High-Frequency Field Measurement of Nitrous oxide (N_2O) Gas Emissions and Influencing Factors at WWTPs under Dry and Wet Weather Conditions

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ABSTRACT

Wastewater treatment plants (WWTPs) contribute to global greenhouse gas emissions. Current knowledge is still insufficient regarding the exact magnitude of the emissions of the powerful greenhouse gas nitrous oxide (N_2O). Also, the complete N_2O production mechanisms remain unclear. In order to shed light on N_2O emissions at real plants, under different weather conditions, continuous field measurements of gaseous nitrous oxide (N_2O), ammonium (NH_4^+), nitrate (NO_3^-) and dissolved oxygen (DO) were carried out at the aeration zone of a 750,000 PE wastewater treatment plant. These were complemented with high-frequency lab analyses of important variables at different locations in the plant. N_2O emissions were analysed by relating it with the aeration flow rate, the DO and other nitrogen-containing components, as well as the influence of dry and wet weather conditions. Spatial differences in N_2O emissions throughout the aerated zone were also investigated. It could be concluded that ammonia-oxidizing bacteria (AOB) can contribute significantly to N_2O production compared to the heterotrophic pathway for N_2O production. Moreover, rather than simply correlating N_2O production by AOB with DO concentration, the investigation revealed the conditions affecting NH_4^+ to be oxidized either more to N_2O or more to NO_3^-. Under regular dry weather conditions, the measured average N_2O emission factor at the summer package aeration zone is 0.96% of influent nitrogen load. The N_2O production by AOB is stimulated by high NH_4^+ concentrations, but it is likely that under high DO conditions the fraction of NH_4^+ converted to N_2O is smaller than under low DO conditions while the NO_3^- production kept increasing. Under rain events, lower N_2O emissions were observed.

KEYWORDS: Activated sludge, aeration, biological nitrogen removal, greenhouse gas emissions

1 INTRODUCTION

Nitrous oxide (N_2O) is produced during biological nitrogen removal process at wastewater treatment plants (WWTPs) and a wide range of N_2O emission rates have been reported (Ahn et al., 2010; Foley et al., 2010; Kampschreur et al., 2009). N_2O is a powerful greenhouse gas (GHG) with a 298-fold global warming potential of CO_2 (IPCC, 2007). Three processes have been identified to produce N_2O (Bremner, 1997; Kampschreur et al., 2011; Wunderlin et al., 2012): production by ammonia-oxidizing bacteria (AOB), heterotrophic denitrification and chemical reactions. The AOB pathway mainly includes the N_2O generated as a side product during ammonia oxidation to nitrite via hydroxylamine and the autotrophic denitrification, i.e. NO_2^- reduction to N_2O. While elucidation of the details of the pathways is still ongoing, also knowledge on the governing mechanisms relating environmental and operational factors with N_2O emissions is still incomplete. Especially, the relation between dissolved oxygen (DO) and N_2O production by AOB is still an issue of debate exemplified by the existence of different models describing N_2O production by AOB, some suggesting that higher DO concentrations stimulate N_2O production while others indicate that, on the contrary, low DO concentrations maximize N_2O production (Ni et al., 2013).

Regardless the details of the AOB pathway, the N_2O obtains its nitrogen (N) from ammonium (NH_4^+). But there are other N-conversion processes which also source N from NH_4^+, e.g. nitrate (NO_3^-) is produced from nitrite (NO_2^-) by nitrite-oxidizing bacteria (NOB) and nitrite (NO_2^-) is a direct product of ammonia oxidation by AOB. Therefore, an internal dependency among various N conversion pathways exists.

To reveal these dependencies dedicated continuous full-scale N_2O measurements under dynamic conditions were conducted at the Eindhoven WWTP (The Netherlands). The relationships between different N species and DO were analysed to better explain the N_2O dynamics. Further, the effect of rain-induced hydraulic shocks on N_2O emissions were studied.

