Effects of untreated or insufficiently treated wastewater discharges on the spatial and temporal variability of nitrous oxide (N$_2$O) emissions from different streams in southeastern Brazil

Renato P. Ribeiro, Luiz Felipe P. Alves, Clara B. de Cerqueira, Leticia M. Mombrini and Heitor Breno P. Ferreira

ABSTRACT

Increasing atmospheric N$_2$O concentrations is of great environmental concern due to the role of this gas in climate change and stratospheric ozone destruction. Nitrogen-enriched lotic water bodies are significant sources of N$_2$O. However, N$_2$O emissions from rivers and streams, particularly those that receive untreated or insufficiently treated wastewater discharge, are poorly understood, especially in Brazil. The present study investigated the effects of the discharge of untreated or insufficiently treated wastewater on the spatial–temporal variability of N$_2$O emissions from different streams in Ilha Grande, located within the Abraão hydrographic system, in southeastern Brazil. Estimated N$_2$O fluxes determined in Abraão streams and upstream of the urbanized stretch ranged from 18.4 and 96.5 μg N m$^{-2}$ h$^{-1}$. Inside the urbanized stretch, estimated N$_2$O fluxes ranged from 110 to 561 μg N m$^{-2}$ h$^{-1}$ under non-limited dissolved oxygen (DO) conditions and 133 to 2,229 μg N m$^{-2}$ h$^{-1}$ under hypoxic conditions (DO < 2 mg O$_2$ L$^{-1}$). High spatial and temporal variability in N$_2$O emissions were noted, with the highest emissions in Abraão urban areas. Therefore, the differences observed between N$_2$O fluxes from the studied streams at Abraão seem to be associated with different lotic water body conditions, such as availability of reactive N and DO.

Key words | dissolved oxygen, nitrogen-enriched water bodies, nitrous oxide, wastewater discharge

HIGHLIGHTS

- Untreated or insufficiently treated wastewater discharges are greatly perturbing N cycling in streams.
- There are significant spatial and temporal N$_2$O emissions variations for all streams studied.
- Diurnal N$_2$O variation was significant within the urban areas of the streams characterized by increased organic, ammoniacal-N input.
- Higher N$_2$O fluxes were observed under limited DO conditions and likely due to nitrification.

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INTRODUCTION

Nitrous oxide (N\textsubscript{2}O) is one of the main gases responsible for global temperature rises, since increasing concentrations in the atmosphere lead to increases in both radiative forcing (greenhouse effect) (IPCC 2014) and the potential for stratospheric ozone (O\textsubscript{3}) consumption (Ravishankara et al. 2009; UNEP 2015). In parallel, N\textsubscript{2}O exhibits a growth rate of 0.8 ppb year\textsuperscript{-1} and a current atmospheric concentration close to 330 ppb (NOAA 2020), representing a 20% increase compared to pre-industrial levels. Thus, increases in the radiative forcing of approximately 35 and 70% are estimated compared to the current average value (0.20 W m\textsuperscript{-2}), for 2050 and 2050, respectively (UNEP 2015). In addition, with decreasing chlorofluorocarbon levels in the atmosphere, N\textsubscript{2}O is expected to become the main stratospheric O\textsubscript{3}-depleting substance emitted by human activities throughout the 21st century (Ravishankara et al. 2009).

The fifth IPCC report indicates that, in 2006, the average N\textsubscript{2}O emission rate from anthropic sources was 6.9 Tg N year\textsuperscript{-1}, of which 9% (0.62 Tg N year\textsuperscript{-1}) were from rivers, estuaries and coastal areas (IPCC 2019). However, Beaulieu et al. (2011) demonstrated that rivers alone represent up to 10% of the anthropogenic N\textsubscript{2}O emissions, which could indicate an underestimation of the values presented by the IPCC (2015). Seitzinger & Kroeze (1998) suggest that 1% of the anthropic nitrogen (N) input is transferred directly from rivers to the atmosphere in the form of N\textsubscript{2}O, which would represent a global anthropic contribution of 0.94 Tg N year\textsuperscript{-1}, higher than the value estimated by Beaulieu et al. (2011) and IPCC (2015).

