

B-51.2.1 Field Observation for CH₄ and N₂O Balance of Solid Waste and Wastewater treatment process

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Abstract As a nation with a low degree of self-sufficiency in food, Japan imports large quantities of nitrogen and organic materials as food or animal feed, and these are released into the environment as contaminated water or waste material. For this reason, according to the operation conditions of the treatment systems that handle the nitrogen that is emitted and the organic material produced from these sources and the changes in the states of these substances after they have been released into the environment, there is a strong possibility of these becoming emission sources with a high potential for emitting CH₄ and N₂O. But it has been pointed out that CH₄ and N₂O inventories for Japan are hampered by their extremely narrow estimation range and low estimation precision for contaminated water and waste material. As a response to this situation, this research project was a survey of an existing sewage treatment plant conducted to study the actual state of emissions of N₂O and based on this, its formation route. The results have revealed that unit quantities of N₂O produced are from 8.33 to 11.2 per person (mgN₂O-N/capita/day) and 21.2 to 29.2 per cubic meter of in flowing water (mgN₂O-N/m³ inflow) and that in some cases the quantity of N₂O-N that is emitted as gas dissolved in the discharged water accounts for almost half of this total. These results suggest that there is a high probability of N₂O dissolved in the discharged water entering the atmosphere as gas. In addition, the higher the N₂O-N accumulation rate, the higher the N₂O formation rate, the N₂O formation rate is accelerated in cases where the NH₄-N concentration is higher than the NO₂-N or NO₃-N concentrations, but that when it is lower, the N₂O formation rate is lower. Consequently, almost all N₂O formation under aerobic conditions is caused by NH₄⁺ oxidization and NO₂⁻ reduction, suggesting that of these, the catabolistic reduction reaction of NO₂ is the principal mechanism.

Key Words CH₄, N₂O, Waste and Wastewater Treatment, Inventory, Biological Reaction

1. Introduction

The Third Conference of the Signatories to the Framework on Climate Change COP3 held in Kyoto in December 1997 set reduction targets not only for CO₂, but also for CH₄, N₂O, hydro-fluorocarbons (HFCs), and per-fluoro carbons (PFCs), and sulfur hexafluoride (SF₆). These reductions are premised on the use of the basket approach that calls for the application of the global warming potential (GWP) to set reduction targets for all greenhouse effect gasses, for the immediate clarification of the quantity emitted and emission properties of each gas, and the development of technology to reduce their emissions at every potential emission source. But although CH₄ and N₂O are the principal greenhouse effect gasses after CO₂, their clarification and reduction are hampered seriously by the fact that compared with the situation for CO₂, the definition of CH₄ and N₂O sources and the precision of estimation of the quantity of these two gasses that are emitted are both at a low level.

In Japan, which is a nation with low self-sufficiency in food, food products are responsible for the emission of large quantities of nitrogen into the environment in the form of contaminated water and waste material, causing eutrophication, mainly in closed bodies of water. This means that contaminated water and waste material are emission sources that account for an extremely large share of emissions of these substances in Japan as a consequence of the processes used to treat nitrogen that has been emitted and the percentage that is converted to CH_4 and to N_2O after it is released. But the second report on Japan states that the precision and the scope of estimation of the quantities of CH_4 and N_2O produced from contaminated water and waste material are both very poor. This research project that has been undertaken to deal with this situation involves a field survey of wastewater treatment processes including digestion and denitrification that are processes assumed to produce and emit N_2O in order to study the N_2O production route based on the results.

2. Research Method

2.1 Observed Wastewater Treatment Plant

The study was carried out at a wastewater treatment plant in Miyagi Prefecture in July and again in December of 1998. The treatment method was combined with the conventional activated sludge process and the sand filtration. In 1996, a total of 13,204 (average m^3/day) of sewage was treated from an area of 1,648.0 ha with a population of 39,600 people.

