Impact of biogenic volatile organic compound emissions on ozone formation in the Kinki region, Japan

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Abstract

The standard Biogenic Volatile Organic Compound (BVOC) emissions from ten Japanese plant species were measured by using a growth chamber where temperature and light intensity can be controlled. These species were selected due to their abundance in the estimated domain of the Kinki region. The BVOC emissions in Kinki region during July 2002 were estimated by revising the standard BVOC emissions from temperature and light intensity which were calculated by MM5. The two types of the ozone calculation were carried out by CMAQ. One was the calculation with BVOC emissions (BIO). Another was the calculation that assumes BVOC emissions to be zero (NOBIO). The maximum ozone concentrations of BIO reasonably reproduced the observed maximum concentrations in especially the fine days. The hourly differences of monthly average ozone concentrations between BIO and NOBIO had the maximum value of 6ppb at 2 p.m. The explicit difference appeared in urban area, though the place where the maximum of difference occurred changed. It was shown that the BVOC emitted from the forest area strongly affected the ozone generation in the urban area.

Keywords: biogenic volatile organic compound, ozone, MM5, CMAQ, growth chamber.

1 Introduction

The photochemical oxidant gives the damage to human and vegetations. In Japan the standard of the photochemical oxidant was regulated in 1970 and due to the useful countermeasure, the photochemical oxidant concentration had decreased until 1990. However, recently the photochemical oxidant concentration has been

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slowly increasing. The increase of the background ozone concentration due to the transboundary transport [1] is pointed out as one of the causes. From another view point, the temperature increase due to the global warming, the urban heat island and the increase of the ultraviolet rays [2] are also pointed out as one of the causes. It is well known that the biogenic volatile organic compound (BVOC) emissions increase accompanied with the temperature increase and that BVOC play the important role of the ozone generation. The BVOC emissions from the plants indigenous to Japan haven't enough been investigated, yet. In this study, the BVOC emissions from the dominant plants were obtained from the growth chamber experiment, the total emissions in the Kinki region were estimated, and the impacts of ozone generation due to the BVOV emissions were assessed by MM5/CMAQ.

2 Growth chamber experiment

2.1 Experimental procedure

Cryptomeria japonica, Chamaecyparis obtusa, Pinus densiflora, *Quercus serrata*, *Quercus crispula, Fagus crenata, Quercus acutissima Carruthers, Quercus glauca* and *Quercus myrsinaefolia,* the nine most abundant plants in the Kinki region, and *Oryza sativa* were selected. Emission measurements were performed by using a growth chamber that can manipulate temperature and light intensity. Plants were then adapted to the following experimental conditions: average temperature of Osaka and PAR was set at 1000 μmol m^{-2} s^{-1} from 6 a.m. to 6 p.m. In order to collect air samples in a growth chamber, a 200 mg Tenax-TA adsorbent tube (Supelco, mesh 60/80) and a vacuum pump (GL Science SP208-1000Dual) with a flow rate of 100 ml min^{-1} were used. The trapped compounds into adsorbent tubes were thermally desorbed at 280ºC by Thermal Desorber (Perkin Elmer ATD-50) connected to GC/MS (Shimadzu GC/MS-QP2010). Isoprene, α-pinene, β-pinene, myrcene, α-phellandrene, α-terpinene, p-cymene, limonene, γ-terpinene and terpinolene were analyzed [3].

2.2 Experimental results

The experiments for ten plant species conducted at several conditions, which were different from temperatures and light intensities. The BVOC emission from ten plant species at several conditions were converted to the standard condition (30ºC, PAR: 1000 μmol m^{-2} s^{-1}) by using the Guenther equation [4] and Tingey equation [5]. Table 1 shows the monoterpenes emission at standard conditions. Table 2 shows the isoprene emission at standard conditions from six deciduous broadleaf trees, which are commonly found in Japan. A large amount of α-pinene and β-pinene was detected from *Cryptomeria japonica, Chamaecyparis obtusa* and *Pinus densiflora*. Previously, *Oryza sativa* has not been reported to emit BVOC, but five kinds of monoterpenes were detected. This detection could be very significant even though the amount is small because a large part of Japan is covered by paddy fields. A large amount of isoprene was detected from *Quercus serrata*.