Recently, in a report published in 2019, the IPCC adjusted the N\textsubscript{2}O emission factor (EF) from rivers to 0.26% (IPCC 2019). However, the study performed by Zhang et al. (2020), who evaluated N\textsubscript{2}O EFs for different rivers draining contrasting landscapes characterized as forested, agricultural field and urban sector areas, demonstrated a wide variation in N\textsubscript{2}O EFs (i.e., 0.066–0.95%). Additionally, the EFs for estimating N\textsubscript{2}O emissions from rivers vary by one order of magnitude (i.e., 0.26–2.5%) (Seitzinger & Kroeze 1998; Beaulieu et al. 2011; Syakila & Kroeze 2011; IPCC 2019). Therefore, due to the wide variety of N\textsubscript{2}O emission rate estimates reported in the literature, the adoption of different N\textsubscript{2}O EFs for lotic water bodies taking into account the drainage of the different watershed landscapes is paramount.

Recent studies have contributed to a greater elucidation of N compound cycling mechanisms in natural aquatic environments (Quick et al. 2019). However, the control factors and the effective contribution of anthropic N\textsubscript{2}O emissions from water bodies (rivers, streams, etc.) enriched with N (untreated or insufficiently treated wastewater discharge) are still not understood, with different interpretations among the few studies reported in the literature (Cébron et al. 2005; Garnier et al. 2009; Rosamond et al. 2012; Burgos et al. 2015; Zhang et al. 2020). In Brazil, only one study on the N\textsubscript{2}O fluxes from a river polluted by urban untreated wastewater discharge is available (Alvim et al. 2014). Alvim et al. (2014) reported an average transfer rate of N\textsubscript{2}O to the atmosphere of 0.62 kg N day\textsuperscript{-1}, positively correlated with ammonium (NH\textsubscript{4}) concentrations.

In this context, the present study aimed to evaluate the effects of reactive N inputs due to the discharge of untreated or insufficiently treated wastewater on the spatial and temporal variability of N\textsubscript{2}O emissions from different streams located in the Ilha Grande hydrographic unit, in southeastern Brazil. It is the first time that these measurements have been released in this area of Brazil.

MATERIAL AND METHODS

Study area

Ilha Grande (193 km\textsuperscript{2}) is located in the municipality of Angra dos Reis, on the southwest coast of the State of Rio de Janeiro, Brazil (Figure 1(a) and 1(b)). It is part of the Atlantic Forest biome covering the Serra do Mar, with a predominant vegetation type of Dense Ombrophilous Forest (INEA 2013). The population comprises approximately 7,000 inhabitants (IBGE 2010), and the region displays a tropical climate (warm and humid) characterized by mean annual temperatures exhibiting little variation (between 20 and 26 °C), with July the coldest (20.2 °C) and February the warmest (26.4 °C) months. The mean annual rainfall is of approximately 2,200 mm, with rainfall predominating during the summer (INEA 2013).

The Abraão district is the main population center of Ilha Grande, with a population of about 4,773 inhabitants (INEA 2015), although this may increase significantly during the holiday and vacation periods, as this is the main gateway for tourists visiting Ilha Grande (Figure 1(c)). Abraão has a wastewater collection network connected to a wastewater treatment plant (WWTP), with an anaerobic system...
(upflow anaerobic sludge blanket reactor) leading to effluent discharge to the sea via a short submarine outfall (INEA 2015). However, there are still residences with their wastewater linked to individual solutions (septic tanks) whose maintenance is often performed precariously (INEA 2015).

**Sampling and analysis**

The present study consisted of the collection of liquid and gas samples from different sampling sites distributed along the courses of the lotic water bodies that are part of the Eastern Ilha Grande hydrographic unit (Figure 2(a)). Four streams were studied and located within the Abraão hydrographic system (HS) (Abraão stream, Bicão stream, tributary stream and an unnamed stream). The sampling sites in these four streams were separated according to their urbanization influence, characterized as upstream of the urbanized stretch (R1P3, R1P4, R1P5, R2P5, R2P6, T2P1, R3P4, R3P5) and within the highly urbanized stretch (R1P1, R1P2, R2P1, R2P2, R2P3, R2P4, R3P1, R3P2, R3P3) (Figure 2(b)). Moreover, the sampling sites within the highly urbanized stretch are the ones near the coast.