2 MATERIALS AND METHODS

2.1 Plant operation and control strategy

The 750,000 PE WWTP of Eindhoven (The Netherlands) has a modified UCT configuration. Each bioreactor consists of an inner ring as anaerobic tank, a middle ring as anoxic tank and an outer ring as aerobic/anoxic tank (Figure 1). Aeration is provided for by a main continuously active “summer package” and by a backup “winter package”, which is activated only occasionally (in winter or under rain events to provide more aerobic volume). The summer package airflow is controlled by a NH_4^+-DO feedback cascade control. A feed-forward correction on the basis of influent flow rate is added to provide sufficient DO for nitrification under increased loading.

2.2 On-line measurements

N_2O gaseous measurements were conducted at three sampling points distributed longitudinally along the summer package aeration zone, respectively at its beg inning, middle and end. Each sampling point was monitored for about 1 week. The temperature was generally between 10-30 ºC during the measurement campaign (6-27 August) except for 17-18 August when the daytime maximum air temperature was above 35 ºC, leading to failures of the on-line N_2O measurement equipment (Emerson). Off-gas was collected by a floating hood and the volume percentages of N_2O in the total emitted gas (ppm) were collected every minute.

The plant is also equipped with several on-line sensors, i.e. for monitoring DO, NH_4^+ and NO_3^- concentrations, and aeration flow rate control. Sensors for DO, NH_4^+, NO_3^- and total suspended solids (TSS) are installed at the outlet of the bioreactor which is close to the N_2O sampling point at the end of the summer package (Figure 1).

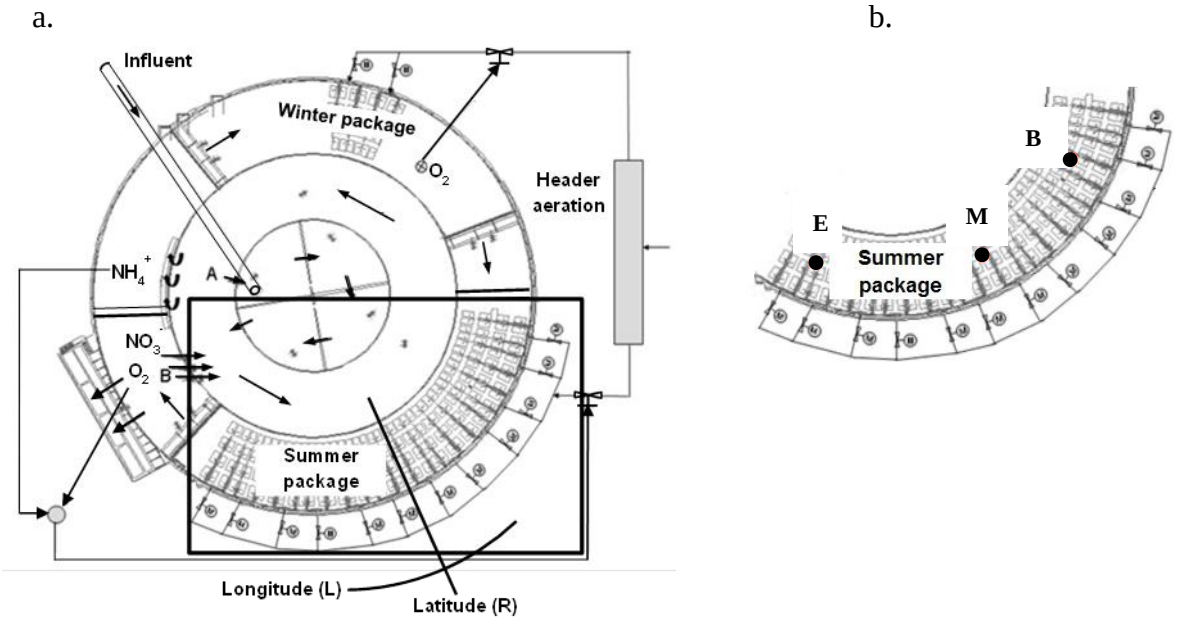


Figure 1 Bird view of bioreactor (a) and location of N_2O sampling points (B: beginning, M: middle, E: end) (b)

