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Comparison of Surface Ozone Simulation among Selected Regional Models in MICS-Asia III – Effect of Chemistry and Vertical Transport for the Causes of Difference-

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Abstract

In order to clarify the cause of variability among the model outputs for surface ozone in the Model Intercomparison Study Asia Phase III (MICS-Asia III), three regional models, CMAQ v.5.0.2, CMAQ v.4.7.1 and NAQPMS (abbreviated as NAQM in this paper) have been selected. The detailed analyses have been made for monthly averaged diurnal variation for select grids covering metropolitan area of Beijing and Tokyo, and at a remote oceanic site, Oki. The chemical reaction mechanism, SAPRC99 used in the CMAQ models tends to give higher net chemical ozone production than CBM-Z used in NAQM agreeing with previous studies. Inclusion of heterogeneous "renoxification" reaction of HNO_3 (on soot) → NO + NO_2 only in NAQM is supposed to give higher NO concentration to give better agreement with observational data for NO and nighttime O_3 mixing ratios. In addition to chemistry, the difference in vertical transport of O_3 was found to affect the simulated results significantly. Particularly, the increase in downward flux of O_3 from upper layer to the surface after the dawn is found to be substantially different among the models. Larger early morning vertical transport of O_3 by CMAQ 5.0.2 would be the reason for higher daytime O_3 by this model in July. All the three models overestimate the daytime ozone by ca. 20 ppbv at the remote site Oki in July, where in situ photochemical activity is minimal.

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Introduction

In the Model Intercomparison Study Asia Phase III (MICS-Asia Phase III), one of the targets was to narrow down the difference in the model simulation results by using the common key input parameters such as precursor emissions, meteorological fields, and boundary conditions to allow more focused discussion on the causes of the difference among model outputs. In most of the past model intercomparison studies for chemical transport models (CTM) for air quality, such key parameters were not common to all the models, which makes difficult the discussion of the causes of the differences among the model outputs, and the results have often been shown to demonstrate that the ensemble mean of simulated mixing ratios agrees reasonably well with observation even though the disagreement among the models are often significantly large (for example, Han et al., 2008; Fiore et al., 2009).

In order to improve the situation of model intercomparison study, participants of the MICS-Asia III studies agreed to use the common emission data (Li, M. et al., 2017), meteorological field (specified Weather Research and Forecasting Model (WRF)) and the boundary conditions by either of two global CTM (GEOS-Chem and CHASER) provided within the project (Wang et al. overview paper to be submitted; Li, J. et al. in this special issue, to be submitted). The following 12 regional models have been submitted to the MICS-Asia III using the designated common emissions, meteorological field and boundary conditions; six WRF-CMAQ (Community Multiscale Air Quality Modeling System, two v.5.0.2, one v.5.0.1 and three v.4.7.1), four WRF-Chem (Weather Research and Forecasting (WRF) model coupled with Chemistry), one WRF-NHM (JMA NonHydrostatic Model)/Chem and one WRF-NAQPMS (Nested Air Quality Prediction Modeling System, which is abbreviated to NAQM in this paper hereafter for simplicity). It turned out, however, that even though these 12 models uses the common specified key input components, large variability in the spatial distribution and absolute mixing ratios among the models were found for ozone (O_3) (Li, J. et al., in this special issue).

In the present study, three regional models, two WRF-CMAQ, v.5.02 and v.4.7.1, and WRF-NAQM were selected among the 12 models to elucidate the causes of difference, and detailed comparison have been made for the selected grids covering metropolitan areas in Beijing and Tokyo, and at a remote oceanic site at Oki in April and July. The reason of the selection of the two models of CMAQ is that CMAQ models have been used widely to assess the air quality for ozone in Asia (e.g. Yamaji et al., 2008; Kurokawa et al., 2009; Fu et al., 2012), and the difference of the simulated results between different version (v. 5.02 and v.4.7.1)

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is of concern. The selection of WRF-NAQM is that this is one of the regional CTM developed in Asia, and give substantially lower mixing ratios of surface ozone as compared to the most of WRF-CMAQ including the selected two models (Li, J. et al., in this special issue). The metropolitan areas of two megacities of Beijing and Tokyo have been selected for the comparison because of the concern on the application of the regional models to the mitigation policy of urban ozone pollution. Oki, an EANET (Acid Deposition Monitoring Network in East Asia) monitoring station located in the southern part of the Sea of Japan, is selected as a remote reference site between the two megacities, where in situ photochemical production of O_3 is known to be minimal (Jaffe et al., 1996). April and July have been selected as months for comparison since in situ photochemical production of O_3 is expected to be substantial in July in Beijing and Tokyo, whereas it is thought to be much less in April.

Models

Basic features and the simulated whole domain of the regional models used in this study, CMAQ v.4.7 (Foley et al., 2010), v.5.0 (CMAS, 2011), and NAQM (Li, J. et al., 2012) are given elsewhere in this issue (Li, J. et al., in this special issue). The employed horizontal resolution is 45 km for all the models, and the highest height and number of vertical layers are 45 km and 40 layers for the CMAQ models and 20 km and 20 layers for the NAQM so that the vertical resolution in the troposphere is about the same. The lowest layer for which the simulated data of ozone were extracted in this paper has the vertical height of ~50 m from the ground. Model calculations by the CMAQ v. 5.0.2, v.4.7.1, and NAQM were conducted at University of Tennessee, National Institute for Environmental Studies, and Institute of Atmospheric Physics, respectively. All the models used the common meteorological fields from WRF (Wang et al., overview paper in this special issue) simulation and common emissions of MIX (0.25°× 0.25°) for 2010 (Li, M. et al., 2017) developed in the MICS-Asia III project. The initial and boundary conditions were supplied by the global models, CHASER for CMAQ v.4.7.1 and NAQM, and GEOS-Chem for CMAQ v.5.0.2. It has been approved that either CHASER or GEOS-Chem may be used in the MICS-Asia III since they were confirmed to give reasonably good agreement for the O_3 field in the Asian domain (Wang et al., overview paper in this special issue).

Other than these three key components (emissions, meteorological field, and boundary conditions), the three models employed different sub-models and parameters for i.e. the gas-phase and aerosol chemistry module, dry deposition parameters, boundary layer scheme, etc.

