

## 10.2 VALIDATION OF THE 3-D AIR QUALITY SIMULATION BASED ON OH REACTIVITY OVER TOKYO METROPOLITAN AREA

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### 1. INTRODUCTION

Air quality in Japan is getting improved. However, NO<sub>2</sub> concentration at some roadside monitoring stations located in urban area exceeds the Japanese air quality standard. O<sub>3</sub> concentration is gradually increasing and the standard has not been met at almost all stations. Though the standard for PM<sub>2.5</sub> is not implemented in Japan, PM<sub>2.5</sub> concentration in urban area is likely above the U.S. standard.

Most of NO<sub>2</sub>, O<sub>3</sub> and PM<sub>2.5</sub> are secondary products through photochemical reactions in the atmosphere. They nonlinearly respond to precursor emissions. 3-D air quality simulations are necessary in order to consider strategies to reduce concentrations. It is inevitably important to validate simulations to make sure that responses of simulations are reliable. Observation data of critical species like O<sub>3</sub> is mainly used for validation. However, more thorough validation is desirable.

Progress in measuring instruments has realized identification of various species. However, a part of species in the atmosphere remains unidentified. Their importance on photochemical reactions should be evaluated. Total OH reactivity of the atmosphere is one of key indicators to see influences of identified and unidentified species on photochemical reactions. A technique to measure total OH reactivity of the atmosphere has been developed by Yoshino *et al.* (2006).

An observation was conducted in summer of 2007 at Tokyo metropolitan area. Total OH reactivity as well as concentrations of various species was measured. The 3-D air quality simulation was executed for the same target period.

This paper describes results of validations and sensitivity analyses of the 3-D air quality simulation in terms of OH reactivity over Tokyo metropolitan area by using observation data of OH reactivity and species concentrations.

### 2. OVERVIEW OF THE SIMULATION

We have developed the simulation framework which consists of The Weather Research and Forecasting (WRF) model, The Community Multi-scale Air Quality (CMAQ) modeling system, and

our emission estimation models. Its overview is described below.

#### 2.1 Target domains

Target domains of the 3-D air quality simulation are shown in Fig. 1. East Asia, Japan, and Kanto domains are nested. Mesh sizes are 64x64km, 16x16km, and 4x4km, respectively.

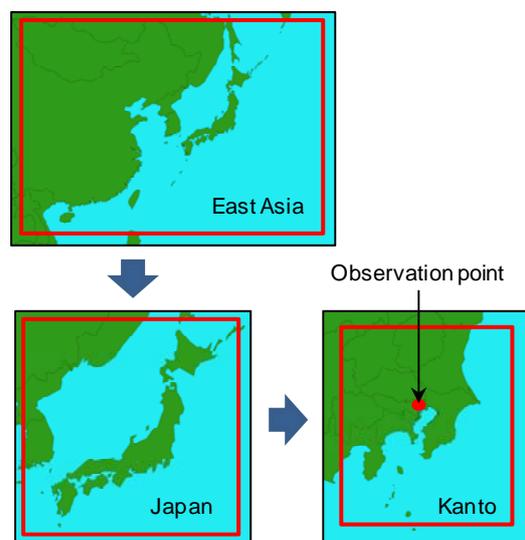


Fig. 1 Target domains of the 3-D air quality simulation.

#### 2.2 Input Emission Data

Japan AuTo-Oil Program (JATOP) vehicle emission estimation model was used to prepare vehicle emissions in Japan. It can estimate running, start and evaporative vehicle emissions. Georeference-Based Emission Activity Modeling System (GBEAMS) was used to prepare emissions from sources except for vehicles in Japan. Regional Emission inventory in ASia (REAS) ver 1.11 (Ohara *et al.*, 2007) was used for anthropogenic emissions in East Asia domain. Model of Emissions of Gases and Aerosols from Nature (MEGAN) v2.04 (Guenther *et al.*, 2006) was used to estimate biogenic VOC emissions.

#### 2.3 Meteorological Model

WRF-ARW ver. 2.2.1 was used to prepare meteorological field. East Asia domain was treated separately, and Japan and Kanto domains were treated simultaneously by 2-Way nesting. NCEP Final

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Analysis data was used for the initial and boundary condition and grid nudging.

