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A MODELING STUDY ON BEHAVIOUR OF ATMOSPHERIC AMMONIA AS A PRECURSOR FOR $PM_{2.5}$

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Abstract: In order to understand the concentration of atmospheric ammonia, the observation based on by-weekly sampling using passive sampler has been conducted since April 2015 at plural monitoring sites in the Kanto region of Japan, which was the most densely populated area in Japan (40 million people) and consists of seven prefectures including the Tokyo metropolis. Since the area also has many livestock, the density of NH_3 emission derived from urban human activities and agriculture is the highest in Japan. The emission strength of NH_3 based on the volatilization generally increases as the temperature rises. Thus, the observed concentration of NH_3 in the atmosphere showed higher in the summer, especially at urban and agricultural sites. In addition, simulation analysis based on WRF/CMAQ was conducted in order to evaluate relationship among the emission, transport, and deposition of atmospheric ammonia in the local scale. The model overestimated and underestimated the observed NH_3 concentrations in the summer and winter, respectively. It was found that the overestimation was obvious at the rural site, which emission strength of NH_3 in the simulation was lower than that at urban and agricultural sites.

Key words: Air Quality Model, NH_3, $PM_{2.5}$, SIA, Passive Sampler

1 INTRODUCTION

$PM_{2.5}$ is defined as "particulate matter floating in the atmosphere with a particle size of approximately 2.5 μm or less". Practically, $PM_{2.5}$ is created by the accumulation and condensation of various substances such as Secondary Inorganic Aerosol (SIA), Elemental Carbon (EC), Organic Carbon (OC) and Metals. Especially, it is quite important to take measures in the future for SIA in $PM_{2.5}$ as the secondary particles, which cause severe $PM_{2.5}$ pollution in urban area. SIA can be divided into "ammonium sulfate [$(NH_4)_2SO_4$]" and "ammonium nitrate [NH_4NO_3]". They are created in atmosphere by the heterogeneous reaction between acid gases (SO_2 and NOx) and alkaline gases (NH_3) on a particulate nucleus such as EC or Metals (So-called secondary particles).

In order to evaluate the mechanism of increasing the concentrations and consider the control measures for SIA, it is necessary to develop a numerical model, which can take the emissions of precursors and the physical/chemical processes in atmosphere into account properly. Sakurai et al. (2015) reported that the air quality model based on WRF/CMAQ could reproduce the weekly concentration of SO_4^{2-} in $PM_{2.5}$ observed in Tokyo from August 2009 to August 2011. On the other hand, it was also reported that the model overestimated observed NO_3^- in $PM_{2.5}$ in the summer seasons. Previous studies have reported the overestimation of NO_3^- in $PM_{2.5}$, and it has been pointed out that (i) there could be the artifact in observation data based on the volatilization of ammonium nitrate, (ii) uncertainties could exist in the seasonal fluctuation of NH_3 emission as input data for the model, (iii) uncertainties could exist in model performance regarding concentrations and the dry deposition process for the precursors (HNO_3 and NH_3), and (iv) model could reproduce more HNO_3 concentration under the condition of overestimated O_3 (e.g., Sakurai et al., 2015). The artifact due to volatilization means that the ammonium nitrate (particulate) present in the atmosphere volatilizes into nitric acid gas and ammonia gas on the particle collection filter in the official method, so that the actual particle concentration is underestimate.

In Japan, the environmental air quality standard for $PM_{2.5}$ states that both of the hourly and annual averaged concentration should not exceed 35 μg m^{-3} and 15 μg m^{-3}, respectively (established in 2009). However, the achievement rate has been remaining at low level so far in Japan. It seems to be quite important to reduce SIA concentration because it is a major component of $PM_{2.5}$ in urban area. Although a numerical model has an important role for the consideration of the counter measure, various model uncertainties regarding NH_3 exist and prevent it. Since NH_3 is not regarded as an air pollution, its monitoring network and official observation method have not been established yet in Japan. In this context, this study aims at an assessment of NH_3 behaviors as a precursors of $PM_{2.5}$. Observation for atmospheric NH_3 concentration has been conducted at plural sites in Tokyo metropolitan area. In addition, simulation analysis based on WRF/CMAQ was conducted in order to evaluate relationship among the emission, transport and deposition of atmospheric NH_3 in the local scale. The observed concentrations were utilized for the verification of model performance and the accuracy of the emission inventories.

