Discussion about Cause of Nitrous Oxide (N$_2$O) Emission in Wastewater Treatment Plant, Based on Long-Term Continuous Measurement

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ABSTRACT

The Bureau of Sewerage, Tokyo Metropolitan Government, has been implementing various measures to reduce greenhouse gas (GHG) emissions. However, measures to reduce Nitrous Oxide (N$_2$O) emission from wastewater treatment, which amounts to about 16% of the GHG emission from the Bureau, has been delayed since little is known about its behaviors and factors which affect its emission.

The Bureau installed continuous N$_2$O analyzer in a wastewater treatment plant (WWTP), and conducted continuous measurement of N$_2$O emission for one year. The results showed that N$_2$O emission fluctuated significantly and was affected by nitrogen load of influent and nitrification condition in reaction tank.

KEYWORDS : Green House Gas, Nitrous Oxide, Continuous Measurement, Wastewater treatment, Nitrite

INTRODUCTION

In recent low carbon society, not only water quality improvement, but also GHG reduction has become essential for WWTP. WWTP emits GHGs such as Carbon Dioxide (CO$_2$) due to electricity consumption and N$_2$O, which has 310-fold-stronger greenhouse effect than CO$_2$, from wastewater treatment and sludge incineration. The Bureau of Sewerage, Tokyo Metropolitan Government, has initiated proactive set of measures for reducing GHG emissions, calling it “Earth Plan 2010”. The Bureau has so far implemented GHG countermeasures by reducing electricity consumption and lowering the amount of N$_2$O generated by sludge incineration. However, only little progress has been made to suppress the emission of N$_2$O from wastewater treatment. Thus, reduction of N$_2$O from wastewater treatment will be important for further reduction of GHGs.

N$_2$O is a byproduct in both nitrification and denitrification process, and released into atmosphere by aeration of reaction tank. Nitrite (Zheng et al. 1994), sludge retention time (SRT) (Mizuochi et al. 1999), and dissolved oxygen (DO) (Tallec et al. 2006) have been reported as factors to affect N$_2$O generation in laboratory-scale experiment. In addition, the Bureau reported in WEFTEC2010 that N$_2$O generates in aeration tank and nitrite accumulation during nitrification process caused an increase of N$_2$O emission, in experimental water processing plant. However, there is a lack of knowledge regarding behavior of N$_2$O emission from full-scale WWTPs and detailed factor of its emission based on long-term monitoring and these data are required to advance measures to reduce N$_2$O from wastewater treatment.
Hence we set continuous N\textsubscript{2}O analyzers in the WWTP in March, 2011 and have measured N\textsubscript{2}O emissions. Here we report;
1. Fluctuation of N\textsubscript{2}O emissions based on one year measurement and its relation with influent and effluent water quality.
2. Relation of N\textsubscript{2}O emissions and nitrogen treatment status in each zone of biological reactor, to identify key factors that are correlated with N\textsubscript{2}O emission.
3. Relation of nitrite concentration and N\textsubscript{2}O gas concentration based on continuous measurement.

The Countermeasures against GHG Emission in Japan and Tokyo Metropolitan Government and the Role of Sewage Works
In Japan, “the Act on Promotion of Global Warming Countermeasures” obliges big enterprises which use energy more than 1,500 kL equivalent of petroleum per year to estimate and report the amount of GHG emission annually since April 2006. Emission factors to estimate the emissions are shown in the related regulations of the Act. Emission factors of methane (CH\textsubscript{4}) and N\textsubscript{2}O from wastewater treatment and N\textsubscript{2}O from sludge incineration are the characteristic factors in wastewater field. For example, the emission factor of N\textsubscript{2}O from wastewater treatment is 0.00016 kg of N\textsubscript{2}O emission per 1 m\textsuperscript{3} of wastewater treatment. Although each emitter is allowed to use its actual measured volume instead of the emission factors, almost all of emitters estimate their emission volumes by the emission factors since it is difficult to measure emission volumes of N\textsubscript{2}O and CH\textsubscript{4} in exhaust gas continuously.

These emission factors are specific in Japan and are different from the values shown in such as “2006 IPCC Guidelines for National Greenhouse Gas Inventories” (IPCC, 2006) that is commonly used to estimate official GHG emission. Each specific factor was determined according to the average data sampled from around 1990 to around 2000 in several WWTPs in Japan. For example, the emission factor of N\textsubscript{2}O from wastewater treatment was calculated as the averaged value among eight data from three investigations (Ministry of the Environment Government of Japan, 2006).