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As for the gas-phase chemistry, CMAQ v.4.7.1 and v.5.0.2 incorporated SAPRC99 (Carter, 2000), and NAQM employed CBM-Z (Zaveri and Peters, 1999). In the CMAQ v.4.7.1 (Foley et al., 2010), major upgrades were made on the aerosol treatment from the previous version of CMAQ: (a) updates to the heterogeneous N_2O_5 parameterization, (b) improvement in the treatment of secondary organic aerosol (SOA), (c) inclusion of dynamic mass transfer for coarse-mode aerosol, and (d) revisions to the cloud model. The NAQM and CMAQ v.4.7.1 employed ISORROPIA v.1.7 (Nenes et al, 1998) and CMAQ v.5.0.2 incorporated ISORROPIA v.2.1 (Fountoukis and Nenes, 2007) for inorganic aerosol chemistry modules. In addition, CMAQ v.4.7.1 and v.5.0.2 included AERO6 (Binkowski and Rosselle, 2003) as an organic aerosol chemistry module. As for the advection module, Yamartino (1993), and Walcek and Aleksic (1998) were used for CMAQ (v.4.7.1 and v.5.0.2) and NAQM, respectively. Sub-modules for vertical diffusion, dry deposition, and wet deposition employed in the three models are essentially the same. The Asymmetric Convective Model version 2 (ACM2) for the planetary boundary layer (PBL) (Pleim, 2007) has been employed both in CMAQ v.4.7.1 and v.5.0.2. The Yonsei University (YSU) Boundary Layer (BL) scheme is used for calculating BL height for NAQM (Li, J. et al., 2012).

Comparison Domain and Observational Data

All the comparisons among the model simulation and with observational data are made for monthly averaged diurnal variations for the mixing ratios of O_3, and NO in April and July. April and July are chosen here since in April in situ photochemical buildup of O_3 is insignificant but the daytime maximum mixing ratio of O_3 is relatively high reflecting the well known spring maximum of O_3 for the background in the northern hemisphere including East Asia (Monks, 2000; Pochanart et al., 2003), while in July much higher in situ photochemical build up of O_3 is expected in urban areas in East Asia. Two representative megacities of Beijing and Tokyo has been selected as urban areas for the comparison. As a remote reference site, Oki, an EANET site, was selected between Beijing and Tokyo. Oki site is located on a cliff of an island where the local emissions of NO_x and VOCs are insignificant so that in situ production of O_3 is also minimal (Jaffe et al., 1996; Pochanart et al., 2002). Since the NO levels at Oki are too low to get the meaningful data by the conventional chemiluminescence NO_x instrument used for monitoring, comparison with modeling results are made only for O_3 at this site. All the calculations were conducted for a whole year of 2010 using the meteorological field and the emission data for this year.

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The domains of Beijing and Tokyo and Oki site are centered at 39.9°N, 116.3°E; 36.0°N, 139.3°E and 36.3°N and 133.1°E, respectively. The selected domains for Beijing and Tokyo consist of 9 (3×3), and 3 (2+1) grids, respectively, covering the metropolitan areas of the cities as shown in Fig. 1. Data of a single grid covering the island is used for the Oki site. The observational data used for Tokyo are 1-hr averaged values in 2010 of the average of 118 (for O_3) and 126 (for NO) non-roadside monitoring stations within the selected grid shown in Fig. 1. The data were obtained from Atmospheric Environment Monitoring Data Files in the Environmental Information Database stored in the National Institute for Environmental Studies (NIES), Japan. In Beijing, unfortunately, no routine monitoring data of 1-hr averaged values of O_3 in 2010 is open to the public. Therefore, the unpublished data obtained at two sites (IAP tower campus and Yangfang) obtained by IAP, and literature values published in Xu et al. (2011) and Chen et al. (2015) have been referred in this work. The observational data for Oki is the 1-hr averaged EANET data in 2010 provided on request by the Network Center, Asia Center for Air Pollution Research (ACAP) (http://www.acap.asia).

Fig. 1

Results

Figures 2(a)-(d) depicts the simulated and observed mixing ratios of the monthly averaged diurnal variations of the O_3 and NO concentrations in April and July in Beijing, and Fig. 3(a)-(d) shows the similar results in Tokyo. The comparisons of the simulated values by the CMAQ 5.0.2 and 4.7.1 (hereafter, "v." for version will be omitted for simplicity) and NAQM, and are plotted in each figure together with the observational data.

Fig. 2
Fig. 3

In Beijing, unfortunately observational data of surface ozone at the routine monitoring stations by the Beijing municipal government is not available until 2013 (Chen et al., 2015). The average of two observational data obtained by IAP in 2010 is plotted by the dashed lines with circles in Figs. 2(a) and (b) for O_3 and in Figs. 2(c) and (d) for NO. Another published observational data of diurnal variation of O_3 in Beijing in April is available by Xu et al. (2011) at four sites, two urban (Fengtai and Baolian), one suburban (Shunyi), and one rural (Shangdianzi) in summer (21 June-12 September, mainly covering July and August) in 2007. Since the diurnal variation of the urban and suburban sites are consistent, the average of these three sites are plotted in Fig. 2(b) by a dashed line with triangles. In April in Beijing no monthly average diurnal variation of O_3 is available in a literature. Chen et al (2015) reported the monthly averaged daily maximum mixing ratio of O_3 ca. 60 ppbv at an urban site (Dongsi), and ca. 75 and ca. 65 ppbv at two suburban sites (Daxing and Shunyi) within the selected grids in

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this study. If we simply take the average of these three values, the daily maximum mixing ratio is ca. 65 ppbv (not shown in Fig. 2(a)). Only the IAP data are plotted for NO with solid lines in Fig. 2(c) and (d).

As can be seen in Figs. 2(a), (b), and Figs. 3(a), (b), the diurnal pattern of the simulated surface ozone shows the maximum at late afternoon around 14-16 o'clock of the local time both in Beijing and Tokyo agreeing well with the observation. The simulated mixing ratios of O_3 by CMAQ 4.7.1 are the highest, and those by NAQM are the lowest both in Beijing and Tokyo and in April and July in common. The diurnal variations of O_3 simulated by CMAQ 4.7.1 is in parallel with NAQM for whole days in all cases, but the predicted mixing ratios by CMAQ 4.7.1 are by ca. 20 ppbv and ca. 40 ppbv higher than NAQM in April and July, respectively, both in Beijing and Tokyo. The O_3 mixing ratios predicted by CMAQ 5.0.2 has a peculiar characteristics by season, i.e. the mixing ratio is slightly higher but close to NAQM within 10 ppbv both in Beijing and Tokyo in April, whereas in July the daytime O_3 maximum by CMAQ 5.0.2 is very close to CMAQ 4.7.1, much higher than NAQM. In Tokyo, the simulated mixing ratios of CMAQ 5.0.2 and NAQM are closer to the observation in April, and NAQM gives closer matching with observation in July, while CMAQ 4.7.1 overestimates in both months as shown in Figs. 2 (b) and 3(b). Comparison with the observation will be discussed later including the uncertainty of the observational data in Beijing.

