Abstract

This study conducted analyses on biogenic volatile organic compounds (BVOC) emission sources contributing to urban ozone (O3) concentration in Osaka Prefecture, Japan in summer 2010 by using the Weather Research and Forecasting model (WRF) version 3.5.1 and the Community Multiscale Air Quality model (CMAQ) version 5.0.1. This prefecture is characterized by highly urbanized area with small forest area. The contributions of source regions surrounding Osaka were estimated by comparing the baseline case and zero-out cases for BVOC emissions from each source region. The zero-out emission runs showed that the BVOC emissions substantially contributed to urban O3 concentration in Osaka (10.3 ppb: 15.9% of mean daily maximum 1-h O3 concentration) with day-by-day variations of contributing source regions, which were qualitatively explained by backward trajectory analyses. Although O3 concentrations were especially high on 23 July and 2 August 2010, the contribution of BVOC on 23 July (35.4 ppb: 25.6% of daily maximum O3) was much larger than that on 2 August (20.9 ppb: 14.2% of daily maximum O3). To investigate this difference, additional zero-out cases for anthropogenic VOC (AVOC) emissions from Osaka and for VOC emissions on the target days were performed. On 23 July, the urban O3 concentration in Osaka was dominantly increased by the transport from the northwestern region outside Osaka with large contribution of O3 that was produced through BVOC reactions by the day before and was retained over the nocturnal boundary layer. On 2 August, the concentration was dominantly increased by the local photochemical production inside Osaka under weak wind condition with the particularly large contribution of AVOC emitted from Osaka on the day.

Key words: Photochemical ozone, BVOC, Source contribution, Zero-out emission, WRF/CMAQ

1. INTRODUCTION

Tropospheric ozone (O3) causes a serious damage to crops and human health in countries around the world (Kim et al., 2011; Adams, 2006; Kobayashi et al., 1995; Sun, 1994; Fuhrer et al., 1989). In Japan, although anthropogenic emissions and concentrations of O3 precursors (nitrogen oxides (NOx) and volatile organic compounds (VOC)) have been decreasing for the last few decades, mean O3 concentration has been gradually increasing (Ministry of the Environment of Japan, 2010). The Japanese environmental standard of photochemical oxidants (60 ppb for 1-h concentration) has not been achieved at almost all the air pollution monitoring stations. Along with the increase in O3 concentration in recent decades, photochemical oxidant warnings (1-h concentration > 120 ppb) are often issued (Ministry of the Environment of Japan, 2010).

The tropospheric O3 can be increased by O3 transport from the stratosphere and photochemical reactions of NOx and VOC in the troposphere. The contribution of the stratospheric O3 to the tropospheric O3 is relatively large in regions where the photochemistry is quiescent (Lelieveld and Dentener, 2000), and varies substantially depending on region and season (Nagashima et al., 2010). Meanwhile, huge anthropogenic emissions of air pollutants including O3 precursors cause transboundary air pollution, which can contribute to the increase in background O3 concentration of each region in the global scale (Auvray and Bey, 2005; Li et al., 2002; Wild and Akimoto, 2001). The increase in O3 in Japan may be partly attributed to the transboundary air pollution because the effect of long-range transport of air pollutants from the Asian continent is serious in Japan (Shimadera et al., 2013, 2009).

In addition to the effect of the background O3, the contribution of Biogenic VOC (BVOC) emissions is also important for O3 production over Japan that is dominantly covered by forests. Isoprene and monoterpenes, which are dominant BVOC species, react rapidly in the atmosphere, and contributes to the formation
of the tropospheric O₃ and aerosol, especially in the presence of NOₓ (Claeys et al., 2004; Duane et al., 2002; Yokouchi and Ambe, 1985). BVOC emissions are larger than anthropogenic VOC (AVOC) emissions (IPCC, 2001), and affected by meteorological factors such as temperature and light intensity (Guenther et al., 1993). Air temperature rise due to the global warming and the urban heat island phenomenon may increase O₃ concentration by increasing BVOC emissions as well as by accelerating photochemical reactions. In addition, the relative importance of BVOC in the atmospheric chemistry over Japan has increased with decreasing anthropogenic emissions in the country. It is necessary to reveal the relationship between BVOC emissions from forest areas and O₃ concentrations in urban areas in order to develop reliable strategies to control the photochemical O₃ pollution because BVOC can significantly affect urban O₃ concentrations (Bao et al., 2010; Solomon et al., 2004; Chameides et al., 1988).