The emission factor of N\textsubscript{2}O on wastewater treatment (0.00016 [kg-N\textsubscript{2}O/m\textsuperscript{3}]) can be converted to approximately 30 [g-N\textsubscript{2}O/person/year] using population and actual amount of wastewater treatment in Tokyo’s 23 wards area. This value is larger than 3.2 [g-N\textsubscript{2}O/person/year] in IPCC guideline without intensive nitrification and denitrification and 7 [g-N\textsubscript{2}O/person/year] used in the U.S. with intensive nitrification and denitrification (USEPA, 2012). Since wide range of emission factors (0.28-140 [g-N\textsubscript{2}O/person/year]) and significant temporal variability on various WWTPs were also shown in recent investigation held in the U.S. (Chandran, 2010), emission factor in Japan is not thought to be quite larger than actual emission factor or emission factors in IPCC guideline and in the U.S.

While the Act in Japan obliges the big enterprises to only report estimation of GHG emission, Tokyo Metropolitan Government, a local government with the largest population in Japan, introduces a regulation demanding reduction of GHG emission as obligation. The targets of this obligation are big enterprises which use energy more than 1,500 kL equivalent of petroleum per year. WWTPs and other industries have to reduce more than 6% of the average emission from FY 2010 to FY 2014 in comparison with the average emission of any continuous three years from FY 2002 to FY 2007. All of 13 WWTPs and three of 83 pumping stations which are managed by Bureau of Sewerage, Tokyo Metropolitan Government in Tokyo’s 23 wards are obligatory to reduce GHG emission.
The target GHG to be reduced in this regulation is only CO₂. However, if an enterprise is able to reduce other GHGs emission intentionally, the half of reduced amount of the GHGs (carbon conversion) is counted as the reduced amount of CO₂. As shown in the circle chart below (Figure 1), the proportion of N₂O is rather large on wastewater and sludge treatment and therefore capacity to be reduced is huge. To count the reduction amount of N₂O by this regulation, we need to reveal that actual emission factor is smaller than the defined value in the Act through continuous monitoring of N₂O on actual WWTPs.

![Diagram of GHG emission](image)

**Figure 1 Inventory of GHG emission on Bureau of Sewerage, Tokyo Metropolitan Government (FY2010)**

**METHODOLOGY**

1 **Long Term Continuous N₂O Measurement**
1.1 **Outline of the Wastewater Treatment Plant**

The outline of the WWTP which we installed continuous N₂O analyzers (WWTP-A) is shown in Table 1.

<table>
<thead>
<tr>
<th>Treatment capacity</th>
<th>Removal system</th>
<th>Treatment trains</th>
<th>Treatment method</th>
<th>Sewage volumes (Fiscal 2011)</th>
</tr>
</thead>
<tbody>
<tr>
<td>598,000 m³/day</td>
<td>Combined sewer system</td>
<td>Train 1</td>
<td>Conventional activated sludge process</td>
<td>116,000 m³/ day</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Train 2</td>
<td>Conventional activated sludge process</td>
<td>249,000 m³/ day</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Train 3</td>
<td>Step feed A²/O method</td>
<td>52,000 m³/ day</td>
</tr>
</tbody>
</table>

Continuous N₂O analyzers (METAWATER: ZSU-4) were set at air duct to deodorization equipments in WWTP-A. Amounts of N₂O emission from total plant and each treatment trains were measured every half-hour from April 2011 to March 2012.
1.2 Measurement Items Used to Analyze the Cause of N$_2$O Emission
At WWTPs in Tokyo, water quality tests are conducted at 10 a.m. on weekdays for daily operation and maintenance of the plant. Measurement items shown in Table 2 were used to analyze the cause of N$_2$O emission. Data of treated wastewater volume, supplied air flow, and rainfall were also used for the analysis.

### Table 2. Measurement Items Used to Analyze the Cause of N$_2$O Emission

<table>
<thead>
<tr>
<th>Samples</th>
<th>Measurement Items</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Effluent</td>
<td>Ammonium-nitrogen (NH$_4$-N), (Chemical oxygen demand) COD, Water temperature</td>
</tr>
<tr>
<td>End of Biological Reactor</td>
<td>NH$_4$-N, Nitrite-nitrogen (NO$_2$-N), Nitrate-nitrogen (NO$_3$-N), DO, Mixed liquor suspended solids (MLSS)</td>
</tr>
<tr>
<td>Treated Wastewater</td>
<td>NH$_4$-N, NO$_2$-N, NO$_3$-N, COD</td>
</tr>
</tbody>
</table>

2 Relations of Nitrification Status and N$_2$O Emissions in Each Part of Reactor
Two Biological reactors (one from Train 1 and the other from Train 2 of WWTP-A) with different nitrification status were selected and N$_2$O concentrations in off-gas from 4 parts of the reactors were measured continuously for two days (14$^{th}$ to 15$^{th}$ of September, 2011) (Figure 2). Multi-gas analyzer (HORIBA: VA-3012) was used for measurement of N$_2$O. Activated sludge of each part was sampled at 9:00 a.m., 12:00 p.m., and 3:00 p.m. on September 14$^{th}$ and 9:00 a.m., and 12:00 p.m. on September 15$^{th}$ to measure NH$_4$-N, NO$_2$-N, and NO$_3$-N by ion chromatography analysis (DIONEX: ICS-1000). NH$_4$-N and COD of the primary effluent were also measured. Relations of these measurement items and N$_2$O emissions were analyzed.