Three intensive sampling campaigns were carried out in order to cover the spatial and temporal variability of N$_2$O fluxes from the four Abraão streams (Figure 2). Each campaign comprised a specific goal in order to better understand the control factors and the effective contribution of N$_2$O emissions from N-enriched streams (due to the input of untreated or insufficiently treated wastewater). The sample details alongside the sampling strategies and parameters evaluated in each study period are presented in Table 1.

N$_2$O gas was directly collected at the water–atmosphere interface using a static chamber technique similar to that used by Beaulieu et al. (2010) and Alvim et al. (2014). This technique consists of using a cylindrical floating PVC (polyvinyl chloride) chamber (diameter = 30 cm; height = 15 cm). Immediately after placing the floating chamber, an atmospheric air sample (outside the chamber) was collected through a plastic syringe (ca. 20 mL). The headspace samples in the floating chamber were collected every 5 – 10 minutes (equal time intervals), totaling 20 – 40 minutes, depending on the sampling site.

Gas samples were stored in glass storage vials previously filled with saturated sodium chloride (NaCl) and capped with rubber stoppers and aluminum seals. During the sampling, the gas samples were transferred into the glass storage vials positioned upside-down to allow the escape of the saturated NaCl solution through another needle while the 20 mL gas sample was injected. Thus, the gas sample constituted the headspace in the glass storage vial. The methodology adopted for the gas sample storage is similar to that applied by Bastviken et al. (2010).

In the laboratory, N$_2$O concentration in the headspace was determined by gas chromatography (Shimadzu GC-2014) equipped with a 1 mL injection loop, a packed Porapak Q column and electron capture detector (ECD).
Column oven temperature was set at 80 °C and N₂ (99.999%) was used as a carrier gas and 5% CH₄–argon as a make-up gas for the ECD. Certified N₂O (290, 1,010 and 4,988 ppb) standards (White Martins) were used for calibration. Analytical precision was ±1%.

After determining the N₂O concentrations in headspace and atmospheric air, their respective fluxes (F) were calculated, as follows:

\[ F = h \times \frac{dC}{dt}_{t=0} \]  

where \( h \) represents the height between the liquid surface and the inner of the floating chamber and \( \frac{dC}{dt}_{t=0} \) is the change of N₂O concentration as a function of time at \( t = 0 \). The limit of quantification for the floating chamber technique was 0.05 μg N m⁻² h⁻¹.

In situ dissolved oxygen (DO) concentrations, pH and oxidation-reduction potential (ORP) were obtained for each sampling site using a multiparameter portable meter (Yellow Springs, Professional Plus). In addition, in situ water flow measurements for the streams, following the methodology described by Hindi et al. (1998), were also taken.
Liquid samples for the determination of chemical oxygen demand (COD), total Kjeldahl N (TKN), ammoniacal-N (NH₃), nitrite (NO₂⁻) and nitrate (NO₃⁻) were collected, filtered through 0.47 mm cellulose acetate membrane filters, and stored frozen until their analyses. All methodologies used for the chemical analysis of the liquid samples followed APHA (2012) procedures. COD concentration determinations were performed using the closed reflux colorimetric method (high and low range). TKN was determined by macro Kjeldahl digestion followed by a distillation step and the application of the titrimetric method. NH₃ was determined by a preliminary distillation step and the application of the titrimetric method for concentrations above 5 mg N L⁻¹. Below 5 mg N L⁻¹, NH₃ was determined colorimetrically at 425 nm after nesslerization. NO₂⁻ was determined colorimetrically by the Griess reaction at 540 nm. NO₃⁻ was determined after reduction in a Cd-Cu column to NO₂⁻. The analytical precisions for the analyses, performed in triplicate, were ±5%.

