1 Comparison of Surface Ozone Simulation among Selected Regional Models

2 in MICS-Asia III

3 – Effects of Chemistry and Vertical Transport for the Causes of Difference-

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14 Abstract

15 In order to clarify the causes of variability among the model outputs for surface ozone in the

16 Model Intercomparison Study Asia Phase III (MICS-Asia III), three regional models, CMAQ

17 v.5.0.2, CMAQ v.4.7.1 and NAQPMS (abbreviated as NAQM in this paper) have been selected.

18 Detailed analyses of monthly averaged diurnal variation have been performed for selected grids

19 covering the metropolitan areas of Beijing and Tokyo and at a remote oceanic site, Oki. The

20 chemical reaction mechanism, SAPRC99, used in the CMAQ models tended to give a higher

21 net chemical ozone production than CBM-Z used in NAQM, agreeing with previous studies.

22 Inclusion of the heterogeneous "renoxification" reaction of HNO_3 (on soot surface) $\rightarrow$ NO +

23 NO_2 only in NAQM would give a higher NO concentration resulting in a better agreement with

24 observational data for NO and nighttime O_3 mixing ratios. In addition to chemical processes, the

25 difference in the vertical transport of O_3 was found to affect the simulated results significantly.

26 Particularly, the increase in downward O_3 flux from the upper layer to the surface after dawn

27 was found to be substantially different among the models. Larger early morning vertical

28 transport of O_3 simulated by CMAQ 5.0.2 is thought to be the reason for higher daytime O_3 in

29 July in this model. All the three models overestimated the daytime ozone by ca. 20 ppbv at the

30 remote site Oki in July, where in situ photochemical activity is minimal.

31

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 common key input parameters such as precursor emissions, meteorological fields, and boundary conditions to allow a 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 made the discussion of the causes of the differences among the model outputs difficult, and the results often demonstrated that the ensemble mean of simulated mixing ratios agreed reasonably well with observations even though the disagreement among the models were often significantly large (for example, Han et al., 2008; Fiore et al., 2009).

In order to improve the situation of model intercomparison studies, participants of the MICS-Asia III studies agreed to use common emission data (Li, M. et al., 2017), meteorological fields (specified Weather Research and Forecasting Model (WRF)) and boundary conditions by either of two global CTM (GEOS-Chem and CHASER) provided within the project (Wang et al. overview paper; Li, J. et al. to be published in this special issue). The following 12 regional models have been submitted to the MICS-Asia III using the designated common emissions, meteorological fields 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 used the specified common key input components, large variabilities 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 above mentioned models to elucidate the causes of differences, and detailed comparisons were made for selected grids covering the metropolitan areas of Beijing and Tokyo, and at a remote oceanic site at Oki in April and July in 2010. We selected the two models of CMAQ because CMAQ models have been widely used 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 in the simulated results between different versions (v.5.02 and v.4.7.1) is of concern. Furthermore, we selected WRF-NAQM because this is one of the regional CTMs

65 developed in Asia, giving substantially lower mixing ratios of surface ozone as compared to

66 most of WRF-CMAQ including the selected two models (Li, J. et al., in this special issue). The

67 metropolitan areas of the two megacities of Beijing and Tokyo have been selected for the

68 comparison to test whether regional models can be applied to the mitigation policy of urban

69 ozone pollution. Oki, an EANET (Acid Deposition Monitoring Network in East Asia)

70 monitoring station located in the southern part of the Sea of Japan, was selected as a remote

71 reference site located between the two megacities, as in situ photochemical production of O_3 is

72 known to be minimal there (Jaffe et al., 1996).

