

CONTROLLING FACTORS OF NITROUS OXIDE EMISSIONS FROM A CONVENTIONAL ACTIVATED SLUDGE WASTEWATER TREATMENT PLANT

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Abstract: Nitrous oxide emissions were determined in three campaigns in the aeration tank of a full scale conventional activated sludge wastewater treatment plant. During these experiments, the carbonaceous organic matter (BOD and COD) removal was high and rather constant (97-98% and 93-96%). The results indicate that the concentration of total nitrogen in the influent wastewater, especially NH_4^+ , and the aeration flow rate are key controlling factor of N_2O emissions from the aeration tank. Nitrification was the major source of N_2O , suggested by the behavior of DO concentrations, $\text{NO}_3^-/\text{NH}_4^+$ ratio and pH values along the six interlinked zones of the aeration tank. Excessive air flow intensified N_2O transfer from the liquor to the atmosphere by air stripping.

Keywords: nitrous oxide, wastewater treatment plant, activated sludge.

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1. INTRODUCTION

Tropospheric nitrous oxide (N_2O) is the third gas, in concentration, responsible for the greenhouse effect, and its contribution to radiative forcing was about $+0.16 \text{ W m}^{-2}$ in the period from 1750 to 2005 (6% of the total contribution) (IPCC, 2007). Nitrous oxide is the first gas in relation to global warming potentials with values in the order of 300 and 15 times higher than carbon dioxide (CO_2) and methane (CH_4), respectively (IPCC, 2007). Moreover, N_2O is the major source of nitric oxide (NO) in the stratosphere which implies that it is indirectly responsible for the consumption of stratospheric ozone (O_3) (Crutzen, 1979; Abbat and Molina, 1993; Ravishankara *et al.*, 2009).

In wastewater treatment plants (WWTPs), N_2O emissions occur naturally due to the microbial transformations of nitrogen compounds by the nitrification and denitrification processes (Wrage *et al.*, 2001). Under aerobic conditions, N_2O production occurs, as a by-product, through oxidation of ammonium ions (NH_4^+) to nitrite (NO_2^-), the first stage of the nitrification process. Conversely, in anoxic compartments, N_2O production occurs as an intermediate during reduction of nitrate (NO_3^-) to molecular nitrogen (N_2), i.e., via denitrification. In addition, N_2O produced by denitrification may subsequently come under aerated conditions and is then purged from the system (Czepiel *et al.*, 1995; Ahn *et al.*, 2010; Law *et al.*, 2012a).

It is estimated that there will be an increase of 13% in global N_2O emissions from wastewater treatment for the 2005-2020 period (Law *et al.*, 2012a). However, there is a high variability in emission factors (EFs) (0-25%), based on the load of the influent total nitrogen (TN), available in the literature from studies performed directly at WWTPs (Kampschreur *et al.*, 2009; Law *et al.*, 2012a). This variability is often attributed to the particularities related to operational parameters adopted at the different WWTPs studied, highlighting among

them, the organic matter and TN to be treated, sludge age, dissolved oxygen (DO) concentration and aeration rate (Kampschreur *et al.*, 2009; Brotto *et al.*, 2010; Brotto, 2011; Law *et al.*, 2012a; de Mello *et al.*, 2013; Ribeiro *et al.*, 2013). Recently, Daelman *et al.* (2013) reported that different sampling strategies used at the WWTPs studied can also play an important role as an influencing factor in the observed variability in EFs of N_2O .

In a study performed at an activated sludge WWTP in Brazil, Brotto *et al.* (2010) reported that 90% of the total N_2O emitted originated from the aeration tank. De Mello *et al.* (2013) estimated, through a study at an intermittent aeration activated sludge system of an urban WWTP, with cycles of 60 minutes with aeration and 30 minutes without aeration, that 50-75% of the net production of N_2O was emitted to the atmosphere during the aeration step (aerobic condition). Foley *et al.* (2010) and Ribeiro *et al.* (2013) suggested that lower N_2O emissions are related to the higher removal efficiency of TN when there is complete nitrification and denitrification processes. In a study performed at an activated sludge WWTP with modified aeration, Brotto (2011) found that the sludge age influenced the nitrification process. Also the high N_2O emissions were due to accumulation of NO_2^- in the aeration tank, which indicated incomplete nitrification. These studies highlight the importance of controlling the operating parameters in order to minimize N_2O emissions.