2 METHODOLOGY

2.1 Observation of atmospheric ammonia

As mentioned above, SIA can be divided into "ammonium sulfate [$(NH_4)_2SO_4$]" and "ammonium nitrate [NH_4NO_3]". They are created in atmosphere by the heterogeneous reaction between acid gases (SO_2 and NOx) and alkaline gases (NH_3) on a particulate nucleus such as EC or Metals (So-called secondary particles). In Japan, national standards have been established for the acid gases (SO_2 and NO_2) and their concentrations have been monitored by the national monitoring network which consists of more than 1,500 sites in whole of Japan. On the other hand, since NH_3 is not regarded as an air pollution, its monitoring network and official observation method have not been established yet in Japan. In this context, in this study, the observation for atmospheric NH_3 concentration has been conducted at plural sites in Tokyo metropolitan area. The observation has been conducted at 5 sites shown in Figure 1 since March 2015. Each site is located at urban (Shinjuku), rural (Hino and Komae) and local area (Tsukui and Hiratsuka).

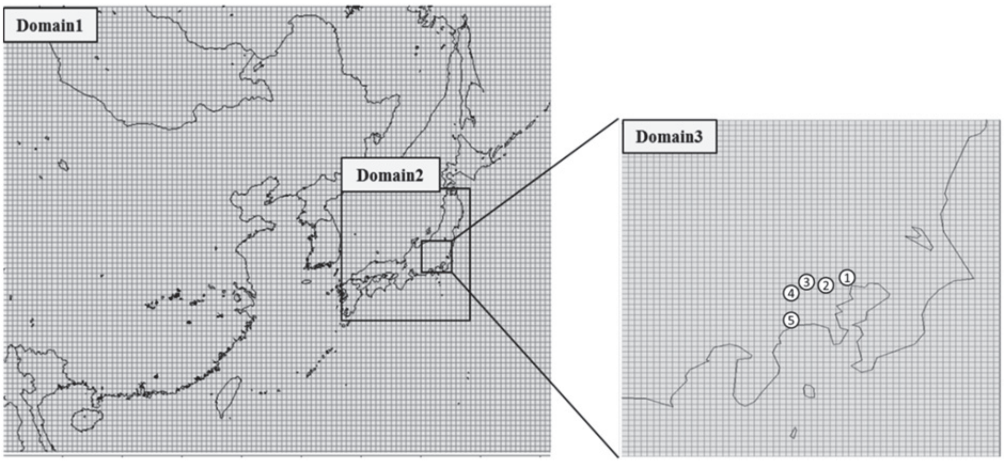

Figure 1 Model domains and locations of 5 monitoring sites to be compared with the calculated concentrations. (1: Shinjuku, 2: Komae, 3: Hino, 4: Tsukui, 5: Hiratsuka)

Passive sampler (manufactured by Ogawa Shokai Co., Ltd.) is adopted as the observation method for NH_3 concentration. The sampling has been carried out every two weeks. Captured NH_3 on the sampling filter was extracted into pure water and the amount was detected by the Flow Injection Analysis method. Atmospheric concentration was calculated according to the instructions published by the supplier.

2.2 Model description

In this study, a modeling analysis was carried out using CMAQ (Community Multiscale Air Quality) version 4.7.1. The selected chemical reaction scheme was the same as Sakurai et al. (2015). Meteorological data in the three-dimensional space was calculated by WRF (Weather Research Forecast model) version 3.7.1. The global objective analysis data (FNL) of National Centers for Environmental Prediction (NCEP) was used in WRF simulation as the initial and boundary condition. In addition, RGT_SST of NCEP was also used for the sea surface temperature. The simulation period was from March 2015 to March 2016. As shown in Figure 1, modeling domain of WRF had a nesting system of 45 km (East Asia as Domain1), 15 km (Japan as Domain2) and 5 km (Kanto region as Domain3) grid resolution, respectively. The domain sizes were 3,825 x 4,950 km^2 for Domain1, 1,095 x 1,200 km^2 for Domain2 and 335 x 335 km^2 for Domain3 with the domain center at 36N and 140E. The vertical layers consisted of 30 sigma-pressure layers from the surface to 100 hPa with the top height of the lowest layer being approximately 22 m.