In addition, same survey was conducted at a biological reactor of another WWTP (WWTP-B), which was expected that N$_2$O emission was low since the center always shows good nitrification, on 24$^{th}$ to 25$^{th}$ of October, 2011. Since biological reactors of WWTP-B are operated by Anaerobic-oxic activated sludge process, we selected 4 parts of aerobic tank to measure N$_2$O emission (Figure 3). Activated sludge of each part was sampled at 9:00 a.m., 12:00 p.m., and 3:00 p.m. on October 24$^{th}$ and 9:00 a.m., and 12:00 p.m. on October 25$^{th}$ to measure NH$_4$-N, NO$_2$-N, and NO$_3$-N by ion chromatography analysis (DIONEX: ICS-1000). NH$_4$-N and COD of the primary effluent were also measured.
3 Continuous Measurements of N$_2$O and NO$_2$-N Concentration in Biological Reactor

UV-vis spectrometer (S::can: Spectro::lyzer™, hereafter NO$_2$-N analyzer) was set in the final zone of a biological reactor of another WWTP (WWTP-C). NO$_2$-N concentration of the activated sludge was continuously measured as well as N$_2$O concentration (HORIBA: VA-3012) at the site.
RESULTS AND DISCUSSION

1 Long Term Continuous N₂O Measurement

Daily N₂O emission from WWTP-A from April 2011 to March 2012 is shown in Figure 5. The data shows that N₂O emission fluctuates widely. It can also be seen that N₂O emission declines after heavy rainfall, which is considered to be due to decrease in ammonia load of primary effluent.

Figure 5. Total N₂O Emission Amount from WWTP-A

To analyze the cause of the fluctuation, we selected Train 1 as a representative and analyzed the relations between N₂O emission and measurement items shown in Table 2, wastewater volume and supplied air flow. No clear interrelations were shown between N₂O emission and wastewater volume, supplied air flow, COD, DO, or MLSS (Data not shown).

Since several reports show that N₂O emissions are affected by nitrification status and N₂O emission amount increases when nitrite remains in the reactor (Miyamoto et al. 2002, and Miyamoto et al. 2010), we analyzed the relation between NO₂-N concentration of the effluent and N₂O emission. To evaluate residual level of nitrite, we defined “Nitrite rate (%)” as shown in following equation.

\[
\text{Nitrite rate (%) = \left\{ \frac{\text{NO}_2-N_{\text{effluent}}}{\text{NH}_4-N_{\text{effluent}} + \text{NO}_2-N_{\text{effluent}} + \text{NO}_3-N_{\text{effluent}}} \right\} \times 100}
\]

Annual N₂O emission and Nitrite rate are shown in Figure 6. Characteristically in dotted circle, Nitrite rate was also high when N₂O emission was high. This long term measurement result indicates that residual level of nitrite greatly affects N₂O emissions in full-scale plant. Thus, we conducted following surveys to analyze further details of the relation between N₂O emissions and nitrite in the reactor.
2 Relations of Nitrification Status and $N_2O$ Emissions in Each Part of Reactor

$N_2O$ emissions and $NH_4-N$, $NO_2-N$, and $NO_3-N$ concentrations of each zone in Train 1 and 2 of WWTP A are shown in Figure 7. Average values of 5 data (9:00 a.m., 12:00 p.m., and 3:00 p.m. on September 14th and 9:00 a.m., and 12:00 p.m. on September 15th) were used since measured data at each time showed similar tendency. In Train 1, accumulation of nitrite was seen after zone B, and $N_2O$ emissions were relatively high. Meanwhile, in Train 2, relatively high amount of ammonia remained while $NO_2-N$ concentrations were very low, and $N_2O$ emissions were lower than Train 1. In Train 1, $N_2O$ emission was the largest at zone C, while it continued to rise until the final zone in Train 2. The differences of these trains were that, nitrification rate (5.6 mg/L/hour) was higher and residual ammonia was relatively low in Train 1, while nitrification rate (4.7 mg/L/hour) was lower and higher amount of ammonia remained in Train 2.