The present study aims to evaluate the relationship of N_2O emissions with the influent TN load, DO concentration, ratio of inorganic nitrogen forms ($\text{NO}_3^-/\text{NH}_4^+$), pH and flow rates of air and wastewater ($Q_{\text{air}}/Q_{\text{wastewater}}$) in an aeration tank of a conventional activated sludge WWTP, aiming to find solutions to mitigate N_2O emissions in this type of system.

2. EXPERIMENTAL

2.1 Location and Characteristics of the WWTP

The WWTP chosen for this study, the same one studied by Ribeiro *et al.* (2013) is located in the metropolitan region of Rio de Janeiro, Southeast Brazil. It is considered a large-scale WWTP and uses a conventional activated sludge system as the wastewater treatment process. During the study period, the plant served approximately 470,000 residents and operated with a hydraulic retention time (HRT) of about 9 hours in the aeration tank and the sludge age varied from 10 to 12 days.

The WWTP has three levels of wastewater treatment: the primary, secondary and sludge treatment. In the secondary treatment, the WWTP has four aeration tanks in operation that are adjacent and independent to each other, but with the same operating characteristics. Each of the four aeration tanks is divided into six interlinked aeration zones (ZNs). The zones have different air flow rates controlled according to the number of diffusers in each of them (ZN1 = 29, ZN2 = 1184, ZN3 = 640, ZN4 = 500, ZN5 = 898, and ZN6 = 612) (Ribeiro *et al.*, 2013).

The ZN1 is differentiated from the other zones by the presence of coarse bubble diffusers applied to mix the effluent from the primary treatment with the biological sludge that returns from the secondary settling (Ribeiro *et al.*, 2013). Furthermore, due to the low HRT, high food/microorganism (F/M) ratio and low DO concentration ($\leq 0.5 \text{ mg L}^{-1}$) employed in the ZN1 compared to the other zones, this zone can be characterized as a biological anoxic selector, which is a system that promotes a better formation of sludge flocs (von Sperling, 2002). The other zones (ZN2 to ZN6) are characterized by having fine bubble diffusers (Ribeiro *et al.*, 2013), whose function is to promote a good mixing capacity and raise the oxygen supply in the liquid (von Sperling, 2002), which characterizes aerobic conditions in these zones, with sufficient sludge age

and HRT for complete nitrification processes.

2.2 Sampling and Analysis

For this study, three sampling campaigns were carried out, on May 18, 2010, and February 17 and June 30, 2011. The study was conducted in only one of the four aeration tanks. This choice was based on the similarity of the aeration tank operations, since the wastewater and air flows are distributed equally in the four aeration tanks that make up the secondary treatment system. The samples were collected only in the morning, between 8:00 and 11:00 h. The sampling took place at 24 equidistant sites distributed along the margins of the six zones of the aeration tank (i.e., four sampling sites per zone) following the direction of the course of the mixed liquor.

During the sampling campaigns, DO concentration and pH were measured *in situ* using a multiparameter probe HI-9828 model (Hanna Instruments). In addition, influent (untreated wastewater) and effluent (treated wastewater) samples were collected for the determination of TN concentrations in the laboratory. Data of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) in influent and effluent samples, and volatile suspended solids (VSS) in each of the six zones of the aeration tank, were provided by the control laboratory of the WWTP.

The procedures for collecting, processing and analyzing N_2O , NH_4^+ and NO_3^- in the wastewater and the mixed liquor samples, and for calculating the N_2O emissions were the same as those described by Ribeiro *et al.* (2013). To determine the N_2O emission at the wastewater-atmosphere interface of each zone of the aeration tank the upturned funnel sampling technique, described in detail by Brotto *et al.* (2010) was used. This same technique was adopted by Ribeiro *et al.* (2013).