The observed mixing ratios of NO shows a peak value at around 7 am, decreases during morning followed by a slow decay in the afternoon, and starts to build up during nighttime both in April and July, and in Beijing and Tokyo. The peak values of mixing ratio in the morning are ca. 13-14 and 6 ppbv in April and ca. 11 and 5-6 ppbv in July in Beijing and Tokyo, respectively. The minimum mixing ratios in the evening are ca. 1.7 and 1.4 ppbv in April and 2.3 and 1.3 ppbv in July in Beijing and Tokyo, respectively. Thus, it can be noted that the NO mixing ratios in Beijing are nearly a double of Tokyo.

The simulated mixing ratios of NO are generally in the order of NAQM > CMAQ 5.0.2 > CMAQ 4.7.1., but are much diverse among the models. In April, CMAQ 5.0.2 gives a morning peak values of 13-14ppbv and ca. 5 ppbv in Beijing and Tokyo, respectively, which agrees well with observation. NAQM overpredicts NO missing ratio in April in Beijing but gives reasonable agreement in Tokyo as shown in Figs 2(c) and 3(c). In contrast, CMAQ 4.7.1 gave a broad daytime peak of only ca. 2 and ca. 1 ppbv in April in Beijing and Tokyo, respectively, which is quite different from other models and much underpredicts the observational data. In July, only NAQM gives a morning peak mixing ratio of ca. 8 and 5.5 ppbv in Beijing and Tokyo agreeing

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196 fairly well with the observation including diurnal variation as seen in Figs. 2(d) and 3(d). In
197 contrast, both CMAQ 5.0.2 and 4.7.1 give a morning peaks as low as 1-2 ppbv and nearly zero
198 mixing ratio during nighttime, which are significantly lower than the observation.
199 It can be noted that the simulated and observed levels of O_3 is highly anti-correlated with
200 those of NO. For example, the reasonably good agreements of O_3 by CMAQ 5.0.2 and NAQM
201 in April, and by NAQM in July in Tokyo correspond to the reasonably good agreement of NO
202 in each case. Much higher overestimate of O_3 by the CMAQ 4.7.1 in April and by both the
203 CMAQ 5.0.2 and 4.7.1 in July correspond the substantial underestimate of NO.
204 Figures. 4(a) and (b) shows monthly averaged diurnal variation of O_3 mixing ratios at Oki in
205 April and July, respectively. As shown in Fig. 4(a), all the three models give consistent mixing
206 ratios of O_3 at 60-65 ppbv in April, which agree well with observation within 10 ppbv. In July,
207 although the simulated mixing ratios of O_3 agree well each other within 10 ppbv, they are in the
208 range of 50-70 ppbv as compared to observational level of 35-45 ppbv. Thus, all the three
209 models overestimate the O_3 mixing ratio by nearly 20 ppbv. Although the characteristics of
210 remote sites showing only a slight daytime build up of O_3 is well reproduced by the models,
211 substantial overestimate of the simulated O_3 mixing ratio compared to the observation should be
212 of concern in July.
213

Fig. 4

214 **Discussion**
215 The causes of the differences of the simulated results among the three models mentioned
216 above must be due to either chemistry or transport processes incorporated in the models. Here,
217 the possible causes of differences of those processes are discussed individually.

218 **Comparison of Chemical Mechanism Sub-Modules**
219 One of the differences in the three models in this study is the chemical reaction mechanism
220 sub-module. CMAQ 5.0.2 and 4.7.1 incorporate SAPRC99 while NAQM employs CBM-Z. It
221 has been well known that different photochemical mechanisms used in the regional chemical
222 transport models produce dissimilar results on the prediction of O_3. Jimenez et al. (2003)
223 compared seven photochemical mechanisms including CBM-IV (Gery et al., 1989) and
224 SAPRC99 using a box model. Comparison of CBM-IV, CBM-V (Sarwar et al., 2008) and
225 SAPRC99 incorporated into a regional chemical transport models have been made by Faraji et
226 al. (2007) and Luecken et al. (2008). The main difference among these mechanisms has been
227 noted to be the lumping technique describing organic compounds into surrogate groups

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(Jemenez et al., 2003), the differences in the products of the reaction of aromatics with OH radical, and the overall branching ratio of radical generation and termination reactions (Faraji et al., 2007). The results of these studies gave a consistent picture that SAPRC99 gives higher concentrations of O_3 than CBM-IV both in the box model calculation and regional model simulation over United States. The O_3 concentration obtained by CBM-V is reported to be in between the CBM-IV and SAPRC99 (Luecken et al., 2008). The reason for giving the higher concentration of O_3 by SAPRC99 has been deduced to be due to the more efficient peroxy radical production in the photochemical reaction scheme of SAPR99 compared to CBM modules.

Figures 5 (a)-(d) show the net chemical production of O_3 in Beijing and Tokyo in April and July calculated in this study. As revealed in the figure, CMAQ models give higher net ozone production than NAQM, which is consistent with the results of earlier studies showing photochemical reaction scheme of SAPRC99 gives higher O_3 production than CBM modules. The reaction scheme of CBM-Z is the revision of CBM-IV, and the major revision is described as (1) including revised inorganic chemistry, (2) explicit treatment of lesser reactive paraffins, (3) revised parameterization for reactive paraffin, olefin, and aromatic reactions, (4) inclusion of alkyl and acyl peroxy radical interactions and their reaction with NO_3, (5) inclusion of organic nitrates and hydroperoxides, and (6) refined isoprene chemistry. Although intercomparison including CBM-Z has not been reported, the overall photochemical reactivity would be assumed to be similar to CBM-V, which gives higher and lower O_3 than CBM-IV and SAPRC99, respectively. Thus, maximum values of daytime net O_3 production of CMAQ 5.0.2 and 4.7.1 in July are ca.10 and 7-9 ppbv hr^{-1} as compared to ca. 6 and ca. 2 ppbv hr^{-1} by NAQM in Beijing and Tokyo, respectively, showing the substantially larger values for CMAQ than NAQM. It can be noted that net O_3 production of NAQM shows a second peak in early morning after breaking of dawn in both Beijing and Tokyo in July, which would be a cause of overestimate of O_3 in the morning by NAQM simulation as seen in Fig. 2(b) and Fig. 3(b). The cause of the early morning peak of net O_3 production in NAQM might be due to the photolysis of higher HONO that is produced by the heterogeneous reaction of NO_2, although it has not been quantified in the present study.