2.3 Calculation of N_2O emissions

The N_2O emission rate is calculated using Eq. (1), assuming that the surface of the summer package is divided into 3 equal parts and so is the local aeration flow rate for each part (beginning, middle and end), i.e. the air flow rate over the summer package shows a longitudinally homogeneous distribution.

$$N_2O\_emission\_min_i = \frac{N_2O\_ppm_i}{10^6\ (ppm)} \times \frac{Q_i}{3} \times \frac{0.028\ (kgN\text{-}N_2O/mol)}{0.0224\ (m^3/mol)} \times 3 \qquad \text{Eq. (1)}$$

where $N_2O\_emission\_min_i$ is the minutely averaged N_2O emission rate (kg N-N_2O/d) at time *i*, $N_2O\_ppm_i$ is the raw measurement of N_2O (ppm) and Q_i is the total aeration flow rate of the summer package (m^3/d).

The N_2O emission factor is calculated using Eq. (2):

$$f_{N2O,i} = \frac{N_2O\_emission\_hour_i}{N\_load_{i-HRT}} \qquad \text{Eq. (2)}$$

where $f_{N2O,i}$ is the hourly averaged N_2O emission factor at time *i*, $N_2O\_emission\_hour_i$ is the hourly averaged N_2O emission rate (kg N-N_2O/d) at time *i*, HRT is hydraulic residence time and $N\_load_{i\text{-}HRT}$ is the influent N load at the current time *i* minus HRT. Note that the N_2O emission rate is calculated every minute as the raw data of N_2O analyser and other plant sensors are provided every minute, giving clear information on the temporal dynamics. The emission factor, however, is calculated as an hourly average because the calculation of the emission factor needs to account for the retention time effect.

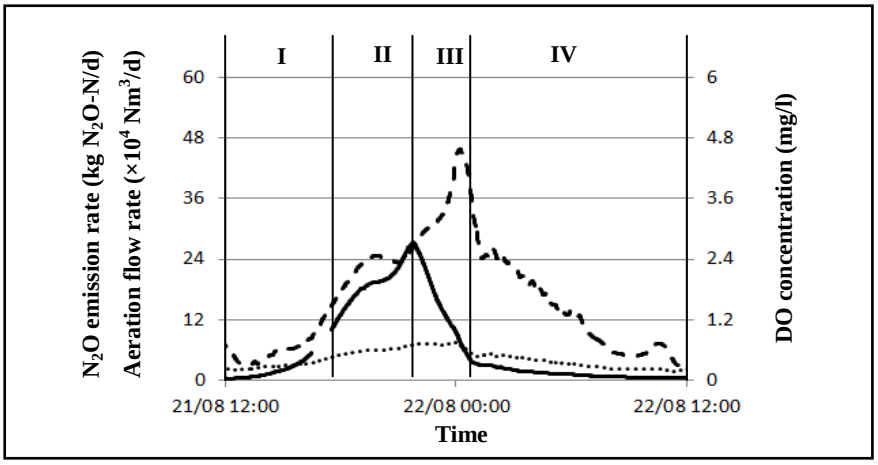
3 RESULTS AND DISCUSSION

3.1 N_2O emissions at different sections of the summer aeration package

Almost all N_2O produced by heterotrophs in the upstream anoxic zones is expected to be stripped at the beginning (and middle) aeration sections. Most N_2O emitted at the end of the summer package is thus probably the result of the AOB pathway. Under dry weather conditions, the end of the summer package showed a significantly higher average N_2O emission rate (6.8 kg N_2O-N/d) compared to the beginning and the middle part (3.6 and 2.6 kg N_2O-N/d). From this observation one can conclude that AOB contribute more to the N_2O emission than heterotrophs.