Air quality simulation based on CMAQ was conducted only in Domain2 and Domain3 due to the limited information regarding the emission inventories in the continental during the recent years. Inland anthropogenic emissions in Domain2&3 were derived from EAGrid-Japan 2010 (Fukui et al., 2014). NOx emission from vehicles was modified by reducing to approximately 75% according to the reduction rate of annual averaged concentration of NOx observed at all of Motor Vehicle Exhaust Monitoring Stations in Japan from 2010 (416 sites) to 2015 (413 sites). Ship emissions were derived from an emission inventories developed by Ocean Policy Research Foundation (2013). In addition, GEIA (Global Emission InitiAtive database) and GFED Ver. 3.1 were applied for vegetable origin VOCs and biomass burning origin, respectively. The volcanic origin SO_2 emissions were also taken into account in the same way as Sakurai et al. (2015). The boundary concentration of air pollutants in Domain2 was derived from MOZART-4 (Model for Ozone and Related chemical Tracers version 4).

3 RESULTS AND DISCUSSION

3.1 Observation results

Figure 2 introduces the seasonal variation of NH_3 concentrations observed from April 2015 to April 2017 at the sites indicated in Figure 1. Since it was found from the observation that the level and the variation for the observed concentrations among Hino, Komae and Tsukui were almost the same each other, the observation at Komae and Tsukui was finished at May 2016.

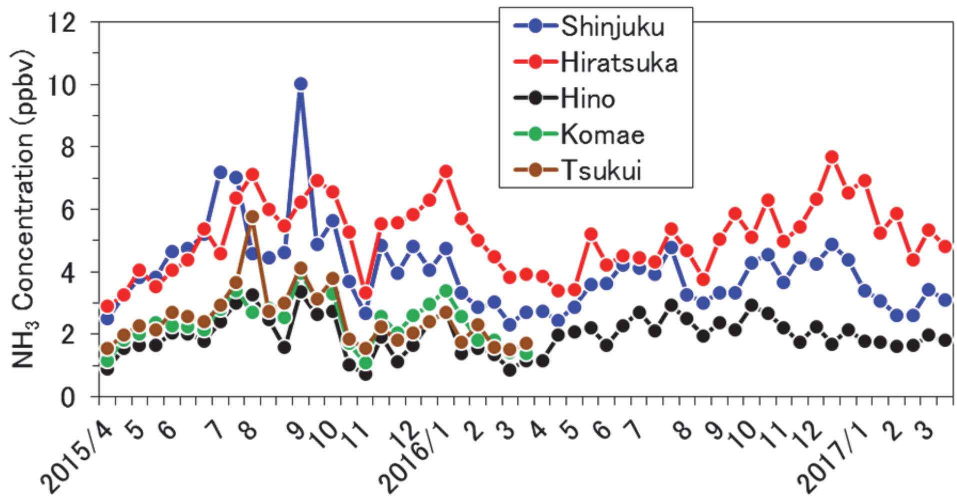

Figure 2 Seasonal variation of NH_3 concentrations observed from April 2015 to April 2017 at the sites indicated in Fig 1.