Fig. 5

In April, net chemical production of O_3 is in general negative for all the models both in Beijing and Tokyo except for CMAQ 4.7.1 around midday and NAQM in early morning showing slight positive values. Tendency of higher net O_3 production is seen particularly for CMAQ 4.7.1, which may be the main cause of higher O_3 by this model both in Beijing and

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Tokyo in April as seen in Fig. 2(a) and Fig. 3(a). The daytime net O_3 production of CMAQ 5.0.2 is similar to CMAQ 4.7.1 in July, but is substantially lower in April. Since the chemistry mechanism of SAPRC99 is used in common to the both CMAQ, the difference may be related to the vertical transport of some relevant species.

Effect of heterogeneous "renoxification" reaction of HNO_3

Figures 2 and 3 show the common feature of anti-correlation of concentrations of O_3 and NO as noted above. This feature is most clearly seen for the comparison of concentrations of O_3 and NO in July in both cities demonstrating the large overestimate of O_3 and large underestimate of NO by CMAQ 4.7.1 and 5.0.2, while the much lower O_3 and much higher NO are estimated by NAQM. The situation in April also supports this contention.

It should be noted that rate constants of the most sensitive gas-phase reactions affecting the balance of O_3 and NO (Finlayson-Pitts and Pitts, 2000; Akimoto, 2016) such as,

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (1)$$

$$NO + HO_2 \rightarrow NO_2 + OH \quad (2)$$

$$NO + RO_2 \rightarrow NO_2 + RO \quad (3)$$

have been well established (Burkholder et al., 2015 and earlier evaluations of the series) and more or less the same reaction rates are employed in both of SAPRC99 and CBM-Z. As for the heterogeneous processes affecting NO_x, the reaction,

$$N_2O_5 + H_2O \text{ (on particle)} \rightarrow 2\ HNO_3 \quad (4)$$

is included in common in the heterogeneous inorganic chemistry sub-module, ISORROPIA and employed in the CMAQ and NAQM models.

It has been noted that the simulated gaseous HNO_3 concentration and HNO_3/NO_x ratio by use of global and regional chemical transport models were found to be 2-10 times higher than the observatiional data during the PEM-West (Singh et al., 1996), TRACE-P (Talbot et al., 2003), and PEM-Tropics A and SONEX (Brunner et al., 2005) aircraft campaigns over the Pacific and Atlantic Ocean. It has also been reported by the ground observations in the remote troposphere at Mauna Loa (Hauglustaine et al., 1996) and in the polluted boundary layer of Beijing-Tianjin-Hebei region (Li, Y. et al., 2015).

Another concern on recent NO_x chemistry has been focused on the high concentration of HONO in the urban atmosphere, which is thought to be produced by heterogeneous reaction of NO_2 and H_2O on the aerosol and ground surface (for example, Li, Y. et al., 2011; Gonçalves et al., 2012; Wong et al., 2013). Inclusion of the additional heterogeneous source of HONO not

only affects the photochemical O_3 formation due to the increase of OH radicals but also increase HNO_3 due to the increase of the reaction, $OH + NO_2 + M \rightarrow HNO_3 + M$. Li, Y. et al. (2015) has shown that the inclusion of heterogeneous formation of HONO gives more HNO_3, which tends to give more overestimate of gaseous HNO_3 in Beijing-Tianjin-Hebei region.

In order to solve the problem of overestimation of HNO_3, heterogeneous reaction of HNO_3 on soot to reproduce NO and NO_2 has been proposed as "renoxification" process early by Lary et al. (1997) in the analysis of the above aircraft observation data. The heterogeneous reaction of HNO_3 on soot to produce NO/NO_2 has been confirmed experimentally in the laboratory studies (Disselkamp et al., 2000; Muñoz and Rossi, 2002), although the product ratio and reaction mechanism has not been well established yet. The steady state uptake coefficient γ_{ss} of this reaction has been reported to be $(4.6 \pm 1{,}6) \times 10^{-3}$ for black soot using geometric surface area (Muñoz and Rossi, 2002).

Only NAQM among the three models studied here incorporates the following heterogeneous non-stoichiometric reactions on soot (Li, J. et al., 2015).

$$HNO_3 + \text{soot} \rightarrow \rightarrow NO + NO_2 \qquad (5)$$

$$NO_2 + \text{soot} \rightarrow \rightarrow 0.5\ HONO + 0.5\ HNO_3. \qquad (6)$$

with $\gamma_{HNO3} = 3.0 \times 10^{-3}$ for Reaction (5) and $\gamma_{HONO} = 1.0 \times 10^{-4}$ for Reaction (6). The "renoxification" by Reaction (5) would have contributed to the increase of NO in Figs. 2(c) and (d) and Figs. 3(c) and (d) to give better agreement with observation. The increase of NO could decrease O_3 by the titration reaction (Reaction (1)), which may also give better agreement for O_3 with the observation particularly during the nighttime. However, quantitative sensitivity analysis has not been made in the present study, and it is highly recommended that the verification of the importance of such heterogeneous renoxification reaction in model simulation against accurate measurement of gaseous HNO_3 together with other NO_y in the polluted urban atmosphere.

Effect of Vertical Transport

Other than the difference in chemical reaction mechanisms, the difference in transport module could give difference in the output of O_3 concentrations. In order to analyze the effect of transport, process analysis of horizontal and vertical transport of O_3 has been made for the three models. Since the horizontal transport has been found to be nearly the same for the three models, only the vertical transport will be discussed here for discussion.

