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Characterization of nitrous oxide and nitric oxide emissions from a full-scale biological aerated filter for secondary nitrification

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HIGHLIGHTS

- N_2O and NO emissions from a full-scale BAF were studied online for the first time.
- N_2O and NO emissions occurred even at DO over 6.9 mg/L in the studied BAF.
- N_2O and NO emission factors were 0.017–0.828% and 0.00017–0.0041%, respectively.
- Influent NO_2^--N concentration was a direct contributor to N_2O and NO production.
- Nitrifier denitrification is a possible N_2O and NO production pathway.

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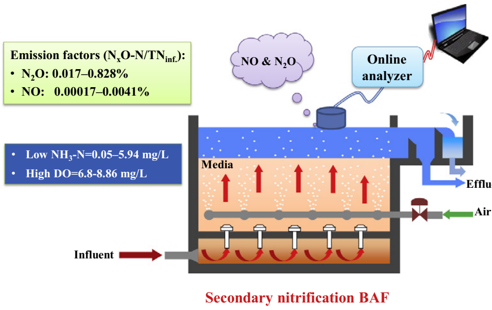
GRAPHICAL ABSTRACT



ABSTRACT

Both nitrous oxide (N_2O) and nitric oxide (NO) (as a N_2O precursor during denitrification) have negative effects on the environment. N_2O is also a potent greenhouse gas. N_2O and NO emissions in full-scale wastewater treatment plants (WWTPs) are mostly from mainstream activated sludge processes, but there are fewer emission studies from biofilm systems. In this study, online monitoring of NO and N_2O emissions from a full-scale biological aerated filter (BAF) for secondary nitrification was performed for the first time over 12 months. Impacts of influent quality (influent NH_4^+-N, NO_3^--N, NO_2^--N) and environmental factors (pH, dissolved oxygen (DO), and water temperature) on N_2O and NO emissions were also evaluated. The results show that N_2O and NO emissions from the BAF occurred even though DO was high at 6.94–8.86 mg/L; they greatly fluctuated with the season that much greater in spring than other seasons (summer, autumn and winter). N_2O and NO emission factors were 0.017–1.261% and 0.00017–0.0041% of influent total nitrogen load, respectively, with an average ammonia removal rate of 60%. The N_2O emission factor for the secondary nitrification BAF was comparable to that of mainstream activated sludge systems in WWTPs, and much lower than that of biofilm reactors in lab-scale. Nevertheless, the low influent ammonia loading of 0.004–0.05 kg NH_4^+-N/m^3 d contributed to the reduced N_2O emissions for the secondary nitrification BAF, compared with that from mainstream wastewater treatment processes. Nitrite seems to be the most important cause of NO and N_2O production, and nitrifier denitrification pathway was postulated to be the main contributor to N_2O and NO production in the studied BAF.

1. Introduction

Nitrous oxide (N_2O) is a major threat to both ozone and climate in the 21st century [37]. N_2O is a potent greenhouse gas for its global warming potential being 298 times stronger than CO_2 for time

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horizon of 100 years [17], and with a rapid emission growth rate of 0.25–0.31% per year. Wastewater treatment plants (WWTPs) are a potential anthropogenic N_2O emission source, accounting for 3.56% of total estimated anthropogenic N_2O emissions in 2010 [19] and 1.3% of total N_2O emissions [41,9,33].

N_2O emissions from WWTPs have received greater attention because of their detrimental environmental effects and increasingly stringent nutrient discharge standards. N_2O emission factors for full-scale WWTPs were reported to be 0–14.6% [22] and 0–25% [28]. This great variation of N_2O emission factors is mainly caused by diverse water qualities, treatment technologies, operating conditions, and environmental factors (e.g., dissolved oxygen (DO), pH, and temperature). Moreover, varying measurements lead to great differences, and offline monitoring is always believed to overestimate or underestimate N_2O emissions [28]. Understanding N_2O emission characteristics and accurate quantification of emission levels are critical for effective N_2O emission mitigation strategies.

Nitric oxide (NO), as a precursor of N_2O during denitrification, is also emitted from WWTPs [23,13]. NO plays an active role in chemical reactions leading to depletion of the ozone layer [10], and has strong biological toxicity for protein denaturation and mutagenicity [48]. Characterizing NO emissions is necessary for clarifying N_2O generation mechanisms [35]. However, NO emissions are less examined than N_2O emissions.

N_2O and NO emissions in full-scale WWTPs are mostly from mainstream activated sludge processes [40,25,11,1]. There are fewer emission studies from biofilm reactors in pilot-studies, such as biological aerated filters (BAFs). A BAF is a reliable and robust biological treatment technology that can provide secondary treatment of municipal and industrial wastewater. BAFs are becoming increasingly popular worldwide, including China, owing to their compactness and favorable performance. In China, secondary nitrification using BAF technology has been used after anaerobic/anoxic/oxic (A^2/O) processes (mainstream) in the upgrade of WWTPs to meet strict permit nutrient effluent limits. In such post-BAFs, nitrification is the main reaction, which is currently considered responsible for the majority of direct NO and N_2O emissions in full-scale WWTPs [25,16,12]. Because of varying influent nitrogen loading (low ammonia loading relative to mainstream treatment processes), sludge morphology (biofilm vs. floc), and related substance and DO diffusion coefficients, N_2O and NO emission characteristics and levels in secondary-nitrification BAFs may differ greatly from those of mainstream activated sludge systems as well as biofilm-based model studies. However, knowledge of N_2O and NO emissions from secondary-nitrification BAFs remains deficient.