2.2 Sampling and Analysis

The sampling performed to obtain specimens for water quality analysis was done in the grit chamber (inflow gate chamber), first settling tank, aeration tank, final settling tank, and its discharge pipe. In the aeration tank, sampling was done at 4 or 5 sampling points set in the flow direction. Gasses produced were sampled in the inflow gate chamber, the grit chamber, the first settling tank, aeration tank, and in the final settling tank. In the aeration tank, sampling was done at 4 sampling points arranged in the flow direction as in the case of the water analysis sampling. A gas collection chamber was used to obtain samples from the inflow gate chamber, aeration tank, and the final settling tank. In the grit chamber and first settling tank, the samples were obtained directly from the deodorizing ducts. The water quality analysis was based on the Wastewater Examination Law and the gasses dissolved in the water were analyzed using the head space method. The N_2O was analyzed using a GC-ECD.

3. Results and Discussions

3.1 State of Emission of N_2O from Wastewater Treatment Processes

Figure 1 shows the quantity of emission and emission percentage of N_2O emitted outside of the system from the wastewater treatment plant as shown by the survey results. Although a relatively large quantity of N_2O was emitted from the grit chamber and first settling tank, which is a finding not seen in past documents, it is assumed that these areas are effected by countercurrent water from sludge treatment processes, and more studies are necessary. The quantity of N_2O -N per capita per day produced by domestic wastewater treatment is 11.2 (mgN_2O -N/capita/day) in the July study results and 8.33 (mgN_2O -N/capita/day) in the December study results. The quantity of N_2O -N generated per m^3 of in flowing water is 29.2 (mgN_2O -N/ m^3 inflow) from the July results and is 21.5 (mgN_2O -N/ m^3 inflow) from the December results. Furthermore, the rate of conversion to N_2O -N per inflowing T-N is 0.06% from the July results and is 0.05% from the December results (documentary values range from 0.001% to 0.05%).

Figure 2 shows the relationship between the Gaseous N_2O (GN_2O) emissions and NH_4^+ , NO_2^- , NO_3^- inorganic N concentration in the aeration tank. The results of both studies show that the N_2O emitted at No. 2 point in the aeration tank declined then later increased. It is

