon to the nitrogen accumulation rate. As with the other cycles, salty water was replaced with fresh water and the biomass preserved. Three carbon additions were carried out at days 113, 120 and 127 using the following procedure: 200 g of a commercial powdered energy drink (Aptonia iso+) was added to 80 L of water (corresponding to a carbohydrate addition of 196 g, of which 134 g sugars). At the beginning of the cycle, it can be observed from **Figure 6** that the nitrogen mass transfer rate was in the same order of magnitude as values recorded for cycles 1-3 ($\phi = 16.8 \pm 3.4 \text{ g}_N \text{ day}^{-1}$ i.e. $\text{SNAR} = 10.1 \pm 2.0 \text{ g}_{\text{NH}_3} \text{ h}^{-1} \text{ m}^{-3}_{\text{packing material}}$ and $\text{SNAR/LR} = 24.3 \pm 4.9\%$). However, from day 120 the nitrogen accumulation rate slowed down ($\phi = 5.2 \pm 1.0 \text{ g}_N \text{ day}^{-1}$ i.e. $\text{SNAR} = 3.31 \pm 0.63 \text{ g}_{\text{NH}_3} \text{ h}^{-1} \text{ m}^{-3}_{\text{packing material}}$ and $\text{SNAR/LR} = 7.5 \pm 1.5\%$), indicating a change in biomass activity, whereas the EC was significantly lower than the critical value. This change is confirmed by the increase in ammonia concentration in the vapor space of the tank and the pH, which stabilized at around 8, indicating that the nitrite generation was disturbed. Additionally, as observed in **Figure 8**, the addition of an organic carbon source to the water led to significant production of N_2O in the vapor space of the water tank. While N_2O production was only marginal during cycles 1-3, each carbon addition during the fourth cycle resulted in peak production of N_2O a few days later. As a result, the presence of an organic carbon source modified the nitrification process. It is possible that the addition of a carbon source led to heterotrophic growth and increased oxygen consumption. Since the dissolved oxygen concentration is recognized an important parameter controlling N_2O emission [32], the nitrous oxide production recorded during cycle 4 could be due to anoxic conditions in the water tank. A specific study should be carried out in order to confirm this assumption. Thus, the records and the interpretation of the change in electrical conductivity of the water once again provide valuable information on how the biotrickling filter worked. Nonetheless, it should be kept in mind that EC measurement is a suitable tool for characterizing nitrogen accumulation rate but offers no explanation as to why the biotrickling filter operates well or otherwise (for mechanisms leading to the N_2O generation please see the literature on this topic [32–39]).