The DO, NH_4^+ and NO_3^- sensors installed at the end of the aeration zone help understanding the AOB-produced N_2O emissions and their relationship with the other N species. The period 20-24 August was a dry weather period and one typical dry day cycle was picked for further analysis. Figure 2.a compares N_2O emission rates at the end section of the summer package with the local aeration flow rate and DO concentrations under one typical dry weather day whereas Figure 2.b compares it with the NH_4^+ and NO_3^- concentrations at the end of the summer package and the influent NH_4^+ loads and concentrations. Figure 3.a shows the comparison under wet weather day.

a.

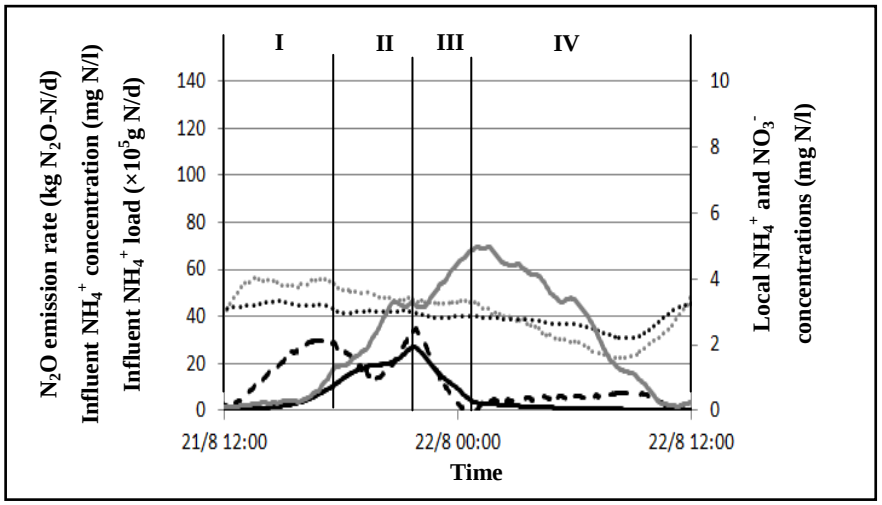


N_2O emission rate (kg N_2O-N/d)

Aeration flow rate of summer package (×10^4 Nm^3/d)

Local DO concentration at summer package (mg/l)

b.



N_2O emission rate (kg N_2O-N/d)

Local NH_4^+ concentration at summer package (mg N/l)

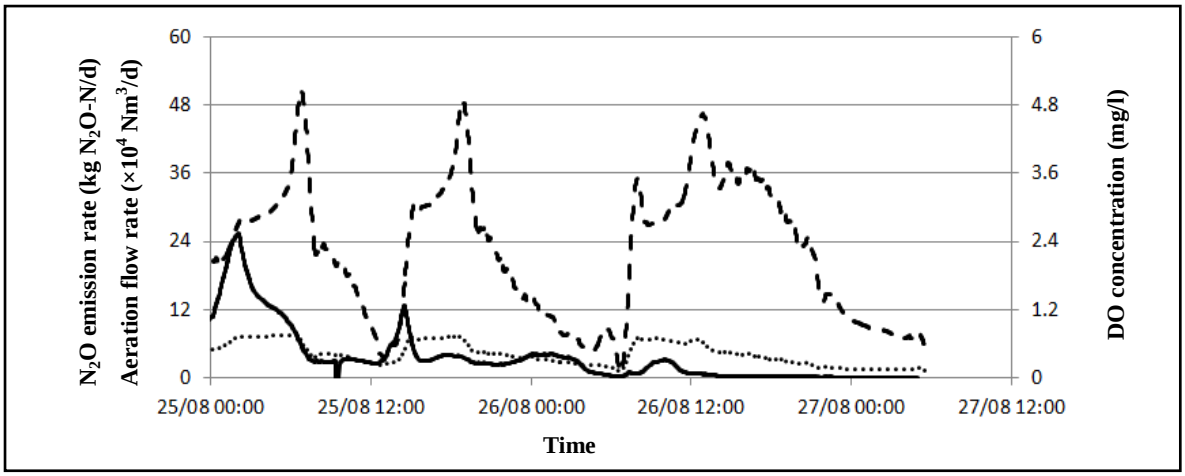
Local NO_3^- concentration at summer package (mg N/l)