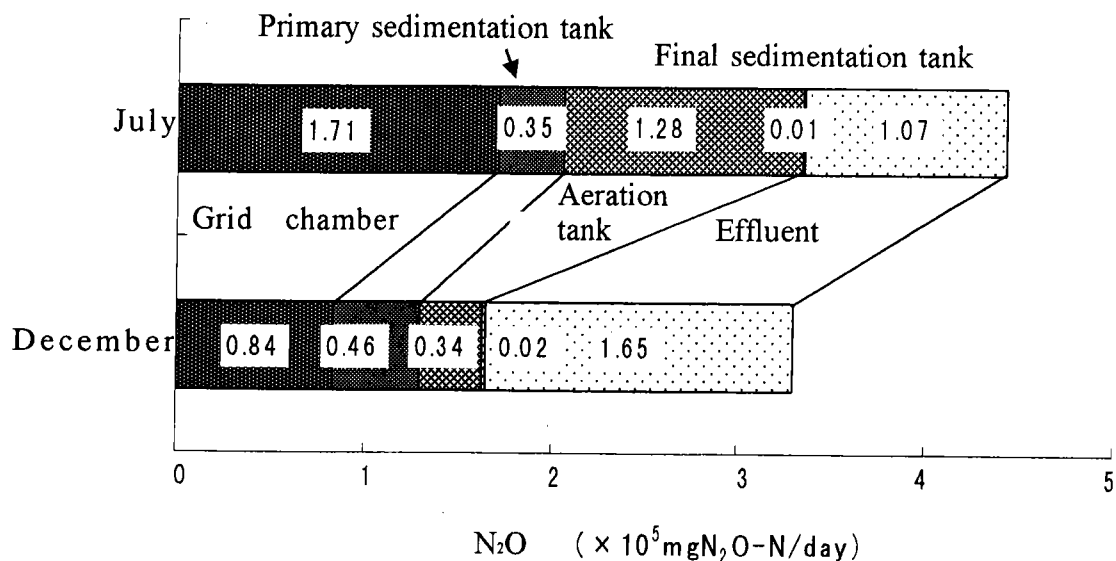


Fig.1 Release amounts of N_2O from each unit process of plant

believed that because there is a low DO content in the front half of the aeration tank, denitrification consumes N_2O . This figure also shows that the quantity of GN_2O emitted rises in proportion to the decline in the NH_4-N concentration. A study of N_2O formation routes shows that there are two, NH_4^+ oxidization and NO_2^- reduction, and based on this result, it is believed that N_2O is formed by the oxidization of NH_4-N . But in parts of the aeration tank that are in an aerobic state, the DO value is approximately 1 (mg/l), it is considered to be fully possible that a reduction reaction is occurring, and it is also possible to conclude that N_2O is also being produced by the reduction of NO_2^- . The temperatures of the water at the time of the July and December surveys were $22.5^\circ C$ and $17^\circ C$, and it is clear that the rate of NH_4 oxidization and N_2O formation are dependent on the temperature.

The saturation factor that represents the value of the measured Dissolved N_2O (DN_2O) as opposed to the DN_2O concentration during vapor-liquid equilibrium ranged from 9.69 to 64.7 in July and from 3.26 to 6.30 in December, showing it was higher in July. Because the fact that the saturation factor is 3.26 for example represents a saturation factor that is 3.26 times as much as in the vapor-liquid equilibrium state, N_2O dissolved in the aeration tank is revealed by this study to be in supersaturated state.

Of the N_2O that is emitted outside the system at the wastewater treatment plant, much is emitted dissolved in the treated water, and the December survey results reveal that this quantity is equal to the total quantity of N_2O that is emitted from all components of the system. The change in the chloride ion concentration shows that the discharged water is diluted about two times when it converges with the water in the river receiving the discharged water, but the DN_2O concentration is about 1/6, suggesting that it is possible that N_2O is emitted into the atmosphere during the convergence of the waters. Further study is necessary to obtain data needed to study the behavior of the DN_2O after it is discharged, but when considering the generation of N_2O at wastewater treatment plants, this is clearly a point that must not be overlooked.

3.2 Analysis of the N_2O formation routes

Along with the results of this study and the results of feed lot waste fluid treatment performed in the past, the N_2 formation routes during aeration that is known to produce large quantities of N_2O was hypothesized to study the formation of N_2O based on this route. The N_2O formation reactions believed to occur during aeration are the NH_2OH oxidization reaction and the NO_2^- reduction reaction caused by aerobic denitrification. To

