SECONDARY GENERATION OF GASEOUS HONO AND ITS EFFECT ON OUR HEALTH

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ABSTRACT

Atmospheric HONO and NO_2 were measured simultaneously at several sites in Osaka area. The HONO / NO_2 ratio at mountain site was almost the same as that at the road side. However, the relationship between HONO concentration and NO_2 concentration at the mountain site was much better than that at the road site. This is probably due to the secondary production of HONO from the reaction of NO_2 with water on particles. The secondary production of HONO was also confirmed in the indoor environment. HONO must be a harmful substance for our health. We investigated the effect of HONO on lungs by exposure experiments to mouse and confirmed the damage on the peripheral bronchus of mouse. HONO concentrations at roadside in Hanoi and at National University of Ho Chi Minh were also measured with an annular denuder system. We found that the HONO concentrations Viet Nam were very high levels.

KEYWORDS

Nitrous acid, Nitrogen Dioxide, Secondary production, Exposure experiment, Peripheral bronchus

INTRODUCTION

Nitrous acid, HONO plays a very important role in the atmospheric photochemistry. HONO is photolized by sunlight to produce OH radicals which are the most important species in the atmospheric chemistry. HONO is a main source of OH radicals early in the morning, and about 24 % of OH radicals per day are produced by the photolysis of HONO (Zhou, 2002). The sources of HONO have not been completely clarified yet. The sources of HONO are reported as follows; i) the reaction of NO with OH, ii) heterogeneous reaction of NO_2 with H_2O on particles, such as soot or salt, iii) direct emission from exhaust gas of vehicles (Finlayson-Pitts, 2000b), etc. However, the concentration of HONO can not be explained only with these sources. HONO is removed from the atmosphere by the photolysis, wet deposition, etc.

A real time measurement of HONO is difficult because NO_2 of which concentration is much higher than HONO interferes the HONO measurement. We reported a new HONO measurement method which is not affected by NO_2 (Takenaka, 2004). HONO concentrations in various sites in Osaka area have been measured by this method. Generally, the concentration of HONO increases in rush hour in the morning, decreases after that, in daytime, increases after sunset, and decreased from midnight. In the measurement at Mt. Ikoma which is located about 10 km east of heavy polluted Osaka City, we found the strong relationship between NO_2 and HONO concentrations. This is probably due to the secondary production of HONO from NO_2. Furthermore, the HONO concentration in the indoor is reported to be higher than the ambient air (Finlayson-Pitts, 2000a). We confirmed the same result, and we found the relationship between NO_2 and HONO concentrations. This is also the result of the secondary production of HONO from NO_2. We report

here the HONO concentration of Osaka and also in Hanoi (intersection of Ton Duc Thang and Kham Thien) and Ho Chi Minh (VNU), Viet Nam, and indoor change in HONO concentration.

HONO is an acid gas and the solubility in water is much higher than NO_2 but much smaller than nitric acid. It is possible to reach to our lung and to damage the lung. We also report here the effect of HONO on the lung by exposure of HONO to mouse. The toxicity of HONO has not been clarified so far. Therefore, the investigations of HONO concentration and effects on our health may become future environmental problems.

MATERIALS AND METHODS

HONO and NO_2 Measurements in the ambient and indoor air

HONO was measured by the method we developed (Takenaka, 2004). Briefly, the measurement system can be divided by two parts. One is a HONO absorption system, and the second is nitrite detection system. The former is called air dragged aqua-membrane type denuder (ADAMD), and HONO is absorbed into an absorption solution in a continuous flow system. Nitrite in the solution is reacted with 2,3-diaminonaphthalene (DAN) to produce strong fluorescent substance, 1-naphthotriazole. The excitation and detection wavelength were 360 and 405 nm, respectively. The diction limit was less than 10 pptv and time resolution was less than 2 minutes. The interference from NO_2 was less than 0.01 %. NO_2 was measured by the Kimoto electric Co., NA623 chemiluminescence NOx analyzer.

Sampling points

The simultaneous measurements of HONO and NO_2 were performed at 4 places. i) General urban inhabited area. The sampling was performed on the roof of No.6 building of the graduate School of Engineering, Osaka Prefecture University. ii) Roadside A. This point was the heavy traffic site in Izumiotsu City. iii) Roadside B. This point is located near the Route which is a very famous traffic pollution road in Japan. The amounts of traffic are very large. iv) Mountain site. This point is located in the mountain at 500 m altitude and about 10 km east from Osaka City which is heavy polluted urban area. The wind in Osaka area blows mainly from west, and the polluted air from Osaka City comes to Ikoma site within a few hours.