RESULTS AND DISCUSSION

Spatial and temporal variability of N₂O emissions: upstream and in the highly urbanized stretches

Figure 3(a) and 3(b) indicate the N₂O flux variations and DO concentrations along the Abraão and Bicão streams, respectively, for the samplings carried out on May 22 and 23, 2017. In the Abraão stream, the three sampling sites upstream of the urbanized stretch (R1P5, R1P4 and R1P3) were characterized by DO values ranging from 7.5 to 7.9 mg L⁻¹, and close to the saturation value (8.2 mg L⁻¹) adjusted by control variables (temperature, altitude and salinity), characterizing the respective sampling sites in areas exhibiting low anthropic influence. The same interpretation is valid for the first two sampling sites of the Bicão stream (R2P6 and R2P5), where the DO ranged from 7.7 to 8.9 mg L⁻¹, with slightly higher values due to the stretch displaying greater turbulence upstream of the first two sampling sites.

N₂O fluxes determined in the Abraão and Bicão streams and upstream of the urbanized stretch ranged from 18.4 to 33.5 μg N m⁻² h⁻¹ and 20.6 to 23.0 μg N m⁻² h⁻¹, respectively. In the urbanized stretch, a sharp drop in DO concentrations was observed, accompanied by an increase in N₂O fluxes (Figure 3(a) and 3(b)). The average N₂O fluxes in the highly urbanized stretch of the Abraão and Bicão streams were 165 and 242 μg N m⁻² h⁻¹, respectively. The N₂O fluxes of the urbanized stretch at the Abraão and Bicão streams were 7- and 11-fold higher than those in the upstream stretch, respectively. These values represent a considerable increase in the amount of N emitted as N₂O, possibly correlated to a greater input of reduced N load (organic and ammoniacal-N), since an abrupt consumption of DO was noted. Hu et al. (2018) reported that the N₂O fluxes of sewage draining rivers in four seasons were 1.1–3.1-fold higher than those in the natural rivers, with DO considered to be one of the main control factors.

Figure 4 displays the variation of N₂O fluxes, DO concentrations and N loads of different forms (NH₃-N-org, NO₂⁻ and NO₃⁻) for each sampling site along the Abraão and Bicão streams and the unnamed stream, for the samplings carried out on October 21, 22 and 23, 2017. As previously noted in May 2017, where an average N₂O flux of 165 μg N m⁻² h⁻¹ was observed within the highly urbanized stretch (Figure 3(a)), during October 2017, the Abraão stream displayed the highest N₂O fluxes in the same area (468 and 561 μg N m⁻² h⁻¹) (Figure 4(a)), although with significantly higher N₂O emissions.
when compared to the previous sampling, with an average N2O flux in the order of 2- to 4-fold higher in the same stretch. The differences observed in N2O emissions can be associated with the higher concentrations of reduced N forms measured during the October sampling, possibly correlated with the greater number of tourists. Zhang et al. (2020) demonstrated that the highest N2O EF was determined for rivers that drain urbanized landscapes (0.95%), correlated with the highest availability of reduced N forms.

The highest N2O fluxes in the urbanized stretch are associated with the untreated wastewater discharge, as observed in Figure 4(b), which exhibits a substantial input of organic N. The discharge of untreated urban wastewater (and a high input of N-rich organic material), with decreased DO concentrations below 1.0 mg O2 L⁻¹, led to the N fraction emitted as N2O being approximately 5-fold higher than the average value in the upstream stretch (Figure 4(b)). Rosamond et al. (2012) reported that N2O emissions were disproportionately high in urban areas influenced by WWTPs, with the highest measured N2O flux (4,859 μg N m⁻² h⁻¹) detected downstream of a WWTP releasing NH₄ to a river site characterized by hypoxia (DO < 2 mg O2 L⁻¹).

Overall, nitrification seems to be the major process responsible for the highest N2O emissions in the urbanized stretch of the Abraão stream. This can be explained by the recovery trend of DO concentrations, with consequent reduction in the organic N coupled with a significant increase in the oxidized N fraction, with NO₃ predominating. Burgos et al. (2015) reported that the N₂O fluxes from coastal rivers influenced by urban and agricultural discharge are a consequence of anthropic inputs, correlated with apparent oxygen utilization assumed by nitrification.