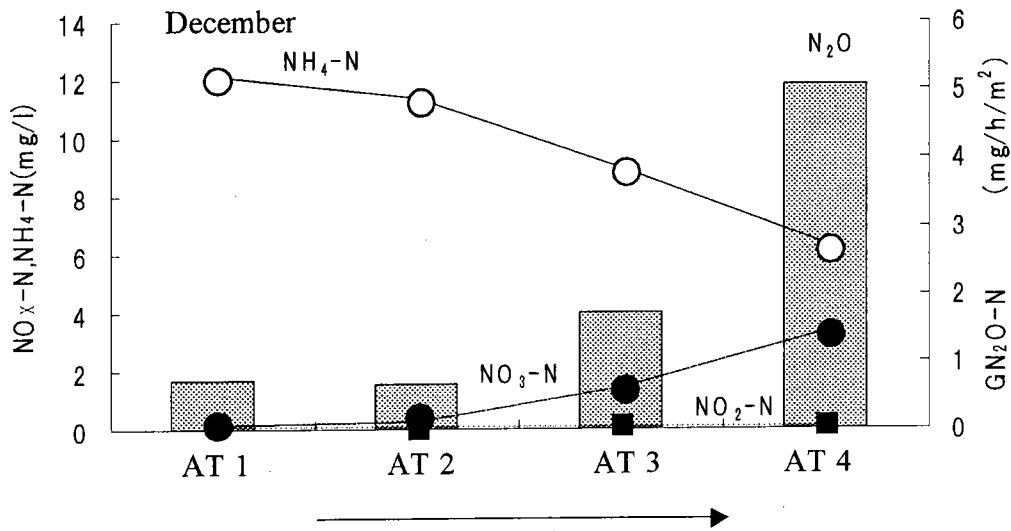
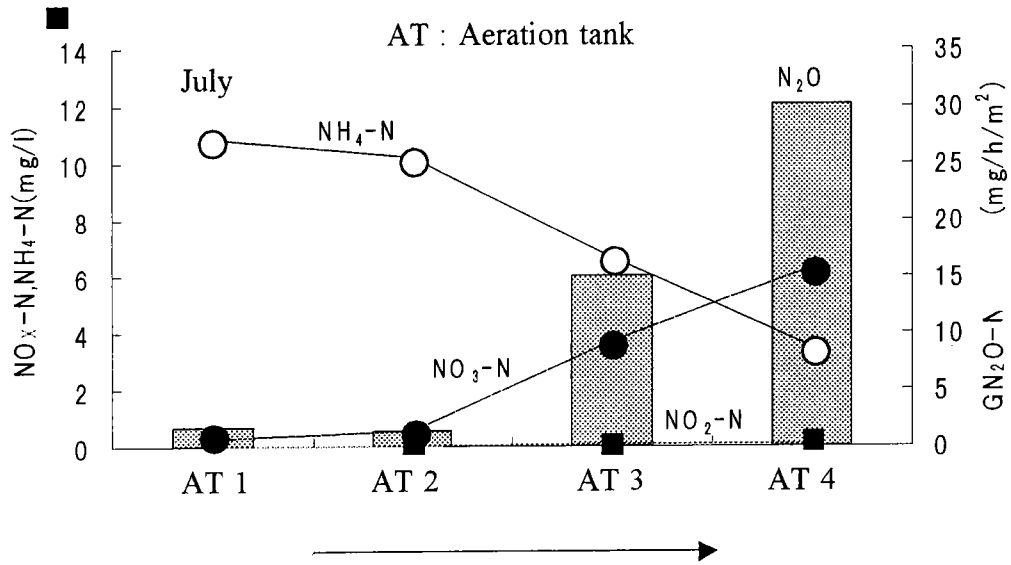


Fig. 2 Relationship between GN₂O and NH₄⁺, NO₂⁻, NO₃⁻

simultaneously account for an oxidization reaction and reduction reaction in this way, it is essential to consider whether this $\text{NO}_2\text{-N}$ comes from the $\text{NH}_4\text{-N}$ or from the $\text{NO}_3\text{-N}$ during the NO_2^- reduction reaction. In an actual system, various reactions are combined to produce N_2O , but if this has been adopted as a formation route, an equation that ultimately cannot be solved is established because a calculation of the balance requires many unknown quantities. Consequently, a formation route that has been simplified by establishing a number of hypotheses as shown below is hypothesized and the formation of the N_2O is analyzed based on this hypothetical route.

- (1) NH_4^+ is not formed.
- (2) NH_4^+ is lowered by NH_4^+ oxidization.
- (3) NO_2^- is formed by NH_4^+ oxidization.
- (4) NO_2^- is lowered by NO_2^- oxidization and by NO_2^- reduction.
- (5) NO_3^- is formed by NO_2^- oxidization.
- (6) NO_3^- reduction does not occur.
- (7) N_2O is formed by NH_4^+ oxidization and by the aerobic denitrification of NO_2^- .
- (8) The N_2O is lowered by its emission outside the system in a gaseous state.

Figure 3 shows the N_2O formation route based on these hypotheses.