Table 1: BVOC emissions from Coniferous trees at standard condition [30ºC, PAR: 1000 μ mol m^{-2} s^{-1}].

compound	BVOC emissions [μg $g_{dw}^{-1}h^{-1}$]			
	Cryptomeria japonica	*Chamaecyparis obtusa*	*Pinus densiflora*	*Oryza sativa*
α-pinene	1.30	1.89	5.33	0.24
β-pinene	0.06	0.22	0.84	0.02
Myrcene	0.32	0.35	1.79	0.03
α-phellandrene	0.20	0.13	0.87	ND
α-terpinene	0.15	0.13	0.23	ND
p-cymene	0.10	0.28	0.14	0.03
Limonene	0.40	ND	0.82	0.08
γ-terpinene	0.21	0.49	ND	ND
Terpinolene	0.08	ND	0.27	ND
Total monoterpenes	2.81	3.48	10.28	0.40

Table 2: Isoprene emissions from broadleaf trees at standard condition [30ºC, PAR: 1000 μ mol m^{-2} s^{-1}].

Plants name	Isoprene emission [μg $g_{dw}^{-1}h^{-1}$]
Quercus serrata	224.21
Quercus crispula	26.04
Fagus crenata	0.79
Quercus acutissima Carruther.	0.18
Quercus glauca	0.04
Quercus myrsinaefolia	0.03

3 Estimation of BVOC Emissions in the Kinki Region

3.1 Standard estimation

At first the emissions of isoprene and monoterpene at the standard conditions in the Kinki regions were estimated by using the forest database including dominant specie of plant, an area, an age, a biomass and so on, In the Kinki region, the deciduous biomass was 1.7 times larger than the broadleaf biomass but *Quercus serrata* emitted a large amount of isoprene. Therefore the emissions of isoprene were extremely larger than the emissions of monoterpene as shown in Fig.1 and Fig.2.

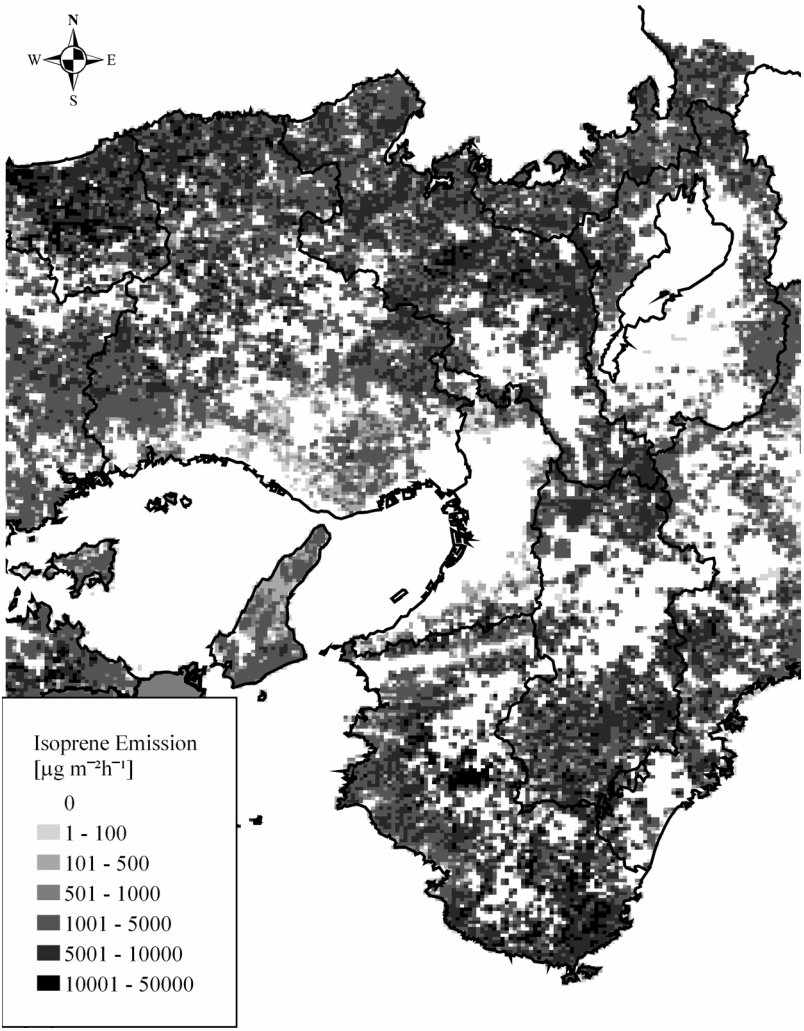

Figure 1: Standard emissions of isoprene in Kinki region.