Exposure experiment to mouse

High concentration of HONO is generated according to the reaction (i). The HONO generation system is shown in Figure 1. Gaseous HCl was produced by using a permeation tube. HCl gas was mixed with humid air (ca. RH=40%), and the mixed air was introduced into the $NaNO_2$ powder. The sample air including HONO is analyzed by NO/O_3 chemiluminescence analyzer. The concentration of HONO is determined from the difference between the NOx value obtained when the sample air was passed thorough a Na_2CO_3 coating denuder and that was not. The sample air was sometimes introduced to the impinger including alkaline solution, and the solution was analyzed by an ionchromatography to determine HCl concentration in the sample air. HCl concentration was several ppbv and less than 1/100 compared to HONO concentration.

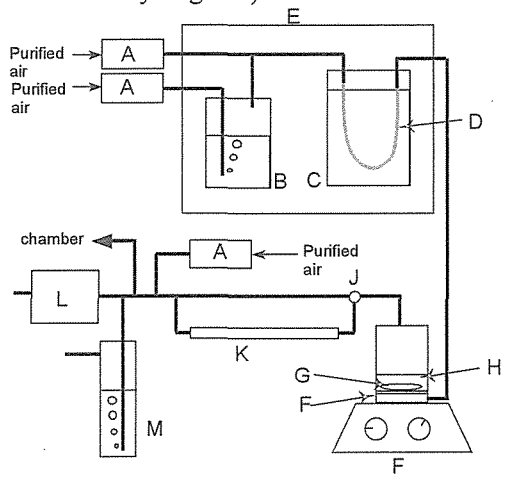


Figure 1 HONO generation and analysis system
A: mass flow controller, B: humidifier, C: 10 N HCl solution, D: Teflon tube, E: magnetic stirrer, F: sintered glass filter, G: stirrer, H: $NaNO_2$ powder, J: three way valve, K: Na_2CO_3 coating denuder, L: NOx analyzer, M: impinger

$$HCl\ (g) + NaNO_2\ (s) \rightarrow NaCl\ (s) + HONO\ (g) \qquad (i)$$

Mice were SPF/VAF mouse (ICR strain) obtained from Oriental Yeast Co., Ltd. The mice were domesticated in a special institution for animals in Osaka Prefecture University for 1 - 2 weeks before the exposure experiments. The mice were divided into the exposure group (4 mice) and the reference group (4 mice). The mice in the reference group were exposed with purified room air with 40 % of the relative humidity. The room temperature was kept at 25 ± 2 °C. The volume of the chamber was 5.6 L, and the flow rate of the exposure gas was 0.5 L / min. The concentration of HONO was 5 ± 1 ppmv at the inlet port of the exposure chamber, and that at outlet port was 0 to 3 ppmv.

RESULTS AND DISCUSSION

The variations of HONO and NO_2 at Osaka Prefecture University are shown in Figure 2-a). The variation pattern of HONO was similar to that of NO_2. HONO concentration increased at rush hour in the morning, decreased in daytime, increased from the evening and decreased from midnight. The result at Mt. Ikoma site is shown in Figure 2-b). Although there is no emission source near the site, the concentration of HONO is almost the same level as that at Osaka Prefecture University. This means that the secondary production of HONO is important. The HONO revels, average HONO/NO_2 ratios and the correlation coefficient of HONO and NO_2 relationships are shown in Table 1. HONO concentration was 3.5 - 6.5 % compared to NO_2 concentration. The relationship between HONO and NO_2 concentrations at Mt. Ikoma site was very high. This result also suggests the secondary production of HONO. HONO is directly emitted from the exhaust gas of vehicles. Therefore, the ratio of HONO/NO_2 is expected to be different near the road side. HONO directly emitted from the vehicles are eliminated from the atmosphere, because HONO is much more water soluble than NO_2. During the transportation, HONO is produced from the reaction of NO_2 with water on particles (eqs. ii) and iii)), and therefore, HONO concentration became to be proportional to NO_2 concentration.