It seems that observed concentrations increased in the warm seasons and the relatively higher concentrations were observed at Shinjuku (urban) and Hiratsuka (local) through the period. Figure 3 shows the horizontal distribution of annual NH_3 emission used in the simulation for Domain 3 (5 km grid resolution). The annual emission amounts of NH_3 in each grid were Shinjuku: 4.92 ton km^{-2} yr^{-1}, Komae: 4.52 ton km^{-2} yr^{-1}, Hino: 3.24 ton km^{-2} yr^{-1}, Tsukui: 1.36 ton km^{-2} yr^{-1} and Hiratsuka: 4.60 ton km^{-2} yr^{-1}. Fukui et al., (2014) estimated that annual emission amount of NH_3 in Japan was 404,393 ton yr^{-1} in 2010 basis and agricultural and human sources contributed 66% and 18% of the total amount, respectively.

Large emission amount at Shinjuku and Hiratsuka were originated in human and agricultural emission sources, respectively. Thus, regarding those 2 sites, it was clarified that there was consistency in the relationship between emissions and the observed concentrations. On the other hand, although the emission amount at Komae , which was originated in human sources, was almost the same as large as that at Shinjuku and Hiratsuka, relatively lower concentration of NH_3 had been observed. This inconsistency between the emission amount and the concentration suggests that the estimated emission might be larger than that in actual.

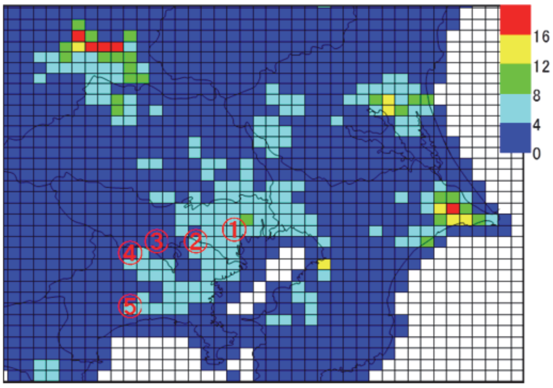

Figure 3 Horizontal distribution of annual NH_3 emission (ton km^{-2} year^{-1}) used in the simulation for Domain 3 (5 km grid resolution).

3.2 Model validation based on the observation

In order to clarify the model performance for the atmospheric ammonia, comparisons between observed and simulated NH_3 were conducted from April 2015 to March 2016 at the 5 sites as shown in Figure 4. It was found that the model generally overestimated the observed NH_3 concentration in the summer season, and underestimated the concentration in the winter season. Especially, the overestimation in the summer was remarkable at Hino and Komae. Regarding the simulation result for Komae, it is suggested from the observation and simulation that the emission amount around Komae seemed to be overestimated especially in summer season.

As for Hino, it was clarified that there was consistency in the relationship between emissions and the observed concentrations as mentioned in the previous section. However, the simulated concentrations at Hino in the summer season became unexpectedly higher despite the smaller emission amount of NH_3 in its grids. Figure 5 indicates the ensemble mean for the diurnal variation of simulated NH_3 in the sampling period from 21st July to 3rd August 2015, when the largest overestimation was simulated at each site. In the simulation, it was configured that the emission strength of NH_3 increased in the daytime according to the temperature rise. Thus, the daily maximum concentration was simulated at Shinjuku, Komae and Tsukui around noon. However, the similar variation was simulated at both of Shinjuku (urban) and Komae (rural) due to almost the same amount of NH_3 emission derived from human sources.