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Figures 6(a) and (b) shows the comparison of vertical transport of O_3 among the three models in Beijing in April and July, respectively, and Figs. 6(c) and (d) shows the similar plots for Tokyo. The daytime downward vertical flux of O_3 for both CMAQ models in Beijing are nearly the same (22-25 ppbv hr^{-1}) in July, which is much larger than the values (ca. 6 ppbv hr^{-1}) in April. In contrast, those values of NAQM are ca. 10 ppbv hr^{-1} both in April and July, which is lager than CMAQ in April, but smaller than CMAQ by a factor of two in July. The diurnal variation of vertical flux of O_3 in Tokyo is quite different from in Beijing in July; downward O_3 flux is positive only in the morning till noon and nearly zero or negative in the afternoon. Such characteristics is in common for the three models. The maximum downward fluxes of O_3 in the morning in Tokyo for the CMAQ 5.0.2 (ca. 17 ppbv hr^{-1}) and CMAQ 4.7.1 (ca. 13 ppbv hr^{-1}) are much higher than for NAQM (< 5 ppbv hr^{-1}). Thus, it would be concluded that at least a part of much higher O_3 concentrations by CMAQ 5.0.2 and 4.7.1 as compared to NAQM shown Fig. 2(b) and Fig. 3(b) in Beijing and Tokyo in July can be ascribed to the higher downward flux of O_3 by the CMAQ models than NAQM.

Fig. 6

Peculiar feature of vertical flux of O_3 shown in Fig. 6 is the strong positive morning peak at around 7 and 6 am for CMAQ 5.0.2 particularly in Beijing in April and July, respectively, and also at 6-7 am in Tokyo in April. Another point to be noted is the delayed rise of vertical downward flux of O_3 by nearly 2 hours for NAQM both in April and July and in Beijing and Tokyo. Although this feature is not scrutinized in this study, it should be reminded here that the vertical transport module affects significantly the simulated results of O_3 in regional chemical transport models.

Comparison of Transport Process for CMAQ v. 5.0.2 and v. 4.7.1

As seen in Fig. 2 and Fig. 3, CMAQ 5.0.2 gives relatively low O_3 and relatively high NO mixing ratios closer to NAQM in April, but relatively high O_3 and low NO closer to CMAQ 4.7.1 in July both in Beijing and Tokyo. Since the chemical mechanisms of CMAQ 5.0.2 and CMAQ 4.7.1 are the same, the difference in the model performance must be ascribed to the difference in transport processes. Figures 7(a) and (b) show the comparison of mixing ratios of O_3 and hourly O_3 mixing ratios change between CMAQ 5.0.2 and observation in Beijing in April and the similar plots in July are shown in Figs. 7(c) and (d), respectively. As for the observational values, the data provided by IAP are used for the plots. The large rise of O_3 concentration change at 7-8 am shown in Figs. 7(b) and (d) clearly correspond to the early morning peak of downward transport flux of O_3 at 6-7 am as seen in Figs. 6(a) and (b). Such a

Fig. 7

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sharp rise at 7 am is not seen for CMAQ 4.7.1 although a small peak is discernable in April. This implies that such a feature is due to the characteristics of the vertical transport module of CMAQ 5.0.2. The similar plots for NO are shown in Figs. 8(a)-(d). In April, NO mixing ratio by CMAQ 5.0.2 rises in early morning, which corresponds well with the observation. The cause of such an early morning rise of NO mixing ratio and hourly mixing ratio change would be due to the increase of traffic in the morning. In July however, although the observation of NO mixing ratio and hourly change shows similar morning peak in April, CMAQ 5.0.2 simulation doesn't give any such morning peak, which would correspond to very low mixing ratio of NO simulated by CMAQ 5.0.2 together with CMAQ 4.7.1 as seen in Fig. 2(d). Although the phenomena could be caused by rapid oxidation of NO to NO_2 in summer, the reason is unknown at this stage.

Fig. 8

It should be noted that after the large rise at 7-8 am, the hourly change of O_3 mixing ratio by CMAQ 5.0.2 agrees well with the observed O_3 change in late morning and afternoon as shown in Fig 7(b) and (d). This implies that the large morning surge give much earlier rise of O_3 compared to observation. It can be noted, however, the morning surge at 7 am in July is ca. 15 ppbv, which is not very much higher than ca.10 ppbv in April. Thus, although the morning surge is larger in July than in April, this would not be the main cause of the much higher predicted O_3 concentration in the morning in July as compared to in April. The large difference in the simulated concentration of nighttime O_3 can be seen between April and July for CMAQ 5.0.2, and also between CMAQ 5.0.2 and CMAQ 4.7.1 in April. The nighttime O_3 is as low as 10-20 ppbv in Beijing, and 20-30 ppbv in Tokyo both for CMAQ 5.0.2 and NAQM in April agreeing with observation. However, the nighttime O_3 by CMAQ 4.7.1 is as high as 30 and 45 ppbv in April in Beijing and Tokyo, respectively. In July, the nighttime O_3 is 20-30 ppbv in Beijing and ca. 20 ppbv in Tokyo by NAQM, which are closer to the observation, while both CMAQ models give 40-50 ppbv both in Beijing and Tokyo, which is substantially higher than observation. The high nighttime O_3 by CMAQ models would contribute at least partly to the daytime high O_3 in July. Although course resolution of 45 km grid may tends to give the higher nighttime O_3 due to less effective NO titration, it would not enough to explain such high nighttime O_3 by CMAQ 4.7.1 both for April and July, and CMAQ 5.0.2 for July since NAQM with the same grid size reproduce the nighttime O_3 as low as 20 ppb, agreeing better with observation. It would be important to quantify the effect of the heterogeneous production of nighttime NO from HNO_3 to evaluate its impact on nighttime O_3.

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Comparison with the observational data of O_3 in Beijing and Tokyo

Both CMAQ 5.0.2 and NAQM give reasonably good agreement of O_3 mixing ratios in April in Tokyo. It can be noted that both of CMAQ 5.0.2 and NAQM gives higher mixing ratio by 10-15 ppb after the dawn. For CMAQ 5.0.2, as mentioned above, the overestimate would be caused by the peak of downward flux of O_3 in early morning. NAQM gives similar overestimate of O_3 mixing ratio by ca. 10 ppbv in early morning, but this phenomenon would be caused by peak of net chemical ozone production (Fig. 5) rather than the vertical transport. Although the cause of the early morning peak of the net O_3 production has not been elucidated in this study, it may be related to the photolysis of HONO accumulated during nighttime, since heterogeneous production of HONO (Eq. 6) is included in NAQM.

In July, NAQM is the sole model giving good agreement with observation in Tokyo. It can be noted, however, that the calculated concentration is higher than observation by ca. 10 ppbv in early morning similar to April. Such higher rise of O_3 mixing ratio in early morning is discernible in July in Tokyo for CMAQ 5.0.2. The same phenomenon can also be seen in July in Tokyo, and the cause would be due the early morning peaks of downward flux and net ozone production for CMAQ5.0.2 and NAQM, respectively. It should be noted that the enhanced mixing ratios of O_3 in early morning are persistent at least till noon giving the higher values of simulated mixing ratios.