High O₃ concentrations exceeding 100 ppb are often observed during summer in Osaka Prefecture, which includes the third largest city in Japan and has higher frequency of photochemical oxidant warnings than the surrounding prefectures (Ministry of the Environment of Japan, 2010). Although this prefecture has the smallest forest area among prefectures in Japan, it is surrounded by prefectures with large forest areas. Therefore, BVOC emitted in the surrounding areas may substantially affect O₃ concentration in Osaka. This study conducted analyses on BVOC emission sources contributing to urban O₃ concentration in Osaka by air quality simulations.

2. METHODOLOGY

2.1 Model Configuration

In order to estimate the effect of BVOC emissions from the Kinki region of Japan on urban O₃ concentration in Osaka, this study utilized the Community Multiscale Air Quality model (CMAQ) (Byun and Schere, 2006) version 5.0.1 driven with meteorological fields produced by the Weather Research and Forecasting model (WRF) (Skamarock and Klemp, 2008) version 3.5.1. The baseline WRF/CMAQ simulation in this study is identical to that of Nishimura et al. (2015). In addition, the Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT) (Draxler and Hess, 1997) version 4 was used with the WRF-simulated wind field for backward trajectory analyses.

The WRF/CMAQ modeling system was run for a period from 6 July to 9 August 2010 with an initial spin-up period of 1 to 5 July 2010. Fig. 1 shows the modeling domains for air quality simulations and location of Kokusetsu Osaka air pollution monitoring station. The horizontal domains consisted of 3 domains: domain 1 (D1) covering a wide area of East Asia, domain 2 (D2) covering the mainland of Japan, and domain 3 (D3) covering the Kinki region. The Kokusetsu Osaka station is located in Osaka City, the most urbanized area in D3. The horizontal resolutions and the number of grid cells in the domains are 64, 16 and 4 km, and 108×96, 68×68 and 76×76 for D1, D2 and D3, respectively. The vertical layers consisted of 30 sigma-pressure coordinated layers from the surface to 100 hPa with the middle height of the first layer being approximately 28 m.

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Fig. 1. Modeling domains for air quality simulations and location of Kokusetsu Osaka air pollution monitoring station.
Table 1 shows WRF and CMAQ configurations in this study. The models were configured with the same physics and chemistry options as those used by Shimadera et al. (2014). The WRF simulation was conducted with on-line one-way nesting in the three domains using the mesoscale model grid point value (MSM-GPV) data by the Japan Meteorological Agency (JMA) and the final analysis (FNL) data by the U.S. National Centers for Environmental Prediction (NCEP). Nishimura et al. (2015) showed that WRF well simulated meteorological variables including air temperature, humidity, wind speed and shortwave radiation at the meteorological observatories in D3; and the WRF-simulated-meteorological fields were applicable to O₃ simulations.

For the CMAQ simulations, the hourly WRF results were processed by the Meteorology-Chemistry Interface Processor (MCIP) version 4.1. The MCIP-processed meteorological data were also used for the estimates of biogenic emission and backward trajectory analyses. CMAQ was configured with the Statewide Air Pollution Research Center version 99 (SAPRC99) (Carter, 2000) mechanism and the fifth generation CMAQ aerosol module (AERO5).