3.2 Hourly emission

Emissions of isoprene and monoterpene vary according to the hourly variations of temperature and light intensity. The emissions on July 2002 were revised from the temperature and light intensity which were calculated by using MM5 (Meteorological Model version 5). Guenther equation for isoprene and Tingey equation for monoterpene were used to calculate the emissions variation due to temperature and light intensity. The equation of isoprene emissions E_{iso} are expressed by

$$E_{iso} = EF_{iso} \cdot C_T \cdot C_L \quad (1)$$

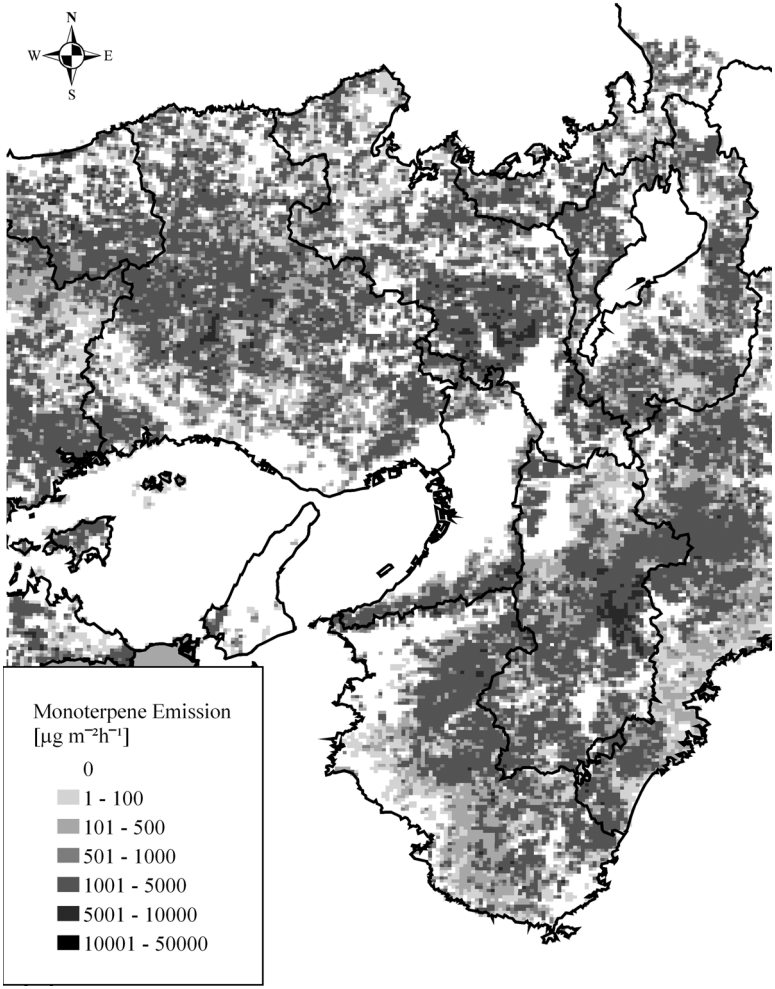

Figure 2: Standard emissions of monoterpene in Kinki region.

where EF_{iso} (μg g_{dw}^{-1} h^{-1}) is the isoprene emission rate at standard conditions. C_T is the correction factor due to temperature and C_L is the correction factor due to PAR. C_T and C_L are defined by

$$C_T = \frac{\exp\frac{C_{T1}\cdot(T-T_s)}{R\cdot T\cdot T_s}}{1+\exp\frac{C_{T2}\cdot(T-T_m)}{R\cdot T_s\cdot T}} \tag{2}$$

$$C_L = \frac{\alpha\cdot C_{L1}\cdot L}{\sqrt{1+\alpha^2\cdot L^2}} \tag{3}$$

where α (0.0027), C_{L1} (1.066), C_{T1} (95000 J/mol), C_{T2} (230000 J/mol) and T_m (314 K) are empirical coefficients, L (μmol m^{-2} s^{-1}) is the PAR flux, T_s (303 K) is the standard reference temperature, R (8.314 J K^{-1} mol^{-1}) is the ideal gas constant and T (K) is the foliar biomass temperature.