An N load transferred to the atmosphere of N₂O of 0.011 ± 0.008 kg N day⁻¹ was estimated, which represents 0.07% of the total dissolved N (TDN) load transferred from the Abraão stream to the sea (15.9 kg N day⁻¹), considering a sampling length of 761 m (from R1P1 to R1P5) and an average width of approximately 2 m.

As observed in Figure 4(c), the Bicão stream presented similar behavior to the Abraão stream, with higher N2O fluxes within the highly urbanized stretch (110 to 780 μg N m⁻² h⁻¹). On the other hand, the total N load determined for the Bicão stream displayed significant increases along the urbanized stretch (Figure 4(d)), indicative of multiple N inputs in different stream locations.

Nitrification appears to be the dominant process in increasing N₂O emissions in the R2P4–R2P3 stretch of the Bicão stream, which displayed a decrease in DO concentrations with increasing NO₃ loads (Figure 4(c) and 4(d)). In addition, a sudden increase in N₂O fluxes was noted when DO concentrations reached levels of approximately 1.0 mg O₂ L⁻¹, as observed for the Abraão stream (Figure 4(a) and 4(b)). This contrasts with what was observed during the
previous sampling (May 2017; Figure 3) for both streams, where DO concentrations remained above 2 mg O₂ L⁻¹ and N₂O emissions did not increase sharply compared with the October 2017 data. Therefore, the differences observed in the magnitude of N₂O emissions between sampling campaigns (May and October 2017) can be associated with higher loads of total N, as previously reported, thus favoring a higher consumption of DO. Cébron et al. (2005) demonstrated that N₂O emissions increase when DO concentrations are limited (i.e. 1.2 mg O₂ L⁻¹) in a study carried out with nitrifying bacterial cultures from Seine river water (in both batch and continuous flow experiments).

However, a reduced nitrification rate from the R2P2 sampling site (559 m distance from the most upstream sampling) was noted due to DO limitations, favoring denitrification in this stretch (R2P2). According to Seitzinger & Kroeze (1998), denitrification requires DO concentrations in freshwater to be less than about 0.2 mg O₂ L⁻¹, slightly close to DO concentrations (DO < 0.6 mg O₂ L⁻¹ and ORP < -86 mV) in the R2P3–R2P1 stretch of the Bicão stream. Additionally, a reduction of NOₓ (NO₂⁻ + NO₃⁻) loads (from 0.32 to 0.01 kg N h⁻¹) was observed downstream of the R2P5 site, reaching values close to those of the initial sampling sites (upstream of the urbanized stretch), although with substantially higher N₂O fluxes (Figure 4(c) and 4(d)).

Therefore, increased TKN loading availability from untreated wastewater discharge increased the DO consumption rate by the nitrification process. However, when the DO concentration reached up to 0.5 mg O₂ L⁻¹, the denitrification process was observed as a replacement for nitrification as the dominant process in N₂O emissions. The average N₂O fluxes associated with the nitrification and denitrification processes were 319 and 601 μg N m⁻² h⁻¹ (within the urbanized stretch), respectively, indicating a greater contribution of the N emitted to the atmosphere by the denitrification process.

An N load transferred to the atmosphere of N₂O of 0.019 ± 0.013 kg N day⁻¹ was estimated, representing 0.08% of the TDN load transferred from the Bicão stream to the sea (22.8 kg N day⁻¹), considering a sampling length of 713 m (from R2P1 to R2P6), an average width of approximately 3 m and an estimated N load transferred from the tributary stream to the Bicão stream of 8.3 kg N day⁻¹.