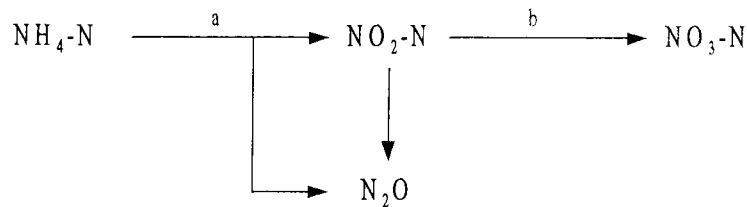


Fig. 3 Simplified N_2O production route

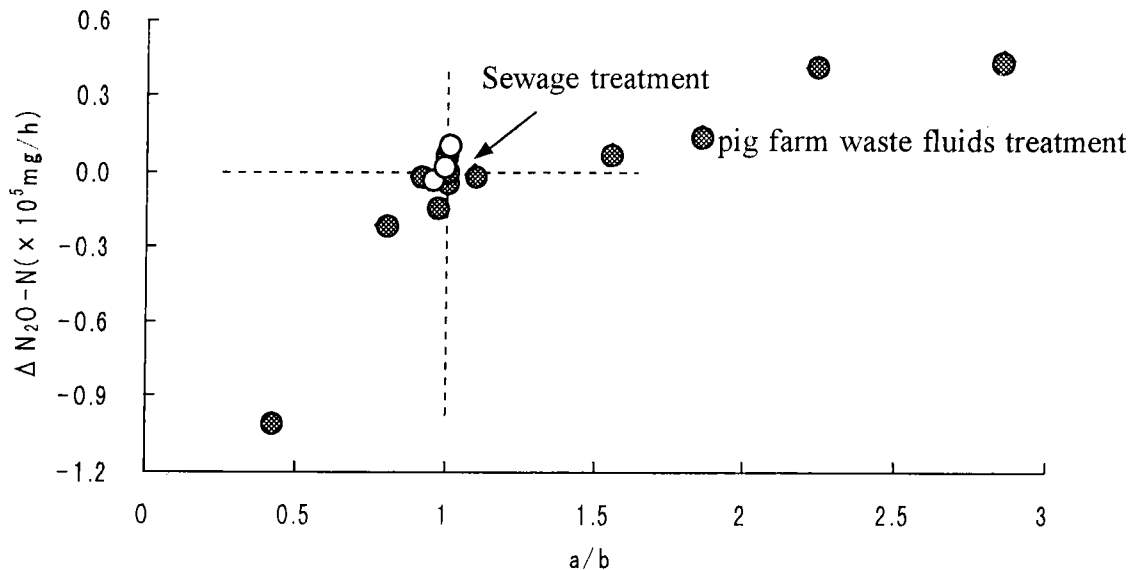


Fig. 4 Relationship between NH_4^+ oxidation rate / NO_2^- oxidation rate (a/b) and N_2O production rate

Although the flux in the oxidization reaction system from $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ in this route can be determined, it is impossible to specify whether the N_2O that is formed was formed by NH_4^+ oxidization or whether it was formed by NO_2^- reduction. So the total of N_2O formed based on NH_4^+ oxidization and NO_2^- reduction was found and an attempt made to

specify the formation route by studying the relationship between this total and the (NH_4^+ oxidization rate (a)) / (NO_2^- oxidization rate (b)) ratio. Figure 4 shows the results combined with the results of the measurement of the pig farm waste fluids. This figure reveals that the larger the a/b ratio, the higher the N_2O formation rate. Because saying that the a/b ratio is large means that NH_4^+ oxidization rate is higher than the NO_2^- oxidization rate, it indicates that NO_2^- has accumulated. In sum, this figure permits the conclusion that the higher the NO_2^- accumulation rate, the higher the N_2O formation rate. In the results for the wastewater treatment plant, $\Delta \text{N}_2\text{O}$ is almost completely concentrated at 0 at an a/b ratio of 1. This is a result of the fact that the measurement results reveal that digestion occurred smoothly without any accumulation of nitrites, but it is recognized that some NO_2^- accumulates according to the operating conditions even when wastewater treatment is done using an activated sludge method of this kind, and it is also known that under such conditions, the quantity of N_2O emitted increases remarkably. In this case, the factors thought to be behind the formation of N_2O include the contribution of NH_2OH . Because NH_2OH is a strong reduction agent, this reaction is the reduction of NO_2^- forming N_2O .

