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Nitric oxide and nitrous oxide emissions from a full-scale activated sludge anaerobic/anoxic/oxic process

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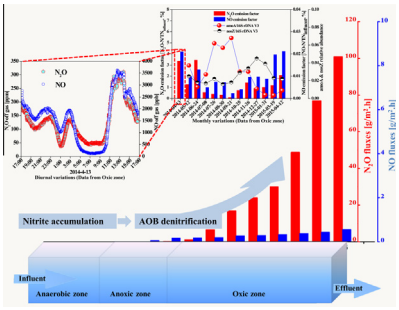
HIGHLIGHTS

- Online monitoring emissions of NO and N_2O from a full-scale A^2/O for the first time.
- NO and N_2O emitted per N load of 0.002–0.021% and 0.095–3.44%.
- NO and N_2O production and emission mainly occurred in oxic zones.
- Nitrite accumulation triggered NO and N_2O production and emissions.
- N_2O emission patterns closely resembled those of NO.

GRAPHICAL ABSTRACT



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ABSTRACT

Both nitric oxide (NO) and nitrous oxide (N_2O) have strong negative effects on the environment. Although N_2O emissions in wastewater water treatment plants (WWTPs) have been widely studied, the concurrence of NO and N_2O emissions has not been well characterized, and their emission status from WWTPs in China is still not clear. In this study, online NO and N_2O analyzers were used to investigate spatial and temporal variations of NO and N_2O emissions in a full-scale activated sludge anaerobic/anoxic/oxic (A^2/O) process over one year. The *amoA* gene of ammonia oxidation bacteria and the *nosZ* gene of denitrifiers were analyzed to identify possible NO and N_2O production pathways. The emission factors of NO and N_2O in the studied A^2/O process were 0.01 ± 0.006% (0.002–0.021%) and 1.29 ± 1.07% (0.095–3.44%) of the nitrogen load, respectively. Both NO and N_2O were mainly emitted from the oxic zone, with emitting levels increasing greatly from the initial oxic zone to the zone end. The N_2O emission pattern closely resembled that of NO emissions, but the emission amounts were 2–3 magnitudes higher than that of NO. Nitrite accumulation directly triggered NO and N_2O production. This study provides novel insights into emission characteristics and the production pathways of both NO and N_2O from a full-scale A^2/O process, which is of great significance toward development of effective mitigation strategies for NO and N_2O emissions from WWTPs.

1. Introduction

Nitric oxide (NO) and nitrous oxide (N_2O) are known to contribute to the depletion of ozone layers [44]. N_2O is a greenhouse gas with a global warming potential approximately 300 times greater than that of CO_2 [20], and is predicted to be the most dominant ozone-depleting substance in the 21st century [44]. According to the United States Environmental Protection Agency, N_2O emissions from wastewater treatment sectors account for 3% of anthropogenic emissions [16]. Nitrous oxide emission factors were reported to range from 0.01% to 0.08% by Ahn et al. [2], 0% to 14.6%

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by Wicht and Beier [54] and 0.6% to 25.3% by Foley et al. [13] during biological nitrogen removal from wastewater treatment plants (WWTPs) (Table 1). Considering that an increase in the N_2O emission factor of 1% could lead to as much as a 30% elevation of the overall carbon footprint in a conventional biological nutrient removal WWTP [11], an accurate calculation of the relative emission factor is essential.

Nitric oxide is the precursor of N_2O production during nitrifier denitrification or heterotrophic denitrification. Recently, other biological processes involved in NO metabolism have also been reported, such as anaerobic ammonium oxidation (anammox) [23] and ammonia oxidation by archaea [37,29,38]. Specially, many archaea are able to reduce nitrate by assimilatory or respiratory pathways, during which NO could be produced as intermediate [38]. Nitric oxide is a known signaling compound, exerting severe biological impacts, e.g., it has an important impact on the metabolism of AOB [58] and many other groups of prokaryotes and eukaryotes [59,60,33]. Accordingly, the formation and subsequent emission of NO and N_2O may interact with each other during biological nitrogen conversion [12]. Besides, nitric oxide participates in regulation of the oxidant balance of the atmosphere, during which time it can be oxidized to NO_2, and the subsequent deposition of NO and NO_2 can lead to serious acidification and eutrophication of ecosystems [52]. However, emissions of NO are less frequently reported in WWTPs. Most studies on NO emissions that have been conducted to date are limited to lab-scale reactors or featured high ammonia loading or conducted with grab sample methods (Table 1). Furthermore, the mechanisms of NO and N_2O emissions during the biological nitrogen removal are process-specific and closely related to operating conditions [2,43]. Therefore, NO emission characteristics and their relationship with N_2O emission are still unclear.