The equation of monoterpene emissions E_{mono} are expressed by

$$E_{mono} = EF_{mono} \cdot \exp(\beta \cdot (T - T_s)) \quad (4)$$

where EF_{mono} (μg g_{dw}^{-1} h^{-1}) is the monoterpene emission rate at standard temperature. β is an empirical coefficient ranging between 0.057 and 0.144 K^{-1}. β can vary according to chemical species and environmental conditions. 0.09^{-1} is a reasonable estimate for monoterpene emissions of most plants.

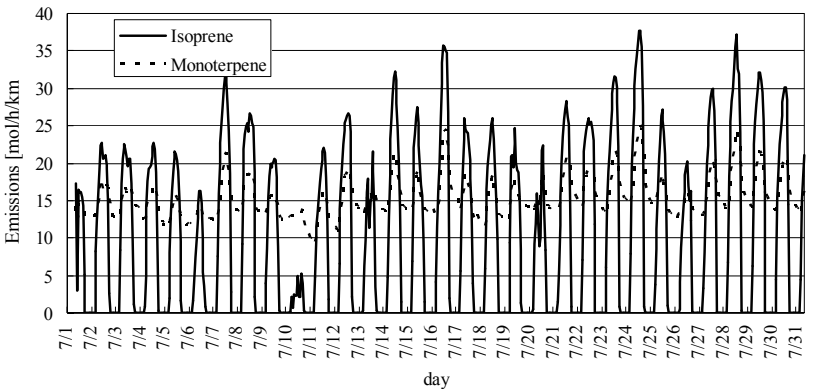

Figure 3: Hourly variations of isoprene and monoterpene.

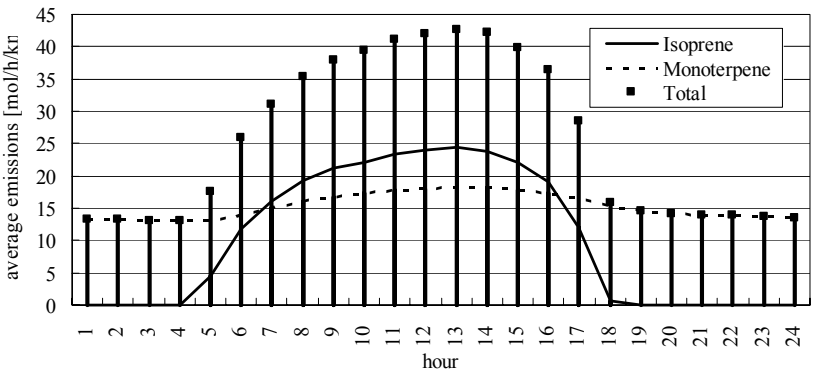

Figure 4: Hourly average emissions.

The hourly variations of isoprene and monoterpene on July 2002 are shown in Fig.3. As there were many days of cloudy or rainy in the first half of this month, the emissions were relatively low. The hourly average emissions are shown in Fig.4. In the daytime, isoprene and monoterpene emissions were almost same, but only monoterpene emitted in the night time.

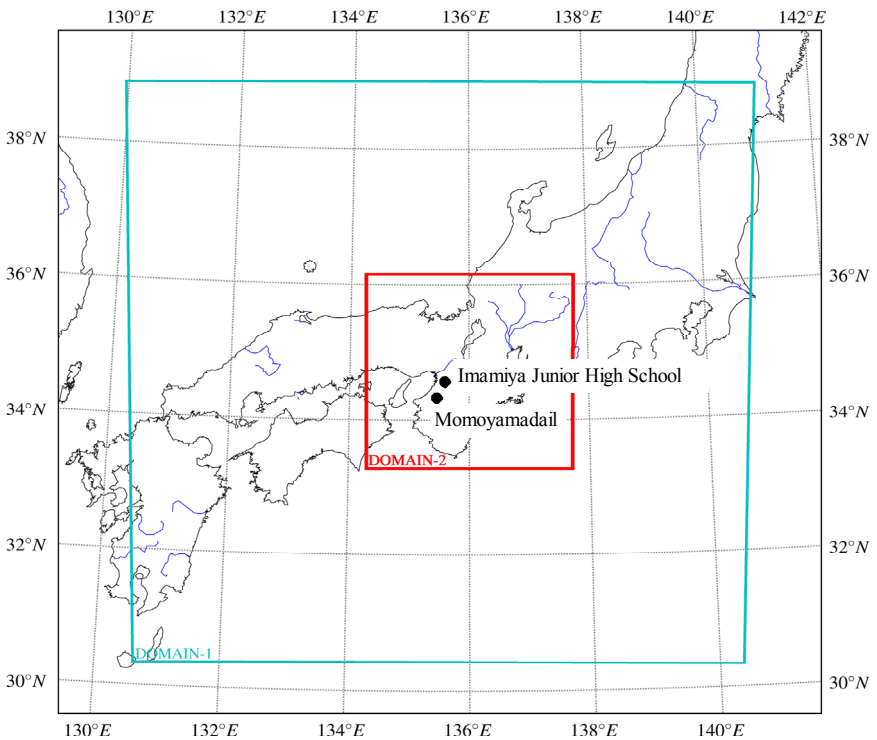

Figure 5: Calculated domain.