In the laboratory, the determination of N_2O was performed in a gas chromatography (GC-17/Shimadzu)

equipped with an electron capture detector (^{63}Ni). The limits of detection and quantification were 30 and 300 ppb, respectively. The quantification limit of the N_2O emission rate using the upturned funnel technique was $4 \times 10^{-3} \text{ g N}_2\text{O h}^{-1}$. The concentrations of NH_4^+ and NO_3^- were determined on filtered samples ($0.22 \mu\text{m}$ pore size filters) and stored in a freezer (-4°C). The TN was determined in unfiltered and acidified ($\text{pH } 2.0$) samples. All analyzes followed the procedures according to APHA (2012). The limit of quantification was 0.2 mg L^{-1} for NH_4^+ and NO_3^- , and 10 mg N L^{-1} for TN. The analytical precisions, for analysis performed in triplicate, of NH_4^+ , NO_3^- and TN were within $\pm 5\%$.

3. RESULTS AND DISCUSSION

The parameters controlling N_2O emissions from activated sludge wastewater treatment systems, which are widely discussed in the literature, derive mainly from laboratory studies (Kim *et al.*, 2010; Rassamee *et al.*, 2011; Law *et al.*, 2012b; Wunderlin *et al.*, 2012). In this work, the key controlling factors are presented and discussed based on data obtained exclusively from the above-described full scale wastewater treatment system.

3.1 Influent BOD, COD and NH_4^+ concentrations

Figure 1 shows the temporal variability in the concentrations of BOD and COD in the influent wastewater of the WWTP for the period January-December 2010. The arithmetic mean concentration (\pm standard deviation) of COD was $600 (\pm 260) \text{ mg L}^{-1}$ ($n = 12$), approximately 2 times higher than the mean BOD concentration. In the summer months lower concentrations were observed probably as a result of increased dilution due to greater domestic water

consumption and a greater input of rainwater in the wastewater collection networks (von Sperling, 2002; Ribeiro *et al.*, 2013). During the period from January to June 2010, Ribeiro *et al.* (2013) observed that the TN concentrations, especially NH_4^+ , had similar behaviour patterns to the BOD and COD concentrations. They also reported lower emissions of N_2O in the summer months and attributed these to the lower concentrations of NH_4^+ in the influent wastewater at that time of the year. The temporal variability of N_2O emissions in activated sludge wastewater treatment systems has been frequently reported in the literature as directly related to the concentration of NH_4^+ in the influent wastewater (Ahn *et al.*, 2010; Lotito *et al.*, 2012; Aboobakar *et al.*, 2013; Hu *et al.*, 2013).

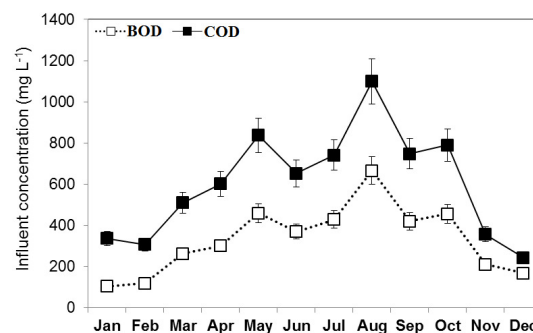


Figure 1. Temporal variability of BOD and COD concentrations (average \pm standard deviation) in wastewater influent to the WWTP, measured from January to December 2010

Table 1 shows the influent (untreated wastewater) loads of BOD, COD and TN to the WWTP, the influent (primary wastewater) NH_4^+ load to the aeration tank and the rate of N_2O emission from the aeration tank on the sampling days. It is noteworthy that on the February 17 and June 30, 2011, the air flow in the aeration tank was approximately 2 times greater than May 18, 2010 (Table 2).