## 2.4 Air Quality Model

CMAQ ver. 4.6 (Byun *et al.*, 1999) was used to simulate pollutant concentrations in the atmosphere. Output from the outer domain was input to the inner domain as the boundary concentration. SAPRC99 was chosen for the chemical mechanism.

## 3. OBSERVATION OF OH REACTIVITY AND SPECIES CONCENTRATIONS

Total OH reactivity is represented by OH decay rate. OH decay rate was measured from August 21 to 27, 2007 in Koto-ku, Tokyo. Data obtained during daytime on August 21, 22, 26 and 27 is used for analyses. Details of measuring instruments and procedures were documented in Yoshino *et al.* (2006). In brief, air was mixed with artificially created OH radicals, and their decay rates were measured by Laser-Induced Fluorescence (LIF). In addition, concentrations of NO<sub>x</sub>, O<sub>3</sub>, CO, SO<sub>2</sub>, and various species of NMHCs (Non-Methane HydroCarbons) and OVOCs (Oxygenated Volatile Organic Compounds) were measured at the same time.

Observed OH decay rate on August 21 is shown in Fig. 2 as an example. OH decay rate can be also calculated from species concentrations and its known reaction coefficients with OH. OH decay rate calculated from all of measured species concentrations and reaction coefficients is also shown in Fig. 2. Observed OH decay rate is higher than calculated one. It implies existence of some unidentified species which react with OH in the atmosphere. They are referred as "missing sinks".

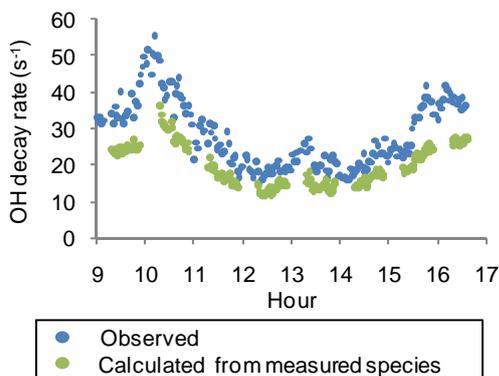


Fig. 2 OH decay rate which was observed directly and calculated from measured species concentrations on August 21, 2007.

Contributions of species to observed OH decay rate averaged over the target period are shown in Fig. 3. NO<sub>2</sub> and anthropogenic VOCs are major contributors, but fraction of missing sinks is larger than them. Therefore, it seems that missing sinks are important for photochemical reactions in the

atmosphere.

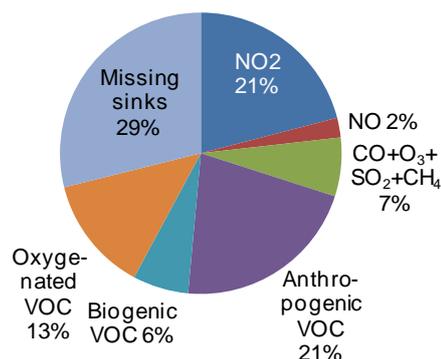


Fig. 3 Contributions of species to observed OH decay rate.

## 4. RESULTS OF THE SIMULATION

The 3-D air quality simulation described in 2. was executed for the period including August 21, 22, 26 and 27, 2007. SAPRC99 species are grouped as shown in Table 1. Measured species are assigned to one of SAPRC99 species. SAPRC99 species which react with OH and no measured species are assigned to are grouped as missing sinks.

Table 1 Grouping of SAPRC99 species.

Group	SAPRC99
NO <sub>2</sub>	NO2
NO	NO
O <sub>3</sub>	O3
CO	CO
SO <sub>2</sub>	SO2
Anthropogenic VOC (AVOC)	ETHENE, ALK1, ALK2, ALK3, ALK4, ALK5, OLE1, OLE2, ARO1, ARO2
Biogenic VOC (BVOC)	ISOPRENE, TRP1
Oxygenated VOC (OVOC)	MEOH, HCHO, CCHO, ACET
Missing sinks	NO3, HNO3, HONO, HO2, HNO4, HO2H, COOH, ROOH, RNO3, MEK, PROD2, CCO_OOH, RCO_OH, PHEN, HCOOH, RCHO, GLY, MGLY, CRES, BALD, METHACRO, MVK, ISOPROD, DCB1, DCB2, DCB3

Observed and simulated OH decay rates are shown in Fig. 4. Simulated OH decay rate is underestimated. OH decay rates of species groups averaged over the target period are shown in Fig. 5. OH decay rates of VOCs are significantly underestimated, and that of missing sinks is lower than the observation. Improvement of emission inventories is necessary.