4 Impact of BVOCs on ozone concentrations

Ozone concentrations were calculated by MM5/CMAQ (Community Multiscale Air Quality). The Grid Point Value–MesoScale Model (GPV–MSM) data from the Japan Meteorological Agency (JMA, http://www.jma.go.jp/jma/index.html) were assimilated as objective analysis data. The data are available for the Japan region and have a high horizontal resolution of 10 km × 10 km. The calculated region is shown in Fig.5. The domain-1 has the resolution of 9 km and includes almost whole of Japan. The domain-2 has the resolution of 3 km and includes all of the Kinki region. The two types of the calculation for one month of July 2002 were carried out. One is the calculation with BVOC emissions (BIO). Another is the calculation that assumes BVOC emissions to be zero (NOBIO).

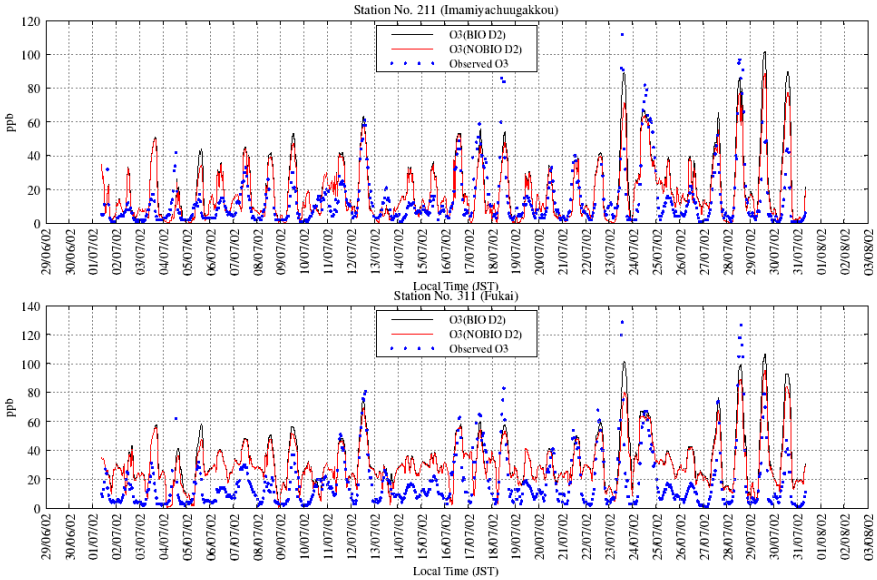

Figure 6: Calculated and observed ozone concentration at Imamiya Junior High School and Momoyamadai.

Table 3: Statistical results of BIO and NOBIO.

Metrics		BIO	NOBIO
Correlation Coefficient		0.41	0.37
Mean Bias	MB	-0.81	-6.03
Mean Normalized Bias	MNB	0.03	-0.06
Normalized Mean Bias	NMB	-0.01	-0.1
Normalized Mean Bias Factor	NMBF	-0.01	-0.11

4.1 Comparison with observations

The calculated ozone concentrations were compared at two observatories; Imamiya Junior High School and Momoyamadai, where the relatively high concentrations were observed. Imamiya Junior High School is located at the center of Osaka City and Momoyamadai is located at the southern part of Osaka Prefecture. The high ozone concentrations were observed on 23, 27, 28, 29, 30, and 31 July as shown in Fig.6. These days were clearly fine and the temperature was relatively high and the light intensity was strong. Consequently a lot of BVOC emitted from the forest area. The ozone concentrations of BIO became higher than NOBIO and reasonably reproduced the observed concentrations. For one example, the observed ozone concentration and the ozone concentration of BIO and NOBIO at Imamiya Junior High School on 23 July were 122 ppb, 110 ppb and 84 ppb, respectively. This means that the BVOC emissions make ozone

concentration of 26 ppb increase. In the first half of this month when BVOC emissions were rather small due to the cloud days, the differences between the ozone concentration of BIO and NOBIO can't be seen.