Table 1. Influent (untreated wastewater) loads of BOD, COD and TN to the WWTP, influent (primary wastewater) NH_4^+ load to the aeration tank, and N_2O emissions from the aeration tank during the study days

Sampling date	BOD (kg day^{-1})	COD (kg day^{-1})	TN (kg day^{-1})	N- NH_4^+ (kg day^{-1})	N- N_2O emitted (kg day^{-1})
May 18, 2010	6.2×10^4	1.1×10^5	7.5×10^3	1.1×10^3	2.4
February 17, 2011	3.2×10^4	7.4×10^4	4.4×10^3	5.5×10^2	2.9
June 30, 2011	4.2×10^4	8.7×10^4	5.4×10^3	7.7×10^2	4.1

In June 30, 2010, the influent loads of BOD, COD, TN and NH_4^+ were respectively 25%, 15%, 20% and 30% higher than those in February 17, 2011, which may explain the higher N_2O emission rate (*ca.* 30%) in June 30 (Table 2). These results suggest that the concentration of TN in the influent wastewater, especially NH_4^+ , is a key controlling factor of N_2O emissions in the

activated sludge wastewater treatment systems. This relationship is in agreement to that reported by Ribeiro *et al.* (2013) in a previous study at the same WWTP. In May 18, 2010, despite the organic load was almost 50% higher, the N_2O emission rate was 70% lower than that found in June 30, 2011, which is attributed due to the lower aeration rate (*air stripping*) in May 18, 2010 (Table 2).

Table 2. Air flow rates per aeration tank, ratios between of air flow and wastewater flow ($Q_{\text{air}}/Q_{\text{wastewater}}$), and BOD, COD and TN removal efficiencies during the study days

Sampling date	Air flow ($\text{m}^3 \text{h}^{-1}$)	($Q_{\text{air}}/Q_{\text{wastewater}}$)	BOD removal efficiency (%)	COD removal efficiency (%)
May 18, 2010	5000	3.6	98	96
February 17, 2011	9500	6.3	98	93
June 30, 2011	9500	6.7	97	96

3.2 Concentration of DO, ratio $\text{NO}_3^-/\text{NH}_4^+$ and pH in the aeration tank

Figure 2a shows the patterns of N_2O emissions and concentrations of NH_4^+ , NO_3^- and DO along the six zones of the aeration tank for the sampling carried out on May 18, 2010. The NH_4^+ concentration decreased from ZN1 to ZN6, whereas N_2O emission increased, culminating in ZN5. Higher N_2O production, due to nitrification mainly, and emission were expected in ZN2 due to both the elevated concentration of NH_4^+ in the prior zone (ZN1) (7.8 mg L^{-1}) and the greatest number of diffusers in ZN2 (1184) compared to other zones. However, observing Figure 2a, it is noticeable that the oxidation of NH_4^+ is much faster in the segment ZN4-ZN6 than that in ZN1-ZN4. In the intersection zone (ZN4), DO concentration and N_2O emission begin to rise. It follows that the rates of NH_4^+ oxidation and concomitant

N_2O production raise sharply in the segment ZN4-ZN6. So, the most plausible hypothesis to explain the pattern of DO and N compounds shown in Figure 2a is that with decreasing concentration of organic matter along the zones, the DO concentration increases, thereby favoring nitrification and N_2O production ($\text{DO} \geq 2 \text{ mg L}^{-1}$) (Surampalli *et al.*, 1997; Ribeiro *et al.*, 2013). Additionally, the greater number of diffusers in ZN5 (898) as compared to ZN4 (500) and ZN6 (612) also contributes to the high N_2O emission rate at ZN5 due to air stripping.

Figure 2b shows the evolution of the nitrification process through the pattern of the $\text{NO}_3^-/\text{NH}_4^+$ ratio and pH throughout the six zones of the aeration tank in the sampling carried out on May 18, 2010. The low values of $\text{NO}_3^-/\text{NH}_4^+$ between ZN1 and ZN4 indicate that complete nitrification was not occurring throughout this segment. The gradual

drop in pH from ZN1 to ZN4 can be attributed to the oxidation of organic matter. The sharp increase in $\text{NO}_3^-/\text{NH}_4^+$ and sudden reduction in pH from ZN4 to ZN6 suggests the occurrence of nitrification (partial or complete) in these zones of the aeration tank. The oxidation of NH_4^+ to NO_2^- , the first step of the nitrification process, releases two H^+ per mol of NH_4^+ oxidized. Subsequently, NO_2^- is rapidly oxidized to NO_3^- (second nitrification step) with no release of H^+ . This is clearly shown by the $\text{NO}_3^-/\text{NH}_4^+$ ratio and pH in the last zones of the aeration tank (Figure 2a).