2.2 Emission Data

Emission data for the CMAQ simulations include NOₓ, sulfur oxides, carbon monoxide, ammonia, non-methane VOC (NMVOC) and particulate matter emissions from anthropogenic, biogenic, biomass burning and volcanic sources. The details are described in the previous study (Nishimura et al., 2015). Anthropogenic emissions in Japan from vehicles, ships and other sectors for the simulations in summer 2010 were respectively derived from the Japan Auto-Oil Program (JATOP) Emission Inventory-Data Base in the year 2010 (JEI-DB) developed by the Japan Petroleum Energy Center (JPEC) (2012), the database in the year 2005 developed by the Ocean Policy Research Foundation (OPRF) (2012) and an emissions inventory in the year 2000 developed by Kannari et al. (2007).

Biogenic isoprene and monoterpene emissions in the Kinki region of Japan were estimated on the basis of Bao et al. (2010). They used the experimentally-derived standard emission rates of the dominant tree species and the forest database in the regions by Bao et al. (2008). The three dominant coniferous trees (Cryptomeria japonica, Chamaecyparis obtusa and Pinus densiflora) and the six dominant broadleaf trees (Quercus serrata, Quercus crispula, Fagus crenata, Quercus acutissima Carruthers, Quercus glauca and Quercus myrsinaefolia) respectively occupy 60% and 18% of the forest area in the region. The other biogenic emissions were estimated with the Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2.04 (Guenther et al., 2006).

2.3 Estimate of BVOC Contribution

The BVOC emission sources contributing to urban O₃ concentration in Osaka were identified by comparing the baseline simulation case of Nishimura et al. (2015) with zero-out emission cases in which emissions from target sources were set to zero. Fig. 2 shows BVOC source regions for zero-out emission cases in D3. The land areas in D3 were divided into 10 source regions: 7 regions in the Kinki region including Mie Prefecture (Reg.1), Shiga Prefecture (Reg.2), Kyoto Prefecture (Reg.3), Osaka Prefecture (Reg.4), Hyogo Prefecture (Reg.5), Nara Prefecture (Reg.6), Fukuoka Prefecture (Reg.7), Aichi Prefecture (Reg.8), Okayama Prefecture (Reg.9) and Yamagata Prefecture (Reg.10).
fecture (Reg.5), Nara Prefecture (Reg.6) and Wakayama Prefecture (Reg.7), the Chubu region in D3 (Reg.8), the Chugoku Region in D3 (Reg.9) and the Shikoku Region in D3 (Reg.10).

Fig. 3 shows spatial distributions of mean NMVOC emission rates and mean fractions of BVOC to the NMVOC emission rates for the simulation period. Major emission sources of NMVOC are stationary evaporative sources and biogenic sources. While the large emissions in the coastal lowland areas are dominated by AVOC from urban areas, large emissions in the mountainous areas are dominated by BVOC from forest vegetation. The temporal mean value of the total NMVOC emission rates for the simulation period in D3 was 3703 molC s⁻¹, 57% of which was accounted for by biogenic isoprene and monoterpenes. In respect of NOₓ, there were large emissions from the coastal urban areas and from ships, and the temporal mean total emission rate in D3 was 360 mol s⁻¹ (Nishimura et al., 2015). Fig. 4 shows temporal variations of the total AVOC and BVOC emissions and mean regional AVOC and BVOC emissions in D3 in the simulation period. Although diurnal, weekday-weekend (vehicles only) and monthly variations were considered in AVOC emissions, the temporal variation of AVOC was much smaller than that of BVOC that was strongly affected by temperature and light intensity. As described by Nishimura et al. (2015), the meteorological conditions in the first 10 days of the simulation period were generally influenced by a seasonal rain front over Japan. Then, the study region tended to be covered with high pressure systems, which resulted in clear sky and high temperature conditions, except on 29 July, when low pressure systems brought precipitation. These variations of the meteorological conditions were reflected in the temporal variation of BVOC emission rate. In respect of the mean regional emissions, the ratios of Reg.4 was the highest for AVOC emissions and the lowest for BVOC emissions because Reg.4 has the most urbanized area and the smallest forest area in D3. However, Reg.4 is surrounded by regions with large BVOC emissions, such as Reg.3, Reg.5 and Reg.7.