Influent NH_4^+ load (g N/d)

Influent NH_4^+ concentration (mg N/l)

Figure 2 Comparison of N_2O emission rate at the end section of the summer package with the local aeration flow rate and the DO concentration (a) and with N-component concentrations at the end of the summer package and influent NH_4^+ concentrations and loads (b) under one typical dry day

a.

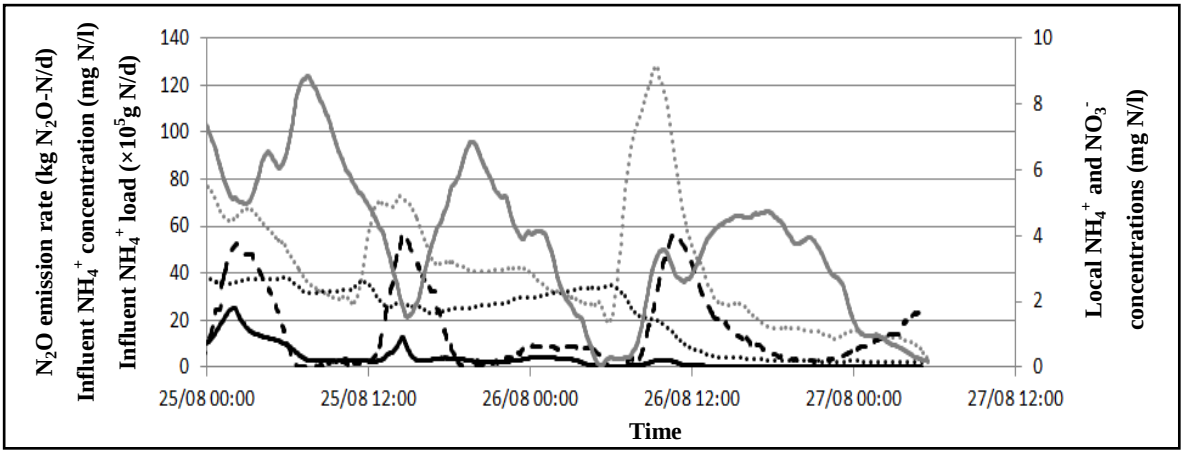


N_2O emission rate (kg N_2O-N/d)

Aeration flow rate of summer package (×10^4 Nm^3/d)

Local DO concentration at summer package (mg/l)

b.



N_2O emission rate (kg N_2O-N/d)

Influent NH_4^+ load (g N/d)

Local NH_4^+ concentration at summer package (mg N/l)

Influent NH_4^+ concentration (mg N/l)

Local NO_3^- concentration at summer package (mg N/l)

Figure 3 Comparison of N_2O emission rate at the end section of the summer package with the local aeration flow rate and the DO concentration (a) and with N-component concentrations at the end of the summer package and influent NH_4^+ concentrations and loads (b) under wet weather days

For the wet weather days (August 25-26), only the emission at the end part of the summer package was recorded. The rain weather HRT was reduced to about 1 hour. The average N_2O emission rate at this location was 11.9 kg N_2O-N/d, leading to an hourly averaged N_2O emission factor of 0.22% (ranging between 0.02 and 0.97%). More measurements should be carried out at the other parts of the summer package to obtain the total N_2O emissions under rain conditions.