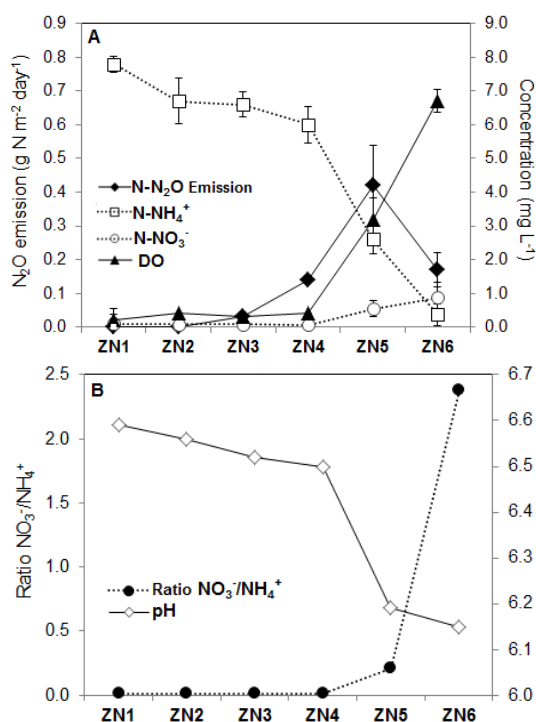


Figure 2. (a) Spatial variability of N_2O emissions and N-NH_4^+ , N-NO_3^- and DO concentrations (average \pm standard deviation) along the six zones of the aeration tank on May 18, 2010. (b) Spatial variability of $\text{N-NO}_3^-/\text{N-NH}_4^+$ (molar) ratio and pH along the six zones of the aeration tank on May 18, 2010.

The Figures 3a and 3b show the results of the sampling carried out on February 17 and June 30, 2011, respectively. On both sampling days, the aeration tank was operated with an influent air flow rate of about 2 times higher than that used on May 18, 2010 (Table 2). Figure 3a (February 17, 2011) shows a different pattern from that observed in Figure 2a (May 18, 2010),

with the largest N_2O emission occurring in ZN2. This outcome may be linked to a more rapid oxidation of NH_4^+ under conditions of higher aeration rate and lower influent organic load (BOD and COD) to the WWTP (Table 1). This condition favors greater availability of DO ($\text{DO} \geq 2 \text{ mg L}^{-1}$) for the oxidation of the organic matter and for the complete nitrification in the initial zones of the aeration tank.

Interestingly, Figure 3b (June 30, 2011) shows a very similar pattern of DO and N compounds to that observed in Figure 2a (May 18, 2010), with higher N_2O emission in ZN5, probably due to *ca.* 30% higher organic loading rate and equivalent aeration rate compared to that on February 17, 2011. These conditions seem to favor the heterotrophic metabolism and the nitrification process in the initial zones of the aeration tank. Similarly as observed on May 18, 2010, the nitrification process on February 17, 2011, intensified in the segment ZN4-ZN5.

Figures 3c and 3d show the evolution of $\text{NO}_3^-/\text{NH}_4^+$ ratio and pH throughout the six aeration zones on February 17 and June 30, 2011, respectively. There is a clear opposite pattern between $\text{NO}_3^-/\text{NH}_4^+$ ratio and pH, supporting the effect of oxidation of organic matter and nitrification on pH. The $\text{NO}_3^-/\text{NH}_4^+$ ratio and pH patterns were strikingly similar during both the May 18, 2010, and June 30, 2011, campaigns. Nevertheless, the $\text{NO}_3^-/\text{NH}_4^+$ values in ZN5-ZN6 were about 1 order of magnitude higher on June 30, 2011, (Figures 2b and 3d) due to the higher influent air flow rate during this campaign (Table 1). This outcome reinforces the hypothesis that with a high influent organic load, DO is restricted to degradation of organic matter and is used by nitrifying organisms only when there is a decrease in organic load along the zones.