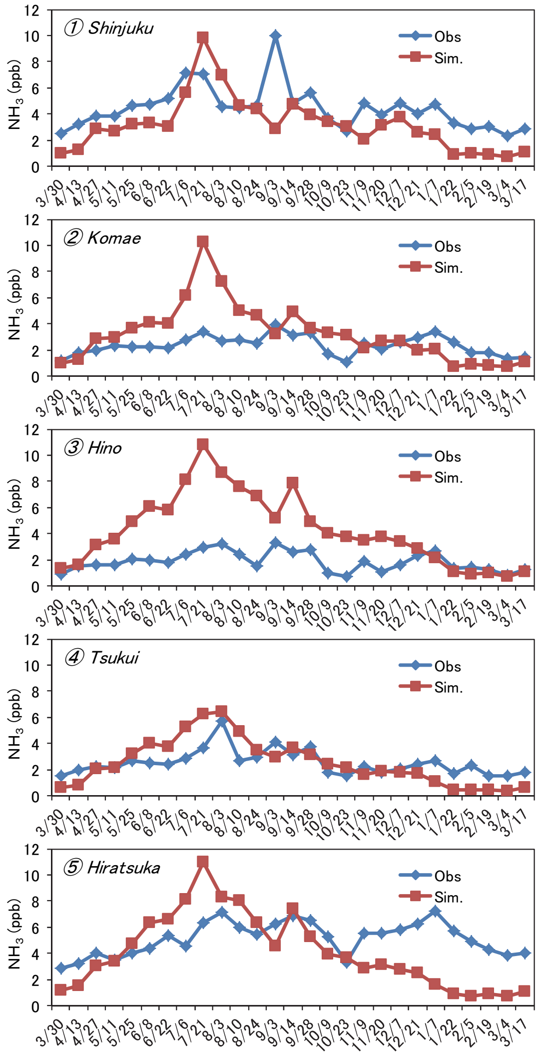

Figure 4 Comparison of observed and simulated NH_3 concentrations from Apr.2015

On the other hand, the daily maximum concentration of NH_3 was simulated in the early morning at Hino and Hiratsuka. The simulated high concentration in the early morning was inconsistent with the diurnal variation of NH_3 emission. In order

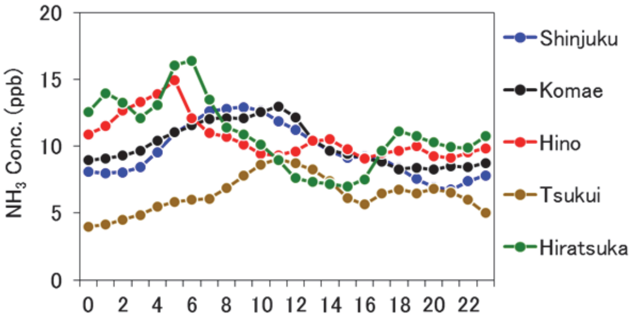

Figure 5 Ensemble mean for the diurnal variation of simulated NH_3 in the sampling period from 21st Jul. to 3rd Aug. 2015.

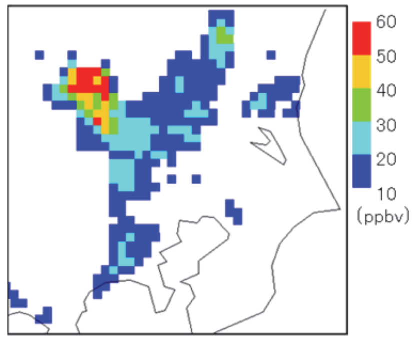

Figure 6 Spatial distributions of simulated NH_3 concentration at 5AM on 1st Aug. 2015

to evaluate the reason why high concentrations appeared at those two sites in the early morning during the summer season, spatial distributions of NH_3 concentration at 5AM on 1st August 2015, simulated by WRF/CMAQ, was illustrated in Figure 6. Sakurai et al. (2003) also reported that the higher concentrations of NH_3 were observed in the nighttime at Shinjuku in summer 2002. As shown in Figure 3, quite large emission area of NH_3 existed at northern part of Kanto region and it was originated in agricultural sources. Since land breeze (north wind) generally prevails in the nighttime in Kanto region, Sakurai et al. (2003) concluded from the simulation analysis that the higher concentration of NH_3 observed at Shinjuku in the nighttime was caused by the transportation of NH_3 emitted in northern part of Kanto region. As shown in Figure 6, it was found that NH_3 emitted around northern part of Kanto region was transported toward south by land breeze and Hino and Hiratsuka were located in the range of the transportation.

In addition, the vertical turbulence is generally reduced due to cooling of the land surface in the nighttime. This likely leads to a law planetary boundary layer as well as the reduction of vertical mixing. Thus, it is also suggested that the higher concentration of NH_3 in the early morning at Komae and Hiratsuka occurred due to the reduced dilution of local NH_3 emission and transported NH_3 in the low planetary boundary layer.

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