Figure 7. Concentrations of Nitrogen Components in Each Zone of Reactors of Train 1 (Ⅰ) and Train 2 (Ⅱ) in WWTP-A and $N_2O$ Emissions from its Off-gas.
Correlations between concentrations of NO$_2$-N and NO$_3$-N in each zone of reactors and N$_2$O emissions from the same place at 9:00 a.m., 12:00 p.m., and 3:00 p.m. on September 14$^{th}$ and 9:00 a.m., and 12:00 p.m. on September 15$^{th}$ are shown in Figure 8. In Train 1, relatively high correlation with N$_2$O was seen for both NO$_2$-N and NO$_3$-N which shows that N$_2$O emits as nitrification proceeds. In Train 2, relatively high correlation with N$_2$O was only seen for NO$_3$-N, while scarce correlation was seen for NO$_2$-N since NO$_2$-N concentration was very low.

Same survey was conducted at a biological reactor of WWTP-B, which was expected that N$_2$O emission is low since the center always shows good nitrification. As seen in Figure 9, nitrification progressed quickly at the latter part of the reactor with no N$_2$O emission.

Figure 8. Correlations between N$_2$O Emissions and NO$_2$-N/NO$_3$-N Concentrations in Train 1 and Train 2 of WWTP-A

Figure 9. Concentrations of Nitrogen Components in Each Zone of a Reactor in WWTP-B and N$_2$O Emissions from its Off-gas.
These results of two WWTPs suggest that N\textsubscript{2}O emits as nitrification proceeds when nitrification status is insufficient, as seen in the results of WWTP-A. It showed especially large emission when nitrite accumulated and there was a correlation between N\textsubscript{2}O emission and NO\textsubscript{2}-N concentration in that case as seen in Train1. In addition, there was no N\textsubscript{2}O emission from a reactor of WWTP-B, which showed ideal complete-nitrification status. These results show that the control of nitrification is a key to reduce N\textsubscript{2}O emissions.

3 Continuous Measurements of N\textsubscript{2}O and NO\textsubscript{2}-N Concentration in Biological Reactor

N\textsubscript{2}O and NO\textsubscript{2}-N concentrations were continuously measured for 10 days (From August 22 to 31, 2011) and data of both analyzers was extracted every 3 hours to analyze the correlation of N\textsubscript{2}O and NO\textsubscript{2}-N. There was a relatively high correlation between N\textsubscript{2}O and NO\textsubscript{2}-N (Figure 10), which shows the link between N\textsubscript{2}O emissions and nitrite accumulation in long-term analysis. This result suggests that NO\textsubscript{2}-N concentration in the part of biological reactor where nitrification is proceeding could be an indicator of N\textsubscript{2}O emission from biological reactor. Especially, since there was almost no emission of N\textsubscript{2}O when NO\textsubscript{2}-N concentration was under 1.0 mg/L, it was confirmed that avoiding nitrite accumulation in biological reactor is important to reduce N\textsubscript{2}O emission.

![Figure 10. Correlation between N\textsubscript{2}O Concentrations and NO\textsubscript{2}-N Concentrations in a Biological Reactor of WWTP-C](image)

**CONCLUSIONS**

N\textsubscript{2}O emissions from a WWTP in Tokyo were continuously measured for one year. N\textsubscript{2}O emissions showed large fluctuations, declined sharply after rainfall, and was affected by nitrification status, especially residual amount of nitrite. So we conducted detailed surveys to confirm the relation of N\textsubscript{2}O emission and NO\textsubscript{2}-N concentration in each zone of biological reactor. The results confirmed that nitrite accumulation in biological reactor greatly affects N\textsubscript{2}O emission. Thus, it is firstly important to achieve perfect nitrification without accumulating nitrite to reduce N\textsubscript{2}O emission from wastewater treatment.
FUTURE PLANS

In addition to WWTP-A, which we started continuous N\textsubscript{2}O measurement from 2011, we started continuous N\textsubscript{2}O measurement at two more WWTPs in Tokyo from July, 2012. These three WWTPs have multiple processing methods (Conventional activated sludge process, A/O process, A\textsuperscript{2}/O process) and this will enable us to compare the difference of N\textsubscript{2}O emission behaviors of each method.

Furthermore, laboratory-scale and pilot plant experiments with different operating conditions, which are controllable in actual plants, are planned to find conditions for N\textsubscript{2}O reduction. These conditions are planned to be adopted into the three WWTPs which we are conducting continuous N\textsubscript{2}O measurement to investigate whether N\textsubscript{2}O emission from wastewater treatment will actually reduce.

After confirming whether it is possible to reduce N\textsubscript{2}O emission by the surveys mentioned above, we would like to take a leading role in establishment of a new system for N\textsubscript{2}O reduction. Concretely, we will propose to the central government to set different emission factors by different processing methods or operating conditions, and we will work on Tokyo Metropolitan Government to apply these different emission factors to GHG reducing obligation by an Ordinance of Tokyo.

REFERENCES