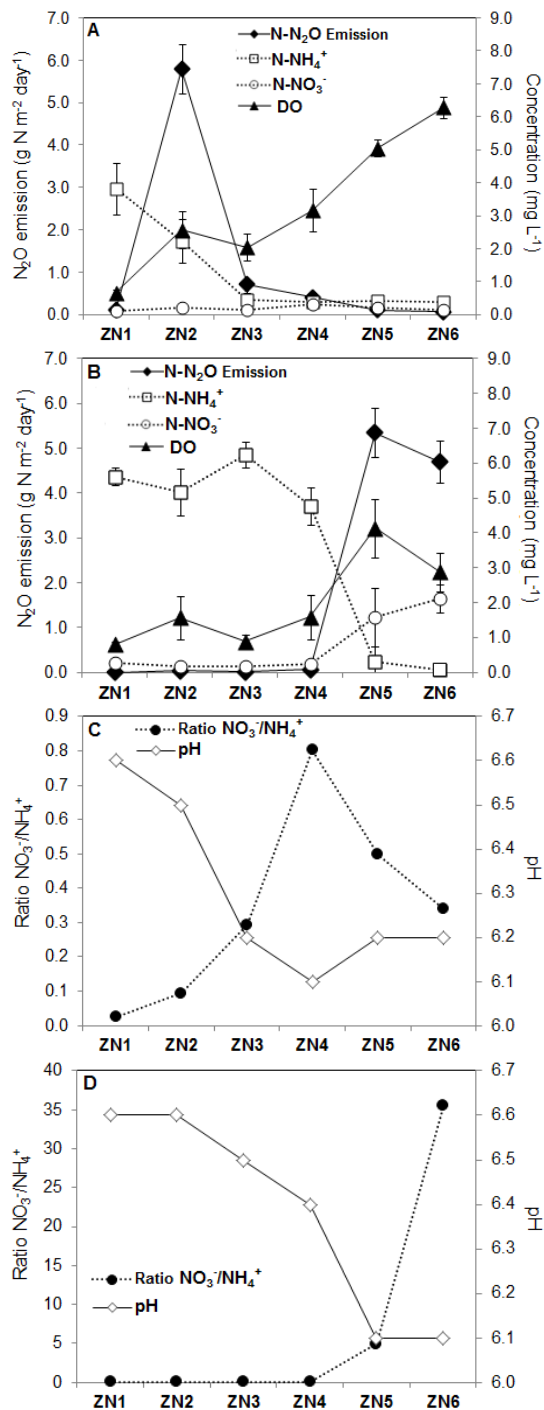


Figure 3. Spatial variability of N₂O emissions and N-NH₄⁺, N-NO₃⁻ and DO

Table 3. Emission factors based on the population served, flow of untreated wastewater and influent TN load during the study days

Sampling date	Emission factors		
	(g N ₂ O person ⁻¹ year ⁻¹)	(g N ₂ O L ⁻¹ wastewater)	(% N ₂ O-N emitted per influent TN load)
May 18, 2010	3.0	3.0 × 10 ⁻⁵	0.04
February 17, 2011	13.8	1.2 × 10 ⁻⁴	0.26
June 30, 2011	19.6	1.9 × 10 ⁻⁴	0.30

The ratio of air flow rate (Q_{air}) to wastewater flow rate ($Q_{\text{wastewater}}$) per tank for May 18, 2010, was almost two times lower than those for February 17 and

concentrations (average \pm standard deviation) along the six zones of the aeration tank on February 17, 2011 (a), and on June 30, 2011 (b). Spatial variability of N-NO₃⁻/N-NH₄⁺ (molar) ratios and pH along the six zones of the aeration tank on February 17, 2011 (c), and on June 30, 2011 (d).