The unnamed stream among the studied lotic water bodies presented lower N₂O fluxes (207 to 258 μg N m⁻² h⁻¹) and higher DO concentrations (0.7 to 6.3 mg O₂ L⁻¹) in the urbanized stretch (Figure 4(e) and 4(f)). Lower N₂O emissions are associated with lower N load inputs into the stream channel (Figure 4(f)). The lowest DO concentration (0.7 mg O₂ L⁻¹) was determined in the final stretch of the stream (R3P1), possibly associated with a small contribution of untreated wastewater from the urbanized stretch. Performing the same calculations for the Abraão and Bicão streams, an estimated N load transferred to the atmosphere of N₂O of 0.005 ± 0.001 kg N day⁻¹ was obtained, representing 0.09% of the TDN load transferred from the unnamed stream to the sea (5.7 kg N day⁻¹), considering a sampling length of 541 m (from R3P1 to R3P5) and an average width of approximately 2 m.

Assuming that DO saturation levels suggest a negligible anthropic N input upstream of the urbanized stretch of the studied streams (Abraão, Bicão, tributary and unnamed), the N load contribution from the discharge of untreated wastewater into water bodies within the urbanized stretch was estimated. Thus, the N load associated with untreated wastewater discharge is the difference between the sums of the total N load transferred to the sea and the total N load upstream of the urbanized stretch. Table 2 displays the total and anthropic N load data for each studied stream and the average N₂O EFs related to the total and anthropic N loads. The anthropic N contribution represented approximately 70% of the total N load of the receiving water bodies during the study period (October 2017). However, the N₂O EF based on the anthropic N load determined in the present study (0.11%) was approximately one order of magnitude lower.

<table>
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<th>Stream</th>
<th>Total N load (kg N d⁻¹)</th>
<th>Anthropic N load (kg N d⁻¹)</th>
<th>N₂O EF (kg N₂O/kg total N load)</th>
<th>N₂O EF (kg N₂O/kg anthropic N load)</th>
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</thead>
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<tr>
<td>Abraão stream</td>
<td>15.9</td>
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<td>0.08</td>
<td>0.11</td>
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<tr>
<td>Bicão stream</td>
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<td>19.4</td>
<td>0.08</td>
<td>0.11</td>
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<tr>
<td>Unnamed stream</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>44.4</td>
<td>30.7</td>
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<td></td>
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</tbody>
</table>

Table 2: Total and anthropic N loads for each Abraão HS stream and the average N₂O EFs relative to their respective N loads (total and anthropic)
lower than the EF proposed by Seitzinger & Kroeze (1998), which represents 1% of the anthropic input of N to lotic water bodies. Additionally, the N₂O EF based on the total N load (0.08%) was lower than the range reported by different studies around the world (0.26–2.5%) (Seitzinger & Kroeze 1998; Beaulieu et al. 2011; Syakila & Kroeze 2011; IPCC 2019).

It is estimated that approximately 3,800 people have their wastewater discharged directly to the receiving water bodies, considering the total anthropic input of N (30.7 kg N day⁻¹) and a per capita contribution of 8 g N day⁻¹ (von Sperling 2005). This estimate represents 80% of the permanent population of Abraão (4,374 inhabitants). In addition, the estimated value may also include an input of wastewater from the collection network, due to operational problems. However, the anthropic N load released to the water bodies is significant regardless of source (direct or indirect), impacting not only water quality but also the atmosphere, with significant increases in N₂O emissions.

Diurnal N₂O variation within the urban area of the Bicão stream

Figure 5 displays the variation of N₂O fluxes and concentrations of DO, COD, TKN and NOₓ (NO₂⁻ + NO₃⁻) at the R2P2 point of the Bicão stream during a sampling period of 11 hours (12:30 to 23:30; May 2018). The R2P2 sampling site was chosen for the temporal evaluation of N₂O fluxes, due to the high input of reduced N (NH₃ and N-org) compared to the other sites, as indicated previously (Figure 4). Figure 5(a) exhibits a high variability of N₂O fluxes throughout the sampling period, ranging from 133 to 2,229 μg N m⁻² h⁻¹. Three well-defined N₂O peaks were noted, with maximum fluxes of 1,099, 1,680 and 2,229 μg N m⁻² h⁻¹. These N₂O peaks caused a 3-fold increase in the average N₂O flux for the sampling period (May 2018). Comparatively, the average and maximum N₂O fluxes were 4- and 10-fold higher, respectively, than the N₂O flux of the previous year and in the same sampling month (May 2017), although determined in the