Substantially higher simulated O_3 mixing ratios than observation by CMAQ 4.7.1 both in April and July, and by CMAQ 5.0.2 in July in Tokyo (Figs. 3(a) and (b)), may at least partially be caused by the higher nighttime mixing ratios of O_3, which would contribute to the baseline mixing ratio for the whole day. It would be expected that if the nighttime O_3 can be reduced to the observational level, better agreement of O_3 with observation would be expected for the whole day.

As for the observational data in Beijing, the daily maximum of O_3 mixing ratio in July is ca. 90 ppbv by Xu et al. (2011) and ca. 60 ppbv by the IAP data, while nighttime minimum are both 10-20 ppbv consistently. Since maximum O_3 mixing ratio in summer is expected to be higher in Beijing than in Tokyo (ca. 60 ppbv) due to the higher NO (see Figs. 2(d) and 3(d)) and NO_2 (not shown) levels by a factor of ~2, the higher observational data than in Tokyo in Fig. 2(c) could be more representative for the average of the calculated grids in Beijing. Although there still is large uncertainty as for the monthly averaged observational data of O_3 in Beijing in 2010, the tendency of the overestimate by CMAQ 5.0.2 and 4.7.1, and the underestimate of NAQM in Beijing in July could be suggested.

421 In April in Beijing, Chen et al. (2016) reported the daily maximum mixing ratio of O_3 at ca.
422 65 ppbv in 2015, which is substantially higher than the IAP data of ca. 40 ppbv in 2010.
423 Meanwhile, the surface ozone increase has been reported in Beijing at the rural sites of
424 Shangdianzi in the period of 2004-2015 with regard to the maximum daily average 8 hr mixing
425 ratios (MDA8) (Ma et al., 2016). Although the long-term increasing trend indicates an average
426 rate of 1.13 ± 0.01 ppb yr^{-1}, no monthly data was reported and the year-by-year variability
427 would be substantial. If we assume the monthly averaged MDA8 values in April in 2010 is
428 lower than 2015 by 10 ppbv, the uncertainty of the daily maximum observational value in April
429 in Beijing would be in the range of 40-55 ppbv. Thus, within the uncertainty range, the
430 tendency of overestimation of CMAQ 4.7.1, and the underestimation by NAQM could be
431 suggested.
432 As for the discussion of reproducibility of the model simulation for observational data,
433 comparison for three-year averaged values in more recent years after 2013, when the routine
434 monitoring data at much more number of sites within the targeted grids are available, would be
435 highly desirable particularly in Beijing.

436 **Overestimate of O_3 at Oki, a remote oceanic site**

437 At the remote site of Oki, overestimate of ca. 20 ppb for daytime O_3 has been seen in July in
438 Fig. 4(b) for all the three models with spatial resolution of 45 km. Such overestimate of
439 summertime O_3 at Oki by CMAQ models has been reported by Lin et al. (2009) with
440 MM5-CMAQ v. 4.6 (27 km × 27 km), while much better agreement with observation is also
441 reported previously by Yamaji et al. (2006) (80 km × 80 km) with RAMS-CMAQ v. 4.4, and Li,
442 J. et al. (2007) with NAQM (81 km × 81 km). The seasonal variation of O_3 at remote sites
443 around Japan has been known well showing springtime monthly maximum of ca. 60 ppb and
444 summertime monthly minimum of 35-40 ppb (Pochanart et al., 1999, 2002), which is consistent
445 with the observational data shown in Fig. 4. The summertime minimum at Oki and other remote
446 islands in this region are well established to be due to prevailing clean marine air in this area
447 (Pochanart et al., 2002; Yamaji et al., 2006).
448 Since the overestimate does not depends on the spatial resolution of the model, and daytime
449 buildup of O_3 due to local photochemical activity is <10 ppbv by the observation and 5-15 ppbv
450 by the simulation as shown in Fig. 4(b), the overestimate of O_3 concentration in July by all the
451 three models cannot by ascribed to the direct influence of nearby terrestrial emissions of
452 precursors in mainland Japan due to the low spatial resolution of the models. Overestimate

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could be either due to more frequent influence of terrestrial air mass by WRF compared to the real meteorology or higher O_3 concentration in the oceanic air around this area affected by the influence of non-episodic terrestrial emissions including long-range transport. The reproduction of observed concentration by models at Oki would be important for the analysis of air quality in Japan since air mass passing through Oki provides a flowing-in background mixing ratio to the mainland of Japan.

Summary

In order to identify substantial variability among the simulated modelling results for surface ozone in MICS-Asia III even though using the same emission, meteorological field and boundary conditions, three regional models, CMAQ 5.0.2, 4.7.1 and NAQM were selected and the detailed comparison have been made in the selected grids covering metropolitan areas in Beijing and Tokyo and at a remote oceanic site of Oki. The analyses were made for the monthly averaged diurnal change of surface ozone in April and July in 2010.

The simulated O_3 concentration was the highest for CMAQ 4.7.1 followed by CMAQ 5.0.2 and NAQM both in Beijing and Tokyo in April, while both CMAQ models gave similar values of O_3 but much higher than NAQM in July. At Oki, simulation for O_3 by all the three models agrees well each other and with observation in April. In July, however, all the models overestimated daytime O_3 by ca. 20 ppb compared to observation.

Three causes of resulting the difference among model outputs have been identified and discussed.

(1) The chemistry mechanism sub-module, SAPRC99 used in the CMAQ was found to give higher net ozone production than CBM-Z in NAQM agreeing with previous studies.

(2) Higher NO concentration have been predicted by NAQM than CMAQ possibly due to the inclusion of heterogeneous "renoxification" reaction of HNO_3 (on soot) → NO + NO_2 giving better agreement with observational concentration particularly for nighttime NO and O_3.

(3) Vertical downward flux of O_3 was found to affect substantially the diurnal pattern and mixing ratios of O_3. The large difference in the performance of O_3 in April and July of CMAQ 5.0.2 would also have been due to the difference in downward flux caused by the difference of meteorological conditions.