3.3 Ratio $Q_{\text{air}}/Q_{\text{wastewater}}$ in the aeration tank

Figures 2 and 3 show that the N₂O production is dependent on DO and NH₄⁺ concentrations. Also, its emission is directly proportional to the aeration rate of wastewater. The average N₂O emissions observed during the two 2011 campaigns (Figures 3a and 3b) were an order of magnitude higher than that in 2010 (Figure 2a), independently of the influent organic load. This is due to the fact that in 2011, the influent air flow rate in the aeration tank was 2 times higher than that used in 2010 (Table 2), which strongly support the hypothesis that the aeration rate influences the N₂O emission rate, due to enhancement of both the nitrification rate and the removal of supersaturated N₂O in the liquid by air stripping, as has already been mentioned by other authors (Czepiel *et al.*, 1995; Ahn *et al.*, 2010; Brotto *et al.*, 2010; Aboobakar *et al.*, 2013; de Mello *et al.*, 2013).

June 30, 2011 (Table 2). The N₂O emission factors (EFs) for the two studies carried out in 2011, based on the population served, flow of untreated

wastewater and influent TN load, were almost one order of magnitude greater than that observed in 2010 (Table 3). Furthermore, the two 2011 EFs were higher than the EF (3.2 (2-8) g N₂O person⁻¹ year⁻¹) proposed by the IPCC guidelines (2006).

The main controlling factors of N₂O emissions in the activated sludge WWTPs are the concentration of influent TN, the sludge age, the DO concentration and aeration rate (Brotto *et al.*, 2010; Brotto, 2011; Lotito *et al.*, 2012; Aboobakar *et al.*, 2013; de Mello *et al.*, 2013; Hu *et al.*, 2013; Ribeiro *et al.*, 2013). Foley *et al.* (2010) and Ribeiro *et al.* (2013) highlighted the importance of precise control in operational parameters regarding to the N₂O production and emission in aeration tanks from activated sludge WWTPs, which is strongly linked with the removal efficiency of TN.

This study shows that besides other factors, the aeration rate has a strong relationship to N₂O emissions because it determines control of DO concentration and physically affects the transfer process of the supersaturated fraction of N₂O from the liquid phase to the atmosphere (Tables 2 and 3). De Mello *et al.* (2013) showed the importance of this operating parameter in controlling N₂O emission of an aeration tank operated with an intermittent aeration system. Table 4 shows the EFs from previous studies carried out in four WWTPs in Rio de Janeiro with distinct values of sludge age and Q_{air}/Q_{wastewater} ratio. Among those four studies, the one with intermediate sludge age and lowest Q_{air}/Q_{wastewater} ratio revealed the lowest N₂O EF. Accordingly, if the aim is to lessen N₂O emissions from activated sludge WWTPs, it is important to control the key operating parameters.

Table 4. Emission factors of N₂O, based on the population served, for studies carried out in WWTPs, located in Southeast Brazil, with activated sludge systems exhibiting diverse operational characteristics

References	Aeration system employed	Sludge age (days)	(Q _{air} /Q _{wastewater})	Emission factor (g N ₂ O person ⁻¹ year ⁻¹)
Brotto <i>et al.</i> (2010)	Extended	25	11.5	13
Brotto (2011)	Modified	3	8.8	8.1
de Mello <i>et al.</i> (2013)	Intermittent	13	25.6	8.8
Ribeiro <i>et al.</i> (2013)	Conventional	10-12	3.3	1.3

The use of N₂O emission as an operational parameter to control the rate of aeration in the activated sludge WWTPs has already been proposed and discussed in the literature by different authors (Burgess *et al.*, 2002; Sivret *et al.*, 2008; Butler *et al.*, 2009). The findings shown in this study reinforce the viability of using systematic measurements of N₂O emissions in aeration tanks of activated sludge WWTPs as an indicator of the aeration rate necessary to promote microbiological processes for the oxidation of organic matter and nitrogen removal.

4. CONCLUSIONS

Three *in situ* experiments, conducted in an activated sludge WWTP, strengthen the influence of the total N loading rate, especially ammonium, and the aeration flow rate on the emission rate of N₂O from the aeration tank. The variation of NH₄⁺, NO₃⁻ and DO concentrations and pH values along the six interlinked aeration zones strongly suggested that N₂O formation occurred mainly through nitrification. During these experiments, the carbonaceous organic matter removal was high and rather constant (93-96%). Excessive air flow intensifies N₂O transfer from liquor to the atmosphere by air stripping, wastes energy and increases plant-operating costs.

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