73

74 **Models**

75 Basic features and the simulated whole domain of the regional models, CMAQ v.4.7 (Foley

76 et al., 2010), v.5.0 (CMAS, 2011), and NAQM (Li, J. et al., 2016) used in this study, are given

77 elsewhere in this issue (Li, J. et al., in this special issue). The employed horizontal resolution

78 was 45 km for all the models, and the maximum height and number of vertical layers were 45

79 km and 40 layers, respectively, in the CMAQ models and 20 km and 20 layers, respectively, in

80 the NAQM, so that the vertical resolution in the troposphere was about the same. The lowest

81 layer for which the simulated data of ozone were extracted in this paper   was 50 m from the

82 ground. Model calculations by the CMAQ v.5.0.2, v.4.7.1, and NAQM were conducted at the

83 University of Tennessee, USA, National Institute for Environmental Studies, Japan, and

84 Institute of Atmospheric Physics, China, respectively. All the models used the common

85 meteorological fields from WRF simulation and common emissions of MIX (0.25°× 0.25°) for

86 2010 (Li, M. et al., 2017) developed in the MICS-Asia III project. The initial and boundary

87 conditions were supplied by global models, CHASER for CMAQ v.4.7.1 and NAQM, and

88 GEOS-Chem for CMAQ v.5.0.2. It was agreed that either CHASER or GEOS-Chem may be

89 used in the MICS-Asia III, since they were confirmed to give reasonably good agreement for

90 the O_3 field in the Asian domain.

91 Other than these three key components (emissions, meteorological field, and boundary

92 conditions), the three models employed different sub-models and parameters for e.g. the

93 gas-phase and aerosol chemistry module, dry deposition parameters, boundary layer scheme, etc.

94 As for the gas-phase chemistry, CMAQ v.4.7.1 and v.5.0.2 incorporated SAPRC99 (Carter,

95 2000), and NAQM employed CBM-Z (Zaveri and Peters, 1999). In the CMAQ v.4.7.1 (Foley et

96 al., 2010), major upgrades were made on the aerosol treatment from the previous version: (a)

97 updates to the heterogeneous N_2O_5 parameterization, (b) improvement in the treatment of

98　secondary organic aerosol (SOA), (c) inclusion of dynamic mass transfer for coarse-mode

99　aerosol, and (d) revisions to the cloud model. The NAQM and CMAQ v.4.7.1 employed

100　ISORROPIA v.1.7 (Nenes et al, 1998), and CMAQ v.5.0.2 incorporated ISORROPIA v.2.1

101　(Fountoukis and Nenes, 2007) for inorganic aerosol chemistry modules. In addition, CMAQ

102　v.4.7.1 and v.5.0.2 included AERO5 and AERO6 (Binkowski and Rosselle, 2003), respectively,

103　as an organic aerosol chemistry module. The sub-modules for dry deposition and wet deposition

104　employed in the three models were essentially the same. The Asymmetric Convective Model

105　version 2 (ACM2) for the planetary boundary layer (PBL) (Pleim, 2007) was employed in both

106　CMAQ v.4.7.1 and v.5.0.2. The Yonsei University (YSU) Boundary Layer (BL) scheme was

107　used for calculating BL height for NAQM (Li, J. et al., 2016). As for the advection module, the

108　models by Yamartino (1993), and Walcek and Aleksic (1998) were used for CMAQ (v.4.7.1

109　and v.5.0.2) and NAQM, respectively. For the computation of the vertical transport for

110　advection, CMAQ v.5.0.2 used the PPM (piecewise parabolic method) scheme, as compared to

111　CMAQ v.4.7.1, which used the vertical velocity directly from WRF.

112

Comparison Domain and Observational Data

113

114　　All the comparisons between the model simulations and the model using observational data

115　were made for monthly averaged diurnal variations in the mixing ratios of O_3 and NO in April

116　and July. April and July were chosen here because in situ photochemical build-up of O_3 in April

117　is insignificant but the daytime maximum mixing ratio of O_3 is relatively high reflecting the

118　well-known spring maximum of O_3 for the background in the northern hemisphere including

119　East Asia (Monks, 2000; Pochanart et al., 2003), while in July, a much higher in situ

120　photochemical build-up of O_3 is observed in urban areas in East Asia. Two representative

121　megacities, Beijing and Tokyo, were selected as urban areas for the comparison. As a remote

122　reference site, Oki, an EANET site situated between Beijing and Tokyo, was selected. The Oki

123　site is located on a cliff of an island where the local emissions of NO_x and VOCs are

124　insignificant so that in situ production of O_3 is also minimal (Jaffe et al., 1996; Pochanart et al.,

125　2002). Since the NO levels at Oki are too low to get any meaningful data using the conventional

126　chemiluminescence NO_x monitoring instrument, comparison with modeling results was made in

127　this study only for O_3 at this site. All the calculations were conducted for the whole year of 2010

128　using the meteorological field and emission data for this year.