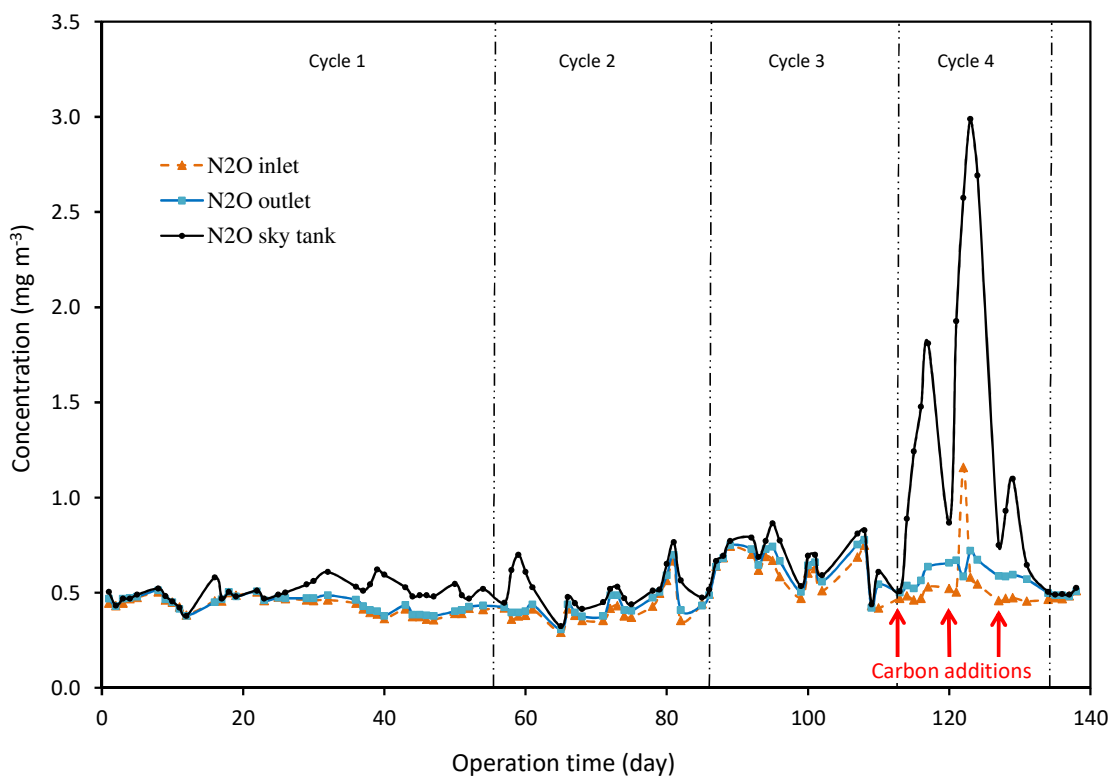


Figure 8 Change in N₂O concentration over time

6. Conclusion

From the findings reported in this study, three main conclusions can be drawn.

1. Since the sum of the main nitrogen salts dissolved in water (NH_4^+ ; NO_2^- ; NO_3^-) correlates to the electrical conductivity (EC) of water, the continuous EC record over time would appear to be a valuable tool in determining the amount of nitrogen actually transferred from the gas phase and accumulated into the liquid. Measurements carried out in the liquid phase do not need to take into account ammonia that is transferred into the water and emitted into the atmosphere in the same form (NH_3) or another form (N_2O). Since EC probes are well adapted to the severe conditions sometimes encountered in livestock facilities, EC measurement therefore appears to be a simple, robust and inexpensive technique for assessing the specific nitrogen accumulation rate (SNAR) of biotrickling filters in treating ammonia in real time without measurement on the gas phase. The technique could be also applied to other industrial plants provided that ammonia is the major pollutant to be removed.

2. The continuous mass transfer of ammonia into water leads to a regular increase in the concentration of nitrogen salts, which increases the ionic strength of the water. Above a critical value (EC around 25 mS cm^{-1}), the ionic strength of the water dramatically affects the nitrogen

accumulation rate. As a result, some of the water has to be regularly removed and replaced with fresh water to control the ionic strength (control being possible via regulation of the electrical conductivity). The amount of fresh water needed to control the electrical conductivity under for a particular value is given in Eq (13). Depending on the air flow rate to be treated, ammonia concentration and desired removal efficiency value, large amounts of fresh water are needed every day. In addition, the same amount of salty water removed from the biotrickling filter must subsequently be treated in an adapted water treatment unit. Electrical conductivity of water would appear to be the parameter to be considered before any other for accomplishing the mass transfer of ammonia. In other words, it is pointless to improve the design of the biotrickling filter if EC control is not taken into account.

3. The second conclusion is valid provided that the water used is organic carbon free (the nitrification process requiring bacteria that uses CO_2 to fulfill the carbon need). In the presence of organic carbon in water, the nitrification process may be disturbed and the nitrogen accumulation rate significantly affected. In addition, some of the ammonia transferred is emitted into the atmosphere in the form of N_2O . As a result, a similar study must be carried out at a pig farm to study the influence of the total organic carbon of the water (TOC) on ammonia removal (via EC analysis) in real conditions.

Further investigations have to be carried out in biotrickling filters *in situ* in order to confirm (i) that the specific nitrogen accumulation rate (SNAR) can be easily determined in real conditions; (ii) that the nitrogen accumulation rate stops as soon as a certain EC value is reached. Moreover, the reasons of the stop of the nitrogen accumulation rate remain to explain (presence of organic carbon, biomass inhibition or mass transfer limitation).

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