Measurements of Gaseous Nitrous Acid Emission from Activated Sludge in a Wastewater Treatment Plant

*Chika Minejima¹, Moe Tejima¹, Tomoyuki Miyashita¹, Norimichi Takenaka², Akihiko Terada³, Masaaki Hosomi³, Masayuki Ohyama⁴, Keiichi Sato⁵

1. International Christian University, 2. Osaka Prefecture University, 3. Tokyo University of Agriculture and Technology, 4. Osaka Institute of Public Health, 5. Asia Center for Air Pollution Research

Introduction & Research Purpose

OH radical is a strong oxidant in the atmosphere and an essential component in the earth' s atmosphere. However, it is difficult to measure its concentration because of its high reactivity and extremely low concentrations¹⁾. Therefore, measuring the precursor of OH radical is useful. Gaseous nitrous acid, HONO, is known as one of the OH sources because of photodissociation²⁾.

 $HONO + h \nu (\lambda < 400 nm) \rightarrow NO + OH$

Despite its importance of HONO, its source is still not well understood. According to previous studies, soil is suggested to be one of the missing sources of HONO³⁾. We focused on activated sludge as a surrogate of soil. Activated sludge commonly exists in the various environments such as lake and rice paddy and is also used in most wastewater treatment plants in Japan. Therefore, our research purpose are a) to investigate whether activated sludge emits HONO or not in both aerobic and anoxic condition and b) to examine influence of pH of activated sludge on HONO emission under a continuous aerobic condition

Methods & Discussion

The first experiment a) was performed in summer (system 1,2) and the second experiment b) was performed in winter (system 3,4) of 2017. Activated sludge was collected from a wastewater treatment plant (system 1, 2) and were acclimated for about 1 month to stabilize the microflora in the systems. They were purged with air at 1.3L/min for 6 hours. After 6 hours of aeration, the purge was stopped for 6 hours to create anoxic condition. On the other hand, system 3,4 were measured from the very next day of collection to see its activity in more similar microflora condition to the wastewater treatment plant. Also, the aeration was kept only as an aerobic condition and no anoxic condition was created. In order to keep the sludge activated, 1 L of 15.1 g⁄L ammonium sulfate solution which contains trace elements was used for nutrient for system 1,2. 1 L of supernatant of the sludge was exchanged with the nutrient every three or four days⁴⁾ for system. For system 3,4, 50 ml of the nutrient was added twice a day. In this experiment, pH of the system 1, 2 were controlled to be 7.0 - 8.0 and system 3,4 were controlled to be pH 5.8 - 6.8 and pH 8.0 - 8.8, respectively, by adding saturated sodium hydrogen carbonate (NaHCO₂). The pH and temperature of each sludge were measured by a pH meter (LAQUA act D-70, Horiba). Also, dissolved oxygen (O_2) (DO) was measured in system 1,2 and oxidation-reduction potential (ORP) was measured in system 3,4 (LAQUA act D-73, Horiba). To capture the emitted HONO, Air Dragged Aqua-Membrane Denuder (ADAMD) method was adopted⁵⁾. To calculate the concentration, Saltzman method was adopted and its absorption was measured by spectrophotometer at 545 nm (UV-1800, Shimazu).

In the first experiment, the large HONO emission was observed in system 1, 2 under aerobic condition.

The average flux was 1.6 ng⁄m²⁄s. In system 2, the HONO emission was higher under aerobic aeration than anoxic aeration; the HONO emission rate increased and the HONO emission rate decreased under the anoxic condition. Therefore, it was suggested that the high availability of O_2 (0.01⁻ mg⁄L) was required for HONO emission, and lack of O_2 would negatively affects HONO emission rate. In the second experiment, the average HONO emission from system 3 (pH 5.8-6.8) was higher than that of system 4 (pH 8.0-8.8) (Fig.1 (b)). However, the HONO emission (0.1-0.9 ng⁄ m²⁄s) was lower than that of experiment 1 with pH 7.0-8.0 (0.1-36.4 ng⁄m²⁄s). Therefore, 2 things were suggested that 1) the lack of O_2 might contribute to the large HONO emission, and the key may be denitrification which occurs under anoxic condition, and 2) the pH 7.2-7.8 where the nitrification bacteria, *Nitrosomonas* and *Nitrobacter*, are both highly active⁶⁾ was possibly the highest pH range to emit HONO.

1) Akimoto et al., 2002. Tairyuken Taiki no Kagaku to Chikyu Kankyo.

2) Kleffmann, 2007. Atmos. Environ. 40, 3640-3652.

- 3) Su et al., 2013. Science., 333, 1616-1618.
- 4) Song et al., 2015. Environ. Sci. Pollut. Res., 22(24):19562-70.
- 5) Takenaka et al., 2004. Analyst., 129 (11), 1130-1136.
- 6) Yoshikura et al., 1999. Seikatsu Eisei., 43, 49-64.

Keywords: HONO, nitrous acid, soil

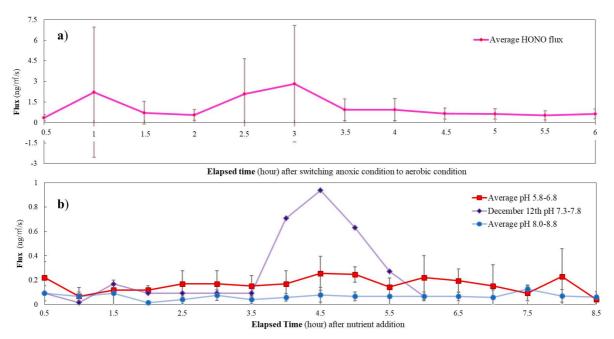


Figure 1. a) Average of HONO flux of 4 measurements at each time vs elapsed time (hour) after switching anoxic condition to aerobic condition. The average flux was 1.6 ng/m²/s in system 1,2. The error bar means standard deviation of each flux at each time (N=8). b) Average HONO flux at each time vs elapsed time (hour) after adding nutrition. The average HONO emission from system 3 (pH 5.8-6.8) was higher than that of system 4 (pH 8.0-8.8). The HONO flux at pH of 7.3-7.8 is also system 3. The error bar means standard deviation of each flux at each time (pH 5.8-6.8; N=3, pH 8.0-8.8). The HONO flux at pH of 7.3-7.8 is also system 3. The error bar means standard deviation of each flux at each time (pH 5.8-6.8; N=3, pH 8.0-8.8). The error bar means standard deviation of each flux at each time (pH 5.8-6.8; N=3, pH 8.0-8.8).