To date, most studies of NO and N_2O emissions from WWTPs have been conducted in Europe, the United States and Australia [2,24,25,7,26,47,54,56]. Online NO and N_2O emission data from full-scale wastewater treatment facilities in China are scant, despite it having the world's second-largest sewage treatment capacity [22]. This absence of online emissions data and poor understanding of the mechanisms that lead to its formation in nitrogen removal processes has greatly hindered steps to further mitigate greenhouse gases emissions from wastewater treatment sectors in China.

Anaerobic/anoxic/oxic (A^2/O) processes account for the largest design treatment capacity (33.2%) in Chinese WWTPs (Data from Urban Drainage Statistics Yearbook 2012 and Ministry of Environmental Protection of the People's Republic of China); however, their NO and N_2O emission characteristics have not been well studied. In this study, the emission dynamic of both NO and N_2O from a full scale A^2/O process were studied over 12 months using online NO and N_2O analyzers. The functional genes encoding ammonia monooxygenase (*amoA*) of ammonia oxidizing bacteria (AOB) and nitrous oxide reductase (*nosZ*) of denitrifiers were quantified by real-time quantitative polymerase chain reaction (RT-qPCR) to explore the contribution of primary bio-contributors for NO and N_2O emission with seasonal dynamics. The main objectives were to: (1) characterize NO and N_2O emissions; (2) identify the main influencing factors and key pathways of NO and N_2O production; (3) demonstrate the relevance between NO and N_2O emissions.

2. Materials and methods

2.1. Monitoring site and operational conditions

This study was carried out at a WWTP located in Shanghai, PR China, which serves an area of around 650 hectares and treats wastewater of 200,000 population equivalents (P. E.). An A^2/O process with a plug-flow pattern was adopted in the WWTP (Fig. 1). The A^2/O module consists of three parallel units, each with four consecutive lanes. One of the three identical parallel units was selected for the NO and N_2O emission study. As shown in Fig. 1, the lanes were divided into three zones according to the locations of air diffusers and returned flow inlets (for returned mixed liquid and sludge), i.e., an anaerobic zone, an anoxic zone and an oxic zone with lengths of 30, 30 and 120 m, respectively. All three individual zones featured with equal width and depth of 6 m.

During the experimental period (a whole year), the average influent flow was 2000 m^3/h with a hydraulic retention time (HRT) of 7.7–10.3 h, the mixed liquor suspended solid (MLSS) level was 2.3–2.5 g/L, and the air fluxes were approximately 7500 m^3/h. The influent and effluent water properties were: $COD_{Cr\ influent}$ = 100–300 mg/L, $COD_{Cr\ effluent}$ < 25 mg/L; $NH_3\text{-}N_{influent}$ = 10–30 mg/L, $NH_3\text{-}N_{effluent}$ = 2–10 mg/L; $TP_{influent}$ = 5–7 mg/L and $TP_{effluent}$ < 3 mg/L. Field gas sample collections were conducted over one year (April 2014 to April 2015), during which time ambient temperatures ranged from 13 °C to 34 °C.

2.2. Sampling campaigns and equipment

2.2.1. Sampling campaigns

A holistic sampling plan was executed on 1 June 2014 to characterize spatial variations in N_2O emissions from the anaerobic/anoxic/oxic zones, while localized sampling plan designed to provide detailed information regarding both NO and N_2O emissions in the oxic zone was conducted monthly. In each plan, appropriate measures were adopted to eliminate potential disturbances caused by fluctuations of incoming water quality. Additionally, 24 h of continuous sampling was conducted monthly from April 2014 to April 2015 at 80 m from the oxic starting point, (S_{80} in Fig. 1) to

Table 1
Comparison of NO and N_2O emission factors in literature and this study.

Configuration	NO emission factor	N_2O emission factor	Sampling method	Reference
Activated sludge	–	0.035%	Grab sample	[7]
Activated sludge	–	0.001%	Grab sample	[47]
25 activated sludge plants	–	0–14.6%	Grab sample	[54]
Seven full-scale BNR WWTPs	–	0.6–25.3%	Grab sample	[13]
Activated sludge	–	0.01–0.08%	On-line measurements	[30]
12 WWTPs in the United States	–	0.01–1.8%	On-line measurements	[2]
Nitritation-anammox sludge water treatment	0.2% (nitritation reactor), 0.003% (anammox reactor)	1.7% (nitritation reactor), 0.6% (anammox reactor)	On-line measurements	[26]
Laboratory scale nitrifying reactor system	0.03%	2.8%	On-line measurements	[27]
A^2/O Activated sludge	0.002–0.021%	0.095–3.37%	On-line measurements	This study (diurnal data in 12 months)
	0.034%	6.54%		This study (5 h data)