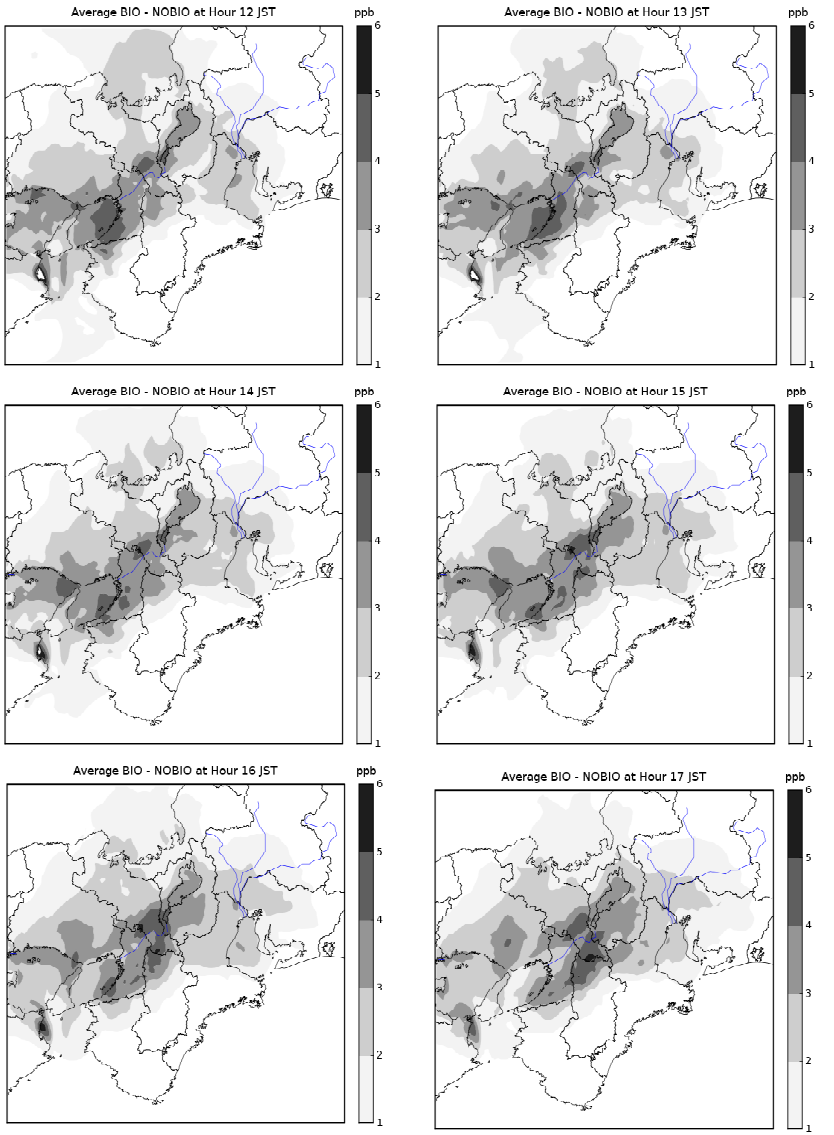

Figure 7: The hourly differences of monthly average ozone concentrations between BIO and NOBIO.

The statistical results are shown in Table 3. The correlation coefficient of BIO was improved to 0.41 from 0.31 (p<0.05) and the mean bias was also improved to -0.81 ppb from -6.05 (p<0.01). Mean normalized bias (MNB), normalized mean bias (NMB) and normalized mean bias factor (NMBF) which are the evaluation index for the ozone prediction by EPA were enhanced.

4.2 Impact of BVOCs on air pollutants concentrations

The hourly differences of monthly average ozone concentrations between BIO and NOBIO were investigated. As the photochemical reaction doesn't occur at night, ozone concentrations of BIO and NOBIO were almost the same. From sunrise, the difference of ozone concentrations appeared and it reached 6ppb at 2 p.m. when the temperature rose. The situation continued until 6 p.m. The differences of ozone concentrations at 12 a.m – 5 p.m. are shown in Fig.7. The difference appeared in the urban area, though the place where the maximum difference occurred changed. In all cases the maximum difference emerged in the border of Osaka City where a lot of NOx was emitted. It was shown that the BVOCs emitted from the forest area strongly affected the ozone generation in the urban area.

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