3.2 N_2O emission under dry-weather conditions

Each dry day was divided into 4 phases (Figure 2). NH_4^+ load peaked at the plant inlet around noon and hit the summer package about 3 hours later. The NH_4^+ concentration at the end of the summer package increased, together with a rise in N_2O emissions (Phase I). This increasing local NH_4^+ concentration also gave rise to an increase in aeration induced by the NH_4-DO cascade control.

In Phase II, aeration kept increasing and N_2O emission increased as well, except that for a short term it increased at a slower pace or even remained constant. At this same time the local NH_4^+ concentrations showed a small afternoon dip and then started to increase again for a short while. Then, just at the beginning of the Phase III when a DO concentration higher than in former phases was reached (around 3 mg/l, see Figure 2.a), N_2O emissions dropped suddenly, coinciding with the drop in the NH_4^+ concentration. The NO_3^- concentration on the other hand kept increasing. Note that the influent NH_4^+ load remained high during this phase which means that the decrease of N_2O emission and NH_4^+ concentration at the summer package cannot be attributed to a reduced influent N load. Rather it must be concluded that the local bio-reactions leading to N_2O formation were affected by the process conditions, resulting in the observed N_2O emission decrease. Since the N source of N_2O formation is NH_4^+ which is also the case for NO_3^- formation, the phenomenon of the turning point of N_2O emission in this phase indicates that under high DO conditions the fraction of NH_4^+ that is converted to N_2O instead of NO_3^- is smaller than under low DO conditions.

In Phase IV, corresponding with the drop in influent NH_4^+ load, the N_2O emissions, the NH_4^+ concentration and the NO_3^- concentration decreased. Concomitantly the aeration was also reduced by the cascade control strategy.

Overall, the measurement results suggest that AOB-produced N_2O emission reaches its maximum in conjunction with both high NH_4^+ concentration and intermediate DO concentrations. This finding is in agreement with other studies (Colliver and Stephenson, 2000; Zhu et al., 2013).

3.3 N_2O emission under wet weather conditions

On August 25th-26th, a rain event occurred, providing information on N_2O emissions under wet weather conditions. At the plant rainfall was observed around 10:30am on the 25th, it stopped in the early afternoon and re-started again in the evening. NH_4^+ peak loads occurred as usual (Figure 3.b). The whole August 26th it rained intensively. However, also early in the morning of August 25th the influent flow rate was higher than the dry weather flow rate. It was therefore concluded that rain already started somewhere else in the catchment at that time.

Interestingly, the NH_4^+ peak loads under wet weather days were equal or higher compared to the ones under dry weather conditions, even though the influent NH_4^+ concentrations were diluted. The maximum NH_4^+ concentrations reached at the end of the summer package were slightly higher during rain events, but, importantly, the N_2O emissions remained relatively low. The N_2O emissions showed a similar relationship, especially on August 25th, with the DO, NH_4^+ and NO_3^- concentrations as during the dry weather days. In other words, the N_2O emissions and the NH_4^+ concentration decreased at a certain point while the NO_3^- concentrations kept increasing.

4 CONCLUSIONS

High frequency N_2O emission data have been collected at a 750,000 PE WWTP and compared with air flow rate data, and on-line measurements of the concentrations of DO and different N species. It could be concluded that a significant fraction of the N_2O is produced in the aerated zone, implying the AOB-mediated production of N_2O. Relationships were observed between N_2O and NO_3^- production, and the NH_4^+ concentrations and load, DO concentration and aeration intensity. Indeed, under dry weather conditions, as local NH_4^+ concentrations increase due to the daily influent NH_4^+ peak load, more N_2O is produced by autotrophs, but at higher DO levels an increasing fraction of the NH_4^+ is converted to NO_3^- than to N_2O. Under wet weather conditions, despite the increased dilution, higher local NH_4^+ concentrations were observed (due to a lack of aeration capacity), but N_2O emissions were lower compared to dry weather conditions. Long-term measurement campaigns hence help in further unraveling the complex mechanisms of N_2O production and emission in WWTPs.

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