Another result of a simulation case is shown in Fig. 4 and 5. In this case, boundary concentrations and emissions were uniformly changed to match

concentrations with observed values. Simulated species concentrations except for secondary products (e.g.  $O_3$  and  $HCHO$ ) are almost the same as the observation. However, missing sinks ( $5.3s^{-1}$ ) are still lower than the observation ( $8.5s^{-1}$ ). It means that about 60% of the observed OH decay rate is explained by secondary products considered in the simulation but 40% remains unexplained. Sensitivity analyses were conducted to investigate impacts of unexplained missing sinks.

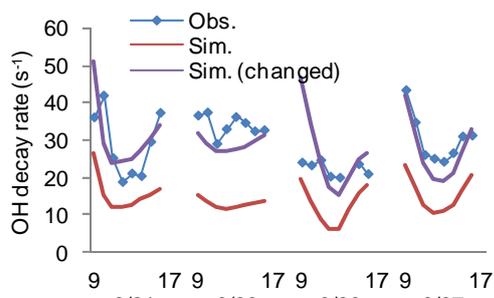


Fig. 4 Observed and simulated OH decay rates.

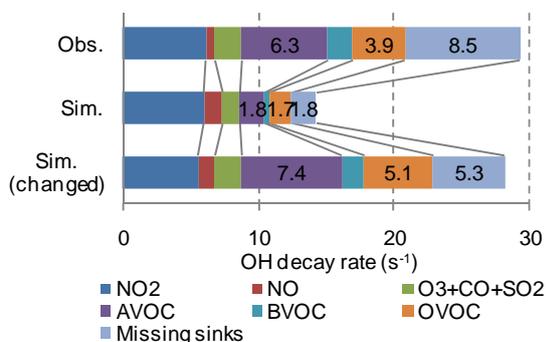


Fig. 5 OH decay rates of species groups averaged over the target period.

## 5. SENSITIVITY ANALYSES

Candidates of unexplained missing sinks are unidentified primary emitted species and unknown secondary products. Their impacts on photochemical reactions were investigated through sensitivity analyses. The simulation in which boundary concentrations and emissions were changed was used as the base case.

### 5.1 Impacts of primary emitted species

In SAPRC99, ALK5, OLE2 and ARO2 are groups to which heavier alkanes, olefins and aromatics are speciated. Unidentified primary species are likely to be included in those groups because it is more difficult to measure heavier hydrocarbons. The simulations in which boundary concentrations and emissions of ALK5, OLE2 and ARO2 were increased were conducted to fill the gap ( $3s^{-1}$ ) of OH decay rate. Fig. 6 shows simulated OH decay rates. OH decay rates increased more than  $3s^{-1}$  due to secondary products.

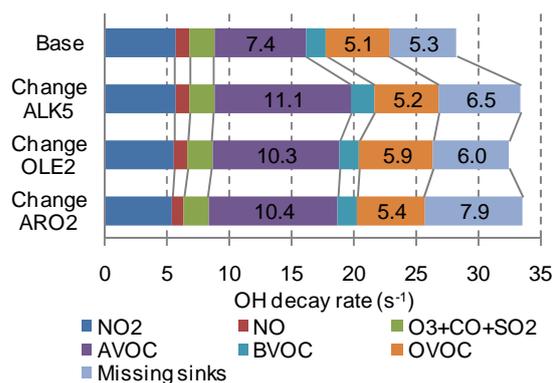


Fig. 6 OH decay rates in cases that boundary concentrations and emissions of primary emitted species are changed.

Incremental ratios of species concentrations including secondary aerosol components from the base case are shown in Fig. 7. Anthropogenic secondary organic aerosol (ASOA) significantly increased when ALK5 and ARO2 increase.  $O_3$  increased slightly. On the other hand,  $NO_3^-$  decreased because oxidation from  $NO_x$  to  $HNO_3$  was suppressed. This is explained by reduction of OH.