Zero-out cases for BVOC emissions were conducted for each source region in D3 with boundary concentra-

![Fig. 2. BVOC source regions for zero-out emission cases in D3.](image)

![Fig. 3. Horizontal distributions of mean NMVOC emission rates (a) and mean fractions of BVOC to the NMVOC emission rates (b) from 6 July to 9 August 2010 in D3.](image)
tions identical to those of the baseline simulation case for the entire simulation period. The contribution of emissions from a source region to O₃ concentration was defined as the difference of O₃ concentration in the baseline case and a zero-out case for the region. In addition, a zero-out case for BVOC emissions in the entire D3 was conducted in order to estimate uncertainty associated with nonlinearity in atmospheric reactions. This study conducted much more detailed analyses than Bao et al. (2010) because the zero-out emission case in the previous study was only a single case for BVOC emissions in the entire Kinki region.

3. RESULTS AND DISCUSSION

3.1 Contribution of BVOC Emissions to Urban O₃ throughout the Simulation Period

Fig. 5 shows hourly time series of observed and simulated wind speed and direction at Osaka meteorological observatory, and nitrogen dioxide (NO₂) and O₃ concentrations (the baseline case) at the Kokusetsu Osaka air pollution monitoring station from 6 July to 9 August 2010. The Osaka meteorological observatory is located at about 2 km west of the Kokusetsu Osaka station. Under clear sky conditions in summer in Osaka, wind speed exhibits a clear diurnal cycle with a peak in the daytime because of prevailing southwesterly sea breeze as shown in Fig. 5a and b. For NO₂, the baseline CMAQ simulation sometimes overestimated diurnal peaks in the morning but well captured day-by-day variation. Consequently, the Pearson’s correlation coefficient between the observation and the baseline simulation was 0.57 for hourly NO₂ concentrations and 0.80 for daily mean values. For O₃, high concentration peaks exceeding 100 ppb were observed on 8, 23 and 25 July, 2 and 3 August under clear sky and high temperature conditions. The baseline CMAQ simulation captured well the temporal variations including the occurrence of the O₃ concentration peaks. Consequently, the Pearson’s correlation coefficient between the observation and the baseline simulation was 0.87 for hourly O₃ concentrations, and the mean simulated daily maximum 1-h concentration (64.5 ppb) was close to the observed value (60.5 ppb). The performance evaluation of the baseline CMAQ simulation was described in greater detail in the previous study (Nishimura et al., 2015). The good CMAQ performance for urban O₃ simulation indicate that the model is applicable to estimates of the contribution of BVOC emissions to urban O₃ concentration.

Fig. 6 shows estimated contributions of BVOC emissions from the 10 source regions in D3 and from the entire D3 to simulated daily maximum 1-h O₃ concentration at the Kokusetsu Osaka station in the simulation period. The BVOC contributions to daily maximum 1-h O₃ concentration at the Kokusetsu Osaka station were large for emissions from Reg.4 including the station and Reg.3, 5, 6 and 7 surrounding Reg.4 with day-by-day variations of contributing source regions. The results indicate that the BVOC emissions in the Kinki region substantially contribute to urban O₃ concentration in Osaka. Considering the finding of Nishimura et al. (2015) that monoterpenes tended to play a role of reducing O₃ concentration in the baseline simulation, the BVOC contribution is dominated by O₃ produced through isoprene reactions.
Although the temporal variation of the sum of estimated BVOC contributions from Reg.1-10 was similar to that of the BVOC contribution from the entire D3, there were some discrepancies between the estimated BVOC contributions. The mean BVOC contribution to daily maximum 1-h O₃ concentration at the Kokusetsu Osaka station was 10.3 ppb (15.9%) for the sum of contributions from Reg.1-10 and 11.8 ppb (18.3%) for the contribution from the entire D3. This difference can be considered as an uncertainty of the estimated BVOC contribution by the zero-out emission method in this study, and is associated with nonlinearity in photo-