129　　The domains of Beijing, Tokyo and Oki site were centered at 39.9°N, 116.3°E; 36.0°N,

130　139.3°E and 36.3°N and 133.1°E, respectively. The selected domains for Beijing and Tokyo

131   consisted of 9 (3×3), and 3 (2+1) grids, respectively, covering the metropolitan areas of the

132   cities as shown in Fig. 1. Data of a single grid covering the island was used for the Oki site. The

133   observational data used for Tokyo were 1-hr averaged values in 2010 of the average of 118 (for

134   O_3) and 126 (for NO) non-roadside monitoring stations within the selected grid (Fig. 1). The

135   data were obtained from Atmospheric Environment Monitoring Data Files in the Environmental

136   Information Database stored at the National Institute for Environmental Studies (NIES), Japan.

137   In Beijing, unfortunately, no routine monitoring data of 1-hr averaged values of O_3 in 2010 are

138   open to the public. Therefore, unpublished data from two sites (IAP tower campus and

139   Yangfang) obtained by IAP, and literature values published in Xu et al. (2011) and Chen et al.

140   (2015) have been referred to in this work. The O_3 and NO_x instruments at the IAP site (39.9N,

141   116.3E), which is an urban site surrounded by residential infrastructure and freeway in the east

142   (ca 200 m), were on the rooftop of a building (10 m above the ground). Yangfang (39.5N,

143   116.7E) is a suburban site in the north of Beijing, ca 40 km away from IAP. The instruments

144   were 10 m above the ground on the campus of a university with little influence from local

145   sources and sinks. The O_3 and NO_x instruments were an ultraviolet photometric analyzer (Model

146   49i, Thermo Fisher Scientific (Thermo), USA) and a chemiluminescence analyzer (Model 42i

147   TL, Thermo, USA), respectively. One of the referred Beijing data is the monthly averaged daily

148   maximum concentration of O_3 in April and July in 2014-2015 averaged over two suburban sites,

149   Daxing (39.7N, 116.4E) and Shunyi (40.1N, 116.7E) presented by Chen et al. (2015). Another

150   data is the averaged diurnal variation at three urban/suburban sites, Fengtai, Shunyi and Baolian,

151   in July and August in 2007, which are given in the paper by Xu et al. (2011). All the denoted

152   observational sites in Beijing are located within the selected nine model grids shown in Fig.1.

153   The observational data for Oki is the 1-hr averaged EANET data in 2010 provided on

154   request by the Network Center, Asia Center for Air Pollution Research (ACAP)

155   (http://www.acap.asia).

156

Results

158   Figures 2(a)-(d) depict the simulated and observed mixing ratios of the monthly averaged

159   diurnal variations of the O_3 and NO concentrations in April and July in Beijing, and Figs.

160   3(a)-(d) show similar results in Tokyo. The comparisons of the values simulated by the CMAQ

161   5.0.2 and 4.7.1 (hereafter, "v." for version will be omitted for simplicity) and NAQM are

162   plotted in each figure together with the observational data.

Fig. 1

Fig. 2

Fig. 3

163   In Beijing, observational data of surface ozone at the routine monitoring stations managed

164   by the Beijing municipal government were, unfortunately, not available until 2013 (Chen et al.,

165   2015). The average of two observational data sets obtained by IAP in 2010 is marked by the

166   dashed lines with filled circles in Figs. 2(a) and (b) for O_3 and in Figs. 2(c) and (d) for