On the other hand, saying that NO_2^- accumulates means that nitrite oxidizing bacteria are impeded to a greater degree than ammonia oxidizing bacteria. And this means that under the effects of the aerobic denitrification, the NO_2^- reduction reaction dominates the NO_2^- oxidization reaction in the N_2O formation reaction process. The former reaction is a chemical reaction while the latter is a biological reaction, but no matter which reaction is assumed to occur, NO_2^- is necessary for the formation of N_2O . Because it is possible to also describe aerobic denitrification as a catabolistic nitrite reduction reaction occurring in aerobic conditions, it is assumed that there is a possibility of an assimilative nitrite reduction reaction that is also a nitrite reduction reaction occurring as aerobic denitrification. If the $\text{NH}_4\text{-N}$ concentration is relatively higher than the $\text{NO}_3\text{-N}$ or $\text{NO}_2\text{-N}$ concentration, the assimilative reduction is restricted, and if it is relatively lower, NO_3^- or NO_2^- is fixed. In brief, because the assimilative nitrite reduction reaction is restricted when $\text{NH}_4\text{-N}/\text{NO}_2\text{-N} > 1$, the catabolistic nitrite reduction reaction is dominant, with the result that N_2O is formed. And because the assimilative reduction reaction is dominant when $\text{NH}_4\text{-N}/\text{NO}_2\text{-N} < 1$, N_2O is not formed. And even when $\text{NH}_4\text{-N}/\text{NO}_2\text{-N} < 1$, the N_2O emission rate gradually declines instead of dropping immediately to 0. This gradual decline occurs because although the assimilative nitrite reduction reaction is dominant, the catabolistic nitrite reduction reaction continues at a reduced level without being completely obstructed and the quantity of NO_2^- that is a substrate falls, resulting in a decline in the quantity of N_2O that is formed.

4. Conclusions

The following facts were clearly demonstrated by the results of this study of the N_2O formation route performed based on a survey of N_2O emissions at a wastewater treatment plant.

- (1) An examination of the quantities of N_2O produced in each component of the facility reveals large quantities emitted from the ducts of the grit chamber and first settling tank, suggesting the possibility of the strong influence of the quality of the countercurrent water on these components.
- (2) A comparison of the quantities of $\text{N}_2\text{O-N}$ emitted outside the system for each process inside the wastewater treatment plant reveals that the quantity of $\text{N}_2\text{O-N}$ emitted as gas dissolved in the discharge water accounts for about half of all that is emitted.
- (3) The unit quantities of N_2O produced are from 8.33 to 11.2 per person ($\text{mgN}_2\text{O-N/capita/day}$) and 21.2 to 29.2 per cubic meter of in flowing water ($\text{mgN}_2\text{O-N/m}^3$ inflow).
- (4) Changes in the water quality at the destination of the water discharged from the plant suggest that N_2O dissolved in the discharged water may be emitted in a gaseous state.
- (5) The higher the $\text{NO}_2\text{-N}$ accumulation rate, the higher the N_2O formation rate, confirming

that NO_2^- is necessary for the formation of N_2O .

- (6) If the $\text{NH}_4\text{-N}$ concentration is relatively higher than the $\text{NO}_2\text{-N}$ concentration or the $\text{NO}_3\text{-N}$ concentration, the N_2O formation rate rises, and inversely, when it is relatively lower, the N_2O formation rate drops.