**Fig. 5.** Hourly time series of observed and simulated wind speed (a) and direction (b) at Osaka meteorological observatory, and NO₂ (c) and O₃ (d) concentrations (baseline case) at Kokusetsu Osaka air pollution monitoring station from 6 July to 9 August 2010.
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chemical O$_3$ production through NO$_x$ and VOC reactions, which has been discussed in a number of earlier literatures (e.g., Zhang et al., 2008; Sillman, 1999).

Fig. 7 shows horizontal distributions of O$_3$ concentration with wind fields and backward trajectories arriving at the Kokusetsu Osaka station on the days with relatively high concentration peaks (Fig. 5b; 14 local time (UTC+9) on 8 July, 15 local time on 23 July, at 14 local time on 2 August and 15 local time on 7 August). The backward trajectories make it easy to understand the transport pathway of an air mass arriving at the Kokusetsu Osaka station. Fig. 8 shows horizontal distributions of estimated contribution of BVOC emissions from the entire D3 to O$_3$ concentration in the same way as Fig. 7. BVOC emissions in D3 substantially contributed to high O$_3$ concentrations over Reg.4. The day-by-day variations of BVOC source regions contributing to O$_3$ concentration at the Kokusetsu Osaka station (Fig. 6) can be qualitatively explained by the backward trajectories. On 8 July, the air mass passed from Reg.5 to near the border of Reg.4, 6 and 7 before arriving at the Kokusetsu Osaka station (Fig. 7a), and the contributions of BVOC emitted from the regions were relatively large. On 23 July and 2 August, the trajectories indicated that air mass arriving at the Kokusetsu Osaka station was transported from the northwesterly direction (Fig. 7b and c), and the BVOC emissions from Reg.3 (the north from Reg.4) and Reg.5 (the west from Reg.4) showed relatively large contributions to O$_3$ concentrations at the station. On 7 August, the air mass passed from Reg.6 to Reg.4 (Fig. 7d), and the BVOC emissions from the regions contributed to O$_3$ concentration at the Kokusetsu Osaka station. In addition, on 16-19 July with prevailing southerly wind in D3 (not shown), although O$_3$ concentrations at the Kokusetsu Osaka were relatively low (Fig. 5d), the BVOC emissions from Reg.7 (the south from Reg.4) dominantly contributed to O$_3$ at the station among those from the 10 source regions.

3.2 Analyses on 23 July and 2 August with Especially High O$_3$ Concentrations

3.2.1 Results on 23 July and 2 August

The O$_3$ concentrations were especially high on 23 July and 2 August (Fig. 5d), with the daily maximum 1-h values being respectively 138.2 ppb at 15 local time and 147.3 ppb at 14 local time in the baseline simulation. However, the estimated BVOC contributions were quite different between 23 July and 2 August (Fig. 6). Among the 10 BVOC source regions, Reg.3 and Reg.5 mainly contributed to urban O$_3$ concentration in Reg.4 on the both days because of the similar transport direction of the air masses (Fig. 7b and c), whereas the contribution of BVOC on 23 July was much larger than that on 2 August. The contributions of BVOC from Reg.3, 4, 5 and 1-10 to daily maximum 1-h O$_3$ concentration at the Kokusetsu Osaka station were 11.4, 0.8, 15.5 and 35.4 ppb (8.2, 0.6, 11.2 and 25.6%) on 23 July, and 7.5, 4.8, 4.2 and 20.9 ppb (5.1, 3.3, 2.9 and 14.2%) on 2 August, respectively. Although the BVOC emissions were slightly larger on 23 July than 2 August (Fig. 4a), this difference does not explain the large difference in the BVOC contributions to O$_3$ concentration between the two days.