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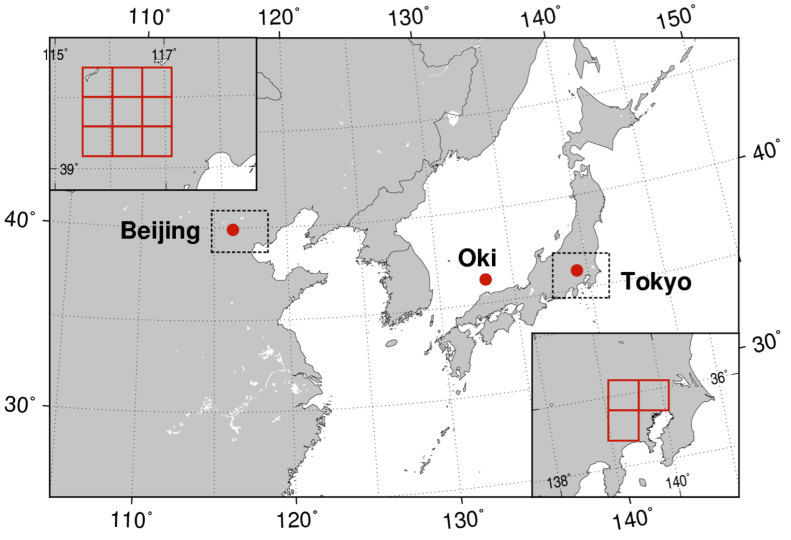

Fig. 1 Grids for comparison of the model simulation and observation; Beijing and Tokyo metropolitan area and Oki EANET site

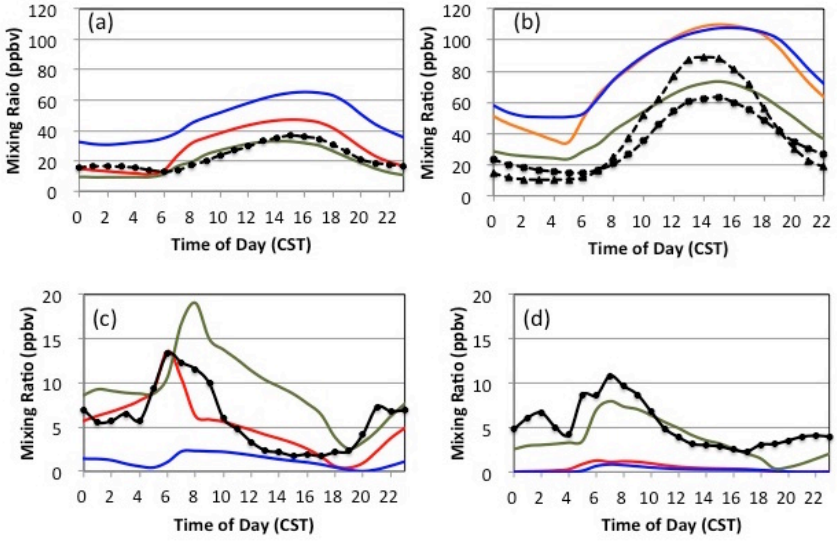

Fig. 2 Monthly averaged diurnal variation in Beijing, (a) O_3 in April, (b) O_3 in July , (c) NO in April, and (d) NO in July. Observation —●— (IAP), —▲— (Xu et al.); CMAQ 5.0.2 ——— ; CMAQ 4.7.1 ——— ; NAQM ———

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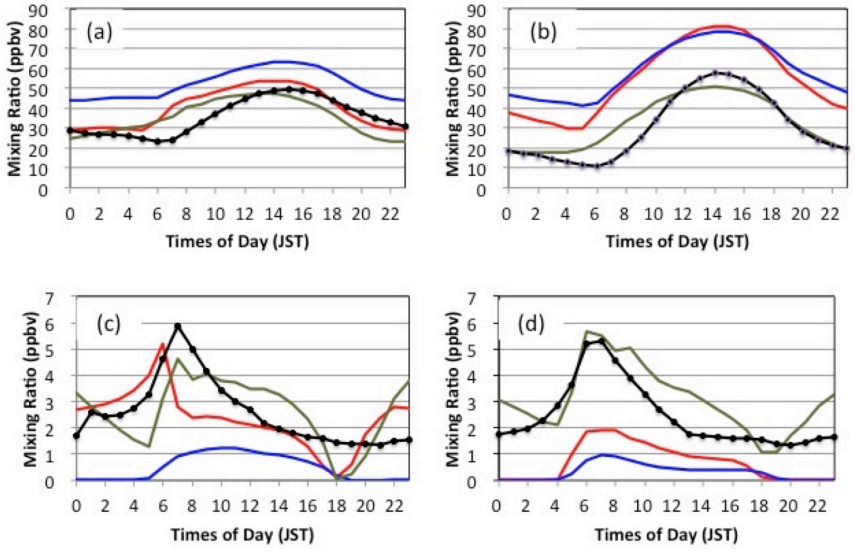

Fig. 3 Monthly averaged diurnal variation in Tokyo, (a) O_3 in April, (b) O_3 in July , (c) NO in April, and (d) NO in July. Observation —●—; CMAQ 5.0.2 ——; CMAQ 4.7.1 ——; NAQM ——

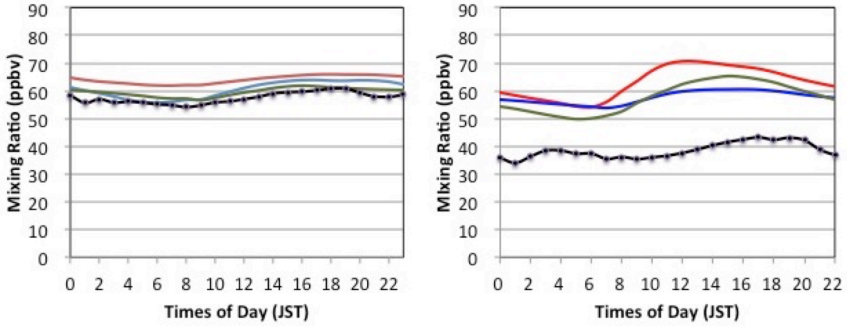

Fig. 4 Monthly averaged diurnal variation of O_3 at Oki (a) in April, (b) in July Observation —●—; CMAQ 5.0.2 ——; CMAQ 4.7.1 ——; NAQM ——