In this study, N_2O and NO emissions from a full-scale, secondary-nitrification BAF were monitored using online N_2O and NO analyzers over 12 months for the first time. The objective was to: (1) characterize diurnal and seasonal emission characteristics of NO and N_2O from the secondary-nitrification BAF; (2) clarify the impact of inflow water quality and environmental conditions on N_2O and NO emission factors (N_xO-N/$TN_{influent}$, %) in BAFs biofilm systems; (3) identify the possible main contribution for N_2O and NO production.

2. Materials and methods

2.1. Plant and BAF process

The monitoring site was a municipal WWTP in Shanghai, China, which serves an area of ~650 hectares and treats wastewater of 200,000 population equivalents (PE). A primarily treatment section of this facility, for biological chemical oxygen demand (COD) and nitrogen (N) removal, consists of three identical A^2/O tanks with operational volume of 19,440 m^3 each (Fig. 1a). During the experimental period, average influent flow was 2000 m^3/h with hydraulic retention time (HRT) 7.7–10.3 h, and the mixed liquor suspended solid level was 2.3–2.5 g/L. Air fluxes were ~7500 m^3/h.

After sedimentation, approximately 50% of the treated wastewater enters the BAF unit for secondary nitrification to polish effluent, and the remaining 50% surpasses BAFs to discharge together with the BAF effluent (Fig. 1a). There are eight BAFs, each of size $L \times W \times H = 8.9\ m \times 9\ m \times 5.8\ m$ (Fig. 1b). For the BAF unit, the inlet flow and the aeration rate were 1000 m^3/h and 2000 m^3/h, respectively, and the HRT was 3 h. During the experimental period, the influent and effluent NH_4^+-N concentrations of the studied BAF were 0.05–5.94 mg/L and 0–1.50 mg/L, respectively. NH_4^+-N and TN loading were 0.0004–0.05 kg NH_4^+-N/m^3 d and 0.09–0.12 kg TN/m^3 d. The influent COD < 25 mg/L. Approximately 25% of the BAF effluent was recycled to the anoxic zone of the prior A^2/O tank. One of the BAFs (spot 1) was selected for study (Fig. 1a). The structure of this BAF and the sampling points are shown in Fig. 1b.

2.2. N_2O and NO monitoring campaigns and equipment

2.2.1. Sampling monitoring campaigns

Both diurnal and seasonal variations in N_2O and NO emissions were investigated. Shanghai features a subtropical monsoon climate with four distinct seasons and abundant rainfall. Temperature is higher than 26 °C in summer (June to August) and falls below 15 °C in winter (December to February the next year). Spring (March to May) and autumn (September to November) has an air temperature range of 15–26 °C. Data of temperature (air and water) and humidity during the sample period was listed in Table S1 as Supporting Materials.

Seasonal monitoring of NO and N_2O emissions was conducted monthly from May to April the next year (generally from 9:00 to 11:00 the following day). The in-situ DO, pH and temperature were measured online at the same time. Corresponding water and sludge samples were collected. Specifically, 5 mL sludge mixed liquor was taken for analysis of dissolved N_2O concentration, and 30 mL water samples for nutrient analysis (i.e., NH_4^+-N, NO_2^--N, and NO_3^--N). The sampling interval was 2–4 h (specifically, at 11:00, 13:00, 15:00, 17:00, 19:00, 21:00, 23:00, 3:00, 7:00, 9:00, and 11:00). Because the HRT for the studied BAF was 3 h, the studied BAF influent (A^2/O tank effluent at spot 2, Fig. 1) was evaluated every 3 h for NH_4^+-N, NO_2^--N, and NO_3^--N analyses.

2.2.2. Sampling device

Two identical floating hoods (FH), each with a circular cross-sectional area of 0.0314 m^2, were used to collect gaseous N (NO and N_2O) fluxes from the surface of the experimental BAF. The FH consisted of floating enclosed spaces through which exhausted gas could be collected in real time (Fig. S1). In the enclosed space, a set of accessories was installed to facilitate gas capture. Two sampling tubes were mounted on the upper spherical space, one ending in the upper space (gas phase sampling tube, tube-G) and another extending to the inside bottom of the cylinder space (liquid phase sampling tube, tube-L) (Fig. S1).

2.2.3. Gas sample collection and determination

Gases isolated from the aeration water columns by the FHs were analyzed in real time using an online NO analyzer (ML410, 2B Technologies, Boulder, Colorado, USA) with a drying unit (Nafion gas drying tube, MD-110, Perma Pure, USA), and an online N_2O analyzer (AO2020 Uras26, ABB Automation GmbH, Germany) with a drying unit and gas conditioning unit (SCC-S, ABB Automation GmbH, Germany). The NO online analyzer has a detection