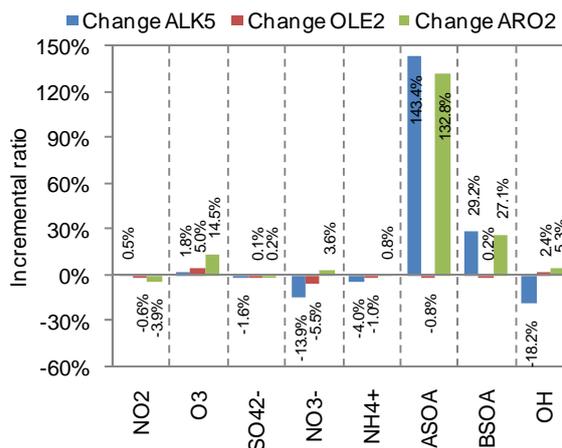


Fig. 7 Incremental ratios of species concentrations from the base case in cases that boundary concentrations and emissions of primary emitted species are changed.

### 5.2 Impacts of secondary products

It is difficult to investigate impacts of unknown secondary products because their reaction paths and coefficients are also unknown. We assumed that unknown secondary products have similar characteristics to existing secondary products. RCHO, DCB1 and PROD2 are major secondary products in our simulation. The simulations in which yields of RCHO, DCB1 and PROD2 in reactions were increased were conducted to fill the gap ( $3s^{-1}$ ) of OH decay rate. Fig. 8 shows simulated OH decay rates.

OH decay rates increased more than  $3\text{s}^{-1}$  due to ternary and subsequent products.

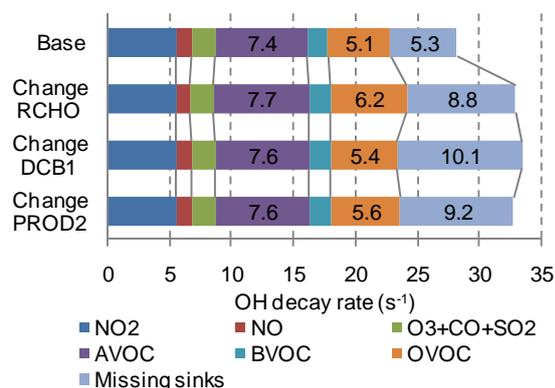


Fig. 8 OH decay rates in cases that yields of secondary products in reactions are changed.

Incremental ratios of species concentrations from the base case are shown in Fig. 9.  $\text{O}_3$  increased slightly, especially when DCB1 increased. All of secondary aerosol components decreased because oxidation of precursors was suppressed. Again, this is explained by reduction of OH. Increases of reactive primary and secondary VOCs reduce OH concentrations and suppress oxidation to secondary aerosols.

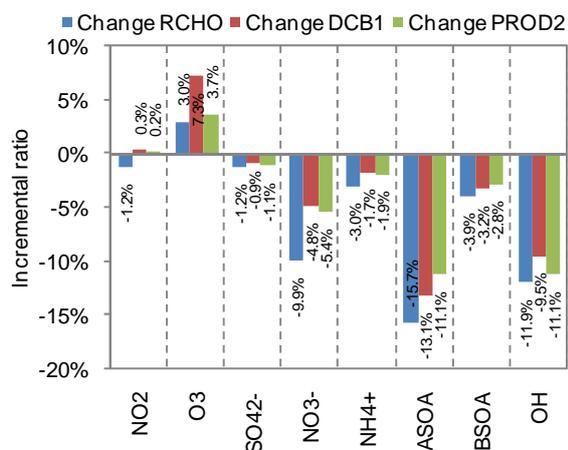


Fig. 9 Incremental ratios of species concentrations from the base case in cases that yields of secondary products in reactions are changed.

## 6. SUMMARY

Simulated OH decay rates and various species concentrations were validated by using observation data. OH decay rates were underestimated. A part of missing sinks remained unexplained even after emissions were improved. Unexplained missing sinks have great impacts on  $\text{O}_3$  and secondary aerosol formations. It was found that validation of simulations in terms of OH reactivity is very useful to know

impacts of secondary products.

## ACKNOWLEDGEMENT

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