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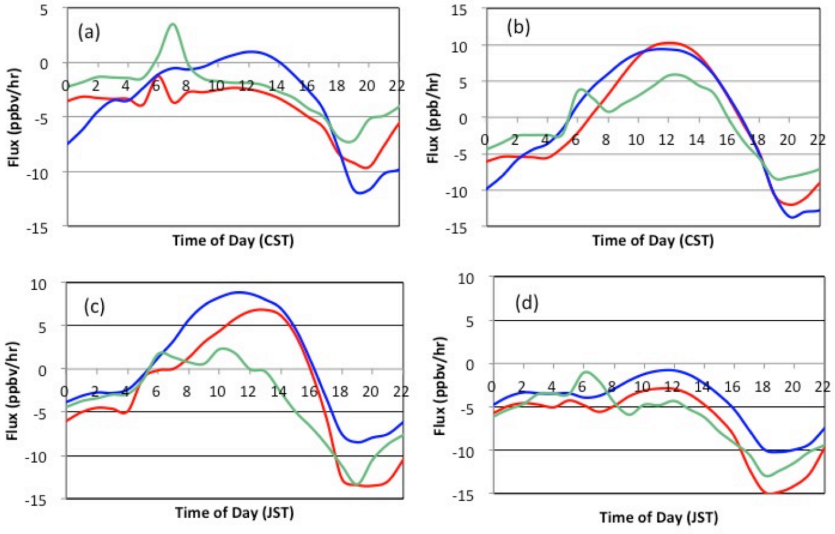

Fig. 5 Comparison of net chemical O_3 production in (a) Beijing in April, (b) Beijing in July, (c) Tokyo in April, and (d) Tokyo in July. CMAQ 5.0.2 ——; CMAQ 4.7.1 ——; NAQM ——

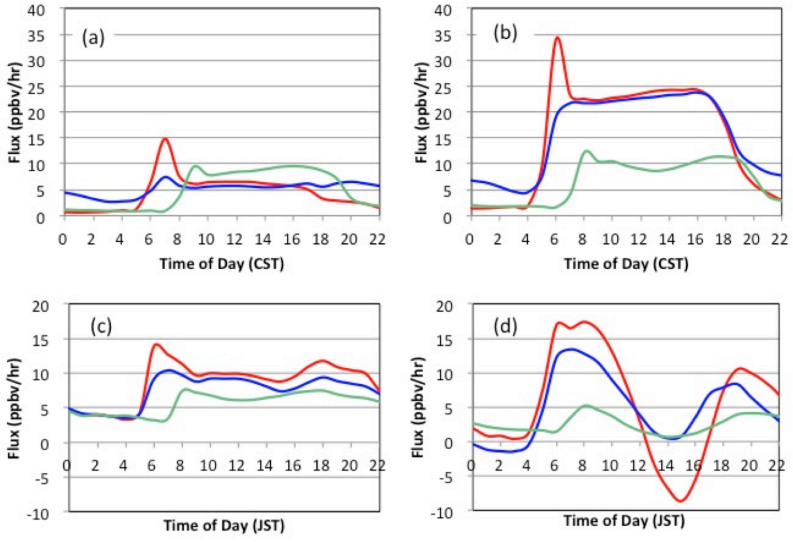

Fig. 6 Comparison of vertical transport of O3 in (a) Beijing in April, (b) Beijing in July, (c) Tokyo in April, and (d) Tokyo in July. . CMAQ 5.0.2 ——; CMAQ 4.7.1 ——; NAQM ——

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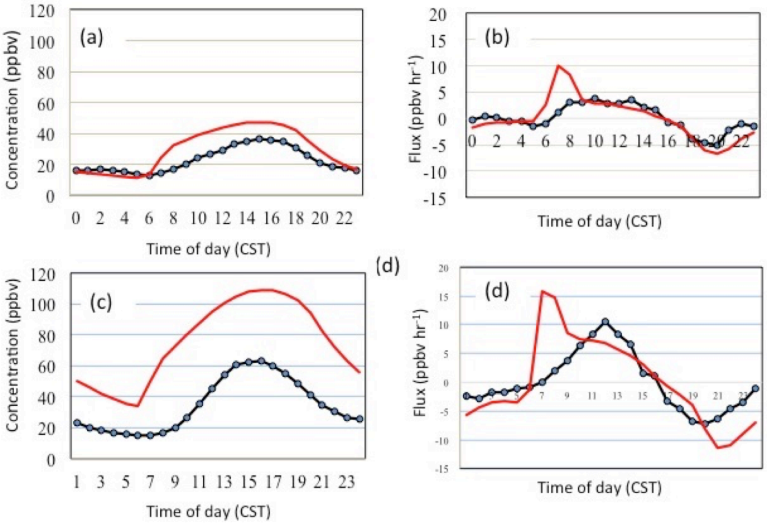

Fig. 7 Monthly averaged diurnal variation of (a) O_3 concentration in April, (b) hourly O_3 concentration change in April, (c) O_3 concentration in July and (d) hourly O_3 concentration change in July in Beijing. CMAQ 5.0.2 ——, Observation —●—

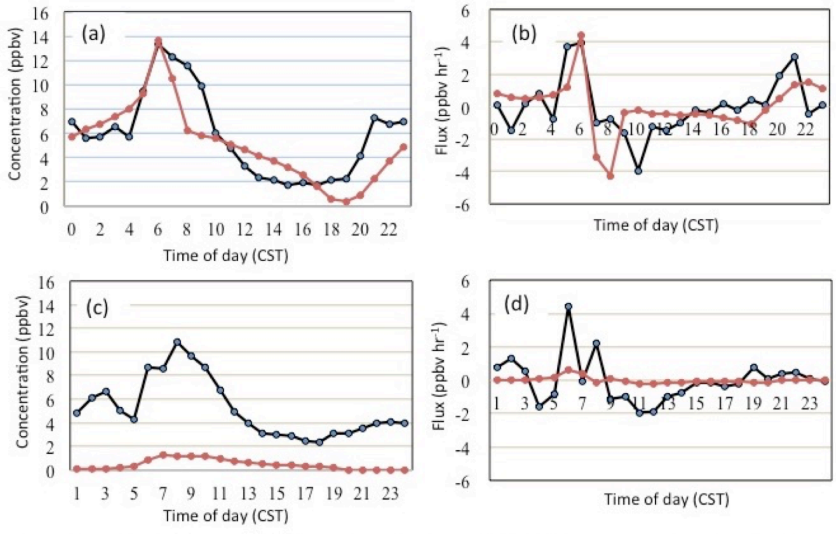

Fig. 8 Monthly averaged diurnal variation of (a) NO concentration in April, (b) hourly NO concentration change in April, (c) NO concentration in July and (d) hourly NO concentration change in July in Beijing. CMAQ 5.0,2 ——; Observation —●—