As shown in Fig. 7b and c, while high O$_3$ concentration was widely spread in the coastal areas including Reg.4 at 15 local time on 23 July, high O$_3$ concentration was limited only in Reg.4 at 14 local time on 2 August. As indicated by the transport distances on the trajectories, wind in morning to daytime on 2 August was weaker than on 23 July. Therefore, pollutants emitted in Reg.4 tended to be retained locally on 2 August. However, NO$_2$ concentration was higher on 23 July.
This was partly because NO\textsubscript{2} was efficiently accumulated in and around Osaka on 22 July which was a weekday compared to on 1 August which was a Sunday with smaller NO\textsubscript{x} emissions. Meanwhile, the increasing rate of NO\textsubscript{2} concentration from the midnight to morning was higher on 2 August (Fig. 5c). This may reflect nitrogen monoxide (NO) titration with O\textsubscript{3} under weak wind condition on 2 August. Additionally, in the daytime in summer, local photochemical activity under weak wind condition efficiently consume local NO\textsubscript{2} to produce O\textsubscript{3}. Aside from the condition in morning to daytime, air masses arriving at the Kokusetsu Osaka station at the times of the daily maximum O\textsubscript{3} concentrations were transported over Reg.5 during the midnight to early morning. Considering low BVOC emission rate and low photochemical activity during the midnight to early morning, the contributions of O\textsubscript{3} produced through BVOC reactions by the previous days are possibly important. The backward trajectory analyses indicate that the difference in the BVOC contributions on 23 July and 2 August may be partly attributed to the difference in the wind fields. The difference between the two days is further discussed in the following subsections.

**3.2.2 Contribution of AVOC and BVOC Emissions**

In order to further investigate the difference of the results on 23 July and 2 August, additional zero-out emission runs were performed in this subsection and the next. The contribution of AVOC emissions from
Reg.4 was estimated by conducting an additional zero-out case because the results described above showed the low BVOC contribution and the possibility of local pollution on 2 August.

Fig. 9 shows diurnal variations of the simulated O₃ concentration in the baseline case and estimated contributions of BVOC emissions from Reg.4, from Reg.3 and 5 and from the other 7 source regions in D3, and AVOC emissions from Reg.4 to the O₃ concentration at the Kokusetsu Osaka station on 23 July and 2 August. The daily maximum VOC contributions occurred before the time of the maximum O₃ concentrations on the both days. The difference between the baseline O₃ concentration and the sum of VOC contributions can be mainly explained by influence of transport from outside D3. The contribution of AVOC emissions from Reg.4 was less than or comparable to that of BVOC emissions from Reg.1-10 on 23 July. On the other hand, the contribution of AVOC emissions from Reg.4 was much larger than the BVOC contributions on 2 August. As well as the AVOC contribution from Reg.4, the BVOC contribution from Reg.4 on 2 August was larger than that on 23 July.

3.2.3 Contribution of VOC emitted by the previous days

The backward trajectory analysis indicated the possible importance of BVOC emitted by the day before
Additional zero-out cases for VOC emitted on 23 July and 2 August were conducted in order to distinguish the contributions of VOC emitted on the target days and by the days before to urban O₃ concentration on the target days.

Fig. 10 shows estimated contributions of BVOC emitted on the target day and by the day before from 10 source regions in D3, and AVOC emitted from Reg.4 to O₃ concentrations at Kokusetsu Osaka air pollution monitoring station on 23 July (a) and 2 August (b).

Fig. 9. Estimated contributions of BVOC emissions from Osaka Prefecture (Reg.4), from Kyoto (Reg.3) and Hyogo Prefecture (Reg.5), from the other 7 source regions in D3, and AVOC emissions from Reg.4 to O₃ concentrations at Kokusetsu Osaka air pollution monitoring station on 23 July (a) and 2 August (b).

23 July. Additional zero-out cases for VOC emitted on 23 July and 2 August were conducted in order to distinguish the contributions of VOC emitted on the target days and by the days before to urban O₃ concentration on the target days.