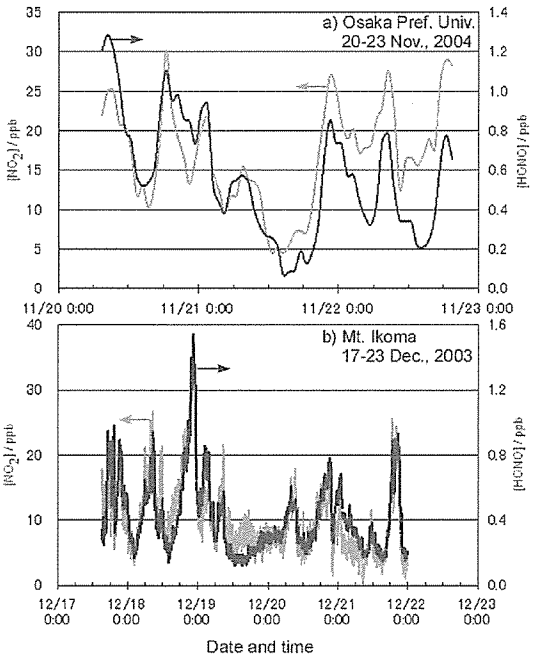


Figure 2 HONO and NO_2 concentrations at Osaka Prefecture University and Mt. Ikoma

$2NO_2 + H_2O \rightarrow HONO + HNO_3$ ii)

NO_2 + Reductant → HONO + Oxidant iii)

Table1 HONO, HNO_3 concentrations and the ratio of HONO/NO_2

Site		HONO ppbv	HNO_3 ppbv	Average HONO/NO_2	correlation of HONO & NO_2 R^2
OPU	20–23 Nov., 2004	00.7– 1.29	------	3.48	0.475
Izumiotsu	25–30 Dec., 2003	0 – 5.00	------	4.92	0.187
Amagasaki	12–17 Mar./ 2005	0.3 – 3.9	------	6.55	0.324
Ikoma	17–23 Dec., 2003	0.12– 1.54	------	4.15	0.727
Hanoi	9 Aug., 2005	3.10	0.53	------	------
Ho Chi Minh	10 Aug., 2005	1.57	0.13	------	------

In order to investigate the secondary production of HONO, HONO and NO_2 were measured in indoor environment. Gas burner was turned on in a closed room for a few hours, and turned off. The measurement result was shown in Figure 3. When the burner was on, HONO increased because of direct emission from the combustion. After the burner was off, HONO concentration decreased gradually. The predominant nitrogen oxides emitted from the combustion is NO. Therefore, when the burner was on, NO emission was very high. After the burner was off, NO was converted to NO_2, and as a result, NO_2 concentrations increased as shown in Figure 3. After NO_2 increased, HONO also increased. This is probably due to the secondary production of HONO from NO_2.

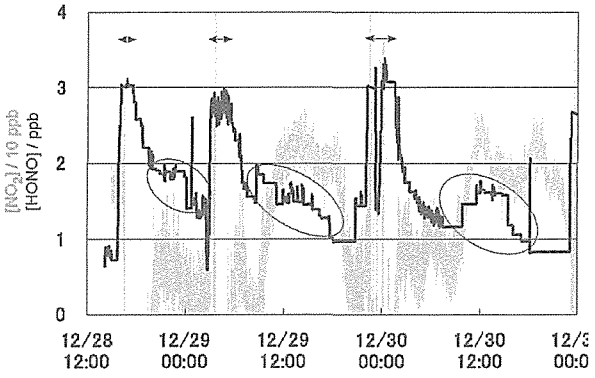
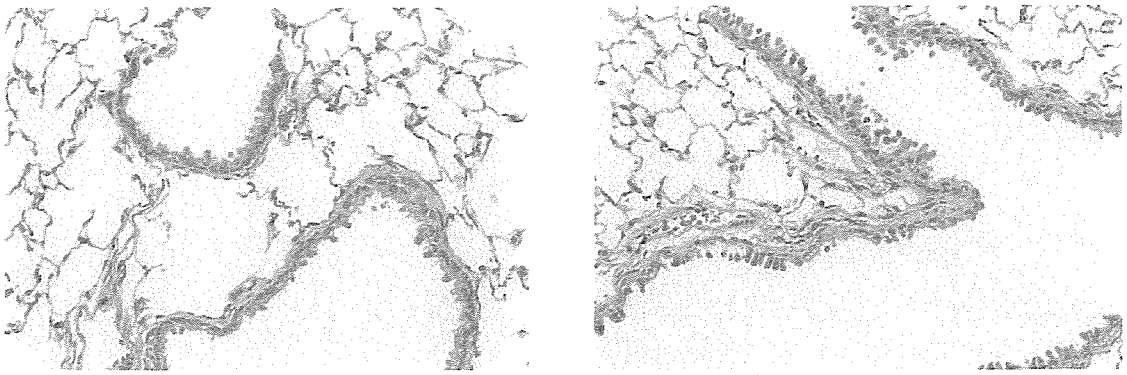