Figure 5 | Variation in N₂O fluxes (black diamond) in relation to (a) DO (white square), (b) COD (gray square), (c) TKN (gray circle) and (d) NOₓ (NO₂⁻ + NO₃⁻) concentrations at point R2P2 at Bicão stream from 12:30 to 23:30.
morning. According to Quick et al. (2019) the estimated N₂O fluxes in rivers or streams during the day are likely underestimated, particularly if large shifts in temperature, DO and pH are observed in the assessed water bodies on a daily basis.

In addition, DO concentrations were higher in the early afternoon (close to 3.0 mg O₂ L⁻¹), displaying a decreasing trend throughout the day, reaching levels below 1.0 mg O₂ L⁻¹ at 14:30 and remaining low (ranging between 0.5 and 0.8 mg O₂ L⁻¹) until the end of the night (Figure 5(a)). Rosamond et al. (2012) suggested that N₂O emissions are more variable in rivers with high daily DO fluctuations, where daily N₂O fluxes can vary by over a factor of 10 at the same site. Our study indicated daily N₂O fluxes varying by a magnitude of 17 times at the same site. In addition, Venkiteswaran et al. (2014) reported that higher N₂O fluxes from rivers in urban areas are characterized by low DO concentrations.

Figure 5(b) and 5(c) display three well-defined COD and TKN peaks at the same times as the N₂O peaks reported previously. Furthermore, an interval of 3 hours between the COD and TKN peaks was noted, leading to increased oxygen consumption rates and, consequently, low DO concentrations throughout the day. The COD and TKN peaks are probably a consequence of higher discharge periods of untreated wastewater into the Bicão stream. These results corroborate our previous observations carried out during the other sampling period for this same site (R2P2) (Figure 4(d)), in which increased TKN availability led to higher N₂O fluxes. Marwick et al. (2014) indicated that the release of untreated wastewater from the city of Nairobi had an impact on DO availability (low levels) of the upper Athi River, due to rapid NH₄ removal accompanied by the downstream production of NO₃ and N₂O. In addition, McMahon & Dennehy (1999) determined high median N₂O emission rates (192 to 1,358 μg N m⁻² h⁻¹) in the South Platte River due to NH₄ inputs from Denver’s largest WWTP. This is similar to that reported herein, ranging from 133 to 2,229 μg N m⁻² h⁻¹ with the highest N₂O fluxes correlated to higher TKN input.

Figure 5(d) indicates that the TKN peaks from the discharge of untreated wastewater were followed by oxidized nitrogen fraction (NOₓ = NO₂ + NO₃) peaks. This is a consequence of nitrification process intensification, resulting in a distinct relationship between high NOₓ concentrations and high N₂O fluxes. Baulch et al. (2011) observed that the sum of NO₂ + NO₃ was a significant predictor of N₂O emissions due to correlations with mean daily fluxes from 10 streams located north and northeast of Toronto, Canada.

CONCLUSIONS

The effects of untreated or insufficiently treated wastewater discharge on the spatial and temporal variability of N₂O were assessed in different streams at Ilha Grande (Abraão HS) and the major conclusions are as follows.

- Untreated or insufficiently treated wastewater discharge is greatly perturbing N cycling in streams, with significant spatial and temporal N₂O emission variation on all streams studied.
- There is high spatial variability of N₂O fluxes for all streams studied, with the highest N₂O emissions in urban areas characterized by input from untreated wastewater or insufficiently treated wastewater discharge.
- Diurnal N₂O variation was significant within the urban areas of the streams characterized by increased organic and ammoniacal-N input.
- Higher N₂O fluxes were observed under limited DO conditions and likely due to organic matter oxidation and nitrification. In addition, denitrification may have contributed to increased N₂O emissions. However, further investigations should be carried out to identify the contribution of the different processes.
- N₂O EFs based on anthropic N and total N loads were 0.11 and 0.08%, respectively.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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