Fig. 10 shows estimated contributions of BVOC emitted on the target day and by the day before from Reg.1-10 in D3, and AVOC emitted from Reg.4 to O₃ concentration at the Kokusetsu Osaka station on 23 July and 2 August. BVOC emitted by the day before 23 July strongly affected the O₃ concentration on 23 July. As mentioned above, air masses arriving at the Kokusetsu Osaka station in the daytime on the day were transported over Reg.5 with large BVOC contributions.
during the midnight to early morning. Therefore, the contributions of BVOC emitted by the day before can be mainly explained by Oz produced by the day before rather than that on the day through the BVOC reactions. On the other hand, almost all the AVOC contributions from Reg.4 on the both days were accounted for by the emissions on the target days. This finding emphasizes the dominant contribution of local photochemical reactions on 2 August to urban Oz concentration in Osaka on the day.

3.2.4 Vertical Profile of BVOC Contribution

Fig. 11 shows altitude-local time cross sections of estimated contributions of BVOC emissions from the entire D3 to Oz concentration with planetary boundary layer (PBL) height at the Kokusetsu Osaka station on 23 July (a) and 2 August (b). While the BVOC contribution was distributed over PBL during the midnight to early morning on 23 July, there was little BVOC contribution at the same period on 2 August. This BVOC contribution on 23 July indicates that Oz produced through daytime BVOC reactions by the day before was retained over the nocturnal boundary layer. Considering the large contribution of BVOC emitted by the day before 23 July (Fig. 10a), the Oz retained over the nocturnal boundary layer contributed to the increase in the ground-level Oz concentration at the Kokusetsu Osaka station through vertical mixing in the daytime. Kiriyama et al. (2015) showed that Oz retained over the nocturnal boundary layer played an important role in increasing ground-level Oz in the inland of the Kanto region of Japan. This study also showed that Oz retained over the nocturnal boundary layer played similar role in increasing urban Oz in Osaka.

Overall, the urban Oz concentration in Osaka on 23 July was dominantly increased by the transport from the northwestern region outside Osaka with large contribution of Oz produced through BVOC reactions by the day before. On the other hand, the concentration on 2 August was dominantly increased by the local photochemical production inside Osaka with particularly large contribution of AVOC emitted on the day.

4. CONCLUSIONS

The WRF/CMAQ modeling system was used to estimate the contribution of BVOC emission sources in the Kinki region of Japan to urban Oz concentration in Osaka Prefecture in summer 2010. This prefecture is characterized by highly urbanized area with small forest area, but is surrounded by prefectures with large forest areas. The BVOC contribution to urban Oz was estimated by conducting zero-out cases for BVOC emissions for the 10 source regions in and around the Kinki region. The BVOC emissions substantially contributed to urban Oz concentration in Osaka with day-by-day variations of contributing source regions, which were qualitatively explained by the transport pathway of air masses shown by the backward trajectory analyses. The sum of BVOC contributions from each source region to mean daily maximum Oz concentration in
urban area in Osaka was 10.3 ppb (15.9%). Although O₃ concentrations were especially high on 23 July and 2 August, the contribution of BVOC emissions on 23 July was much larger than that on 2 August. The BVOC contributions to the daily maximum O₃ concentration on 23 July was 35.4 ppb (25.6%) and on 2 August 20.9 ppb (14.2%).

In order to further investigate the difference of the results on 23 July and 2 August, additional zero-out cases for AVOC emissions from Osaka and for VOC emissions from the 10 source regions on the target days were performed. These analyses revealed that the urban O₃ concentration in Osaka on 23 July was dominantly increased by the transport from the northwestern region outside Osaka with large contribution of O₃ produced through BVOC reactions by the day before, which was retained over the nocturnal boundary layer and transported to the ground-level through vertical mixing in the daytime. On the other hand, the concentration on 2 August was dominantly increased by the local photochemical production inside Osaka under weak wind condition with particularly large contribution of AVOC emitted from urban area in Osaka on the day.

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