Figure 3 Indoor HONO and NO_2 concentration. Black and gray lines show HONO and NO_2 concentrations, respectively. Arrows indocate the time when the burner was on. Circles indicates the secondary production of HONO from NO_2.

NO_2 is known as a harmful compound and regulated by law in various countries. There are mainly two measurement methods of NO_2, that is, a wet method (diazo method) and a dry method (NO / O_3 chemiluminescence). The wet method is principally a determination method of nitrite. In other word, the wet method can measure HONO. In the dry method, only NO can be detected. When NO_2 is measured, NO_2 is reduced to NO by using a converter at a high temperature. However, the converter converts from various kinds of nitrogen oxides to NO. The bond energy of HO-NO is weaker than O-NO, and HONO is easily converted to NO by the converter. As a result, HONO has not been evaluated so far, and even NO_2, it has not been evaluated exactly. In other word, it is possible that HONO is a main cause of damage of our health. Acids are known to damage to bronchus and lung. HONO is much more soluble than NO_2 to produce acid. On the other hand, it is possible to trap until HONO reaches to bronchus and lung. Therefore, we investigate the effect of HONO on bronchus and lung by exposure experiment of HONO to mouse.

The short time exposure experiments of NO_2 or other pollutants are investigated with very high concentration of the pollutants, generally 1000 times higher concentration of the regulations. It is required to produce high concentration of HONO. HONO is generated by the reaction of $NaNO_2$ with HCl, $(COOH)_2$, or other acidic gases. In any case, high concentration of HONO decomposes easily to produce NO_2 and NO. Especially, under dry condition the amount of decomposition is very large. In order to produce high concentration of HONO, we use humid HCl gas as shown in Figure 1. With the setup in Figure 1, 4-6 ppmv HONO with several tens ppbv NO and NO_2 could be obtained. Furthermore, HCl gas concentration was also less than several tens ppbv. Therefore, in short time exposure experiments, the effects of HCl and NO_2 was negligible in our system.

We made four experiments. In all exposures, the concentrations of HONO at inlet port of the chamber were 4-6 ppmv. However, in the first two exposure experiments, the concentration of HONO was almost 0 ppbv. This is probably due to the absorption into small droplets in the chamber which is generated by breath of mice. The droplets formation could be prevented by using large chamber and introducing dry air sometimes. The photograph of the peripheral bronchus of the mouse is shown in Photo 1. Photo 1-a) shows the peripheral bronchus of the mouse of the reference group and photo 1-b) shows the peripheral bronchus of the mouse of the exposure group. The increase in the secretion of bronchial mucus was observed in the peripheral bronchus of the mouse of the exposure group. The increase in the secretion was also observed in the first experiment in which HONO concentration at the outlet of the chamber was almost zero. Even if the



a) the reference group b) the exposure group

Photo 1 Photographs of the peripheral bronchus of the mouse in the a) the reference group and b) the exposure group
HE stein was treated. The increase in the secretion of bronchial mucus was observed in the peripheral bronchus of the mouse of the exposure group.

outlet concentration was zero, enough HONO could be exposed. From the present experiment, it is speculated that HONO is a harmful compound, but the more experiments are required.

CONCLUSIONS

The existence and the health effect of HONO have not been noticed very much so far. As shown in this report, HONO exists about 4-5 % of NO_2 and produced from NO_2, and HONO is possible to affect to our health. The concentration of HONO in Viet Nam has not been measured, but we found that it is very high level. Therefore, the measurement of HONO is required from now to prevent further pollution in Viet Nam. Furthermore, it is necessary to investigate the health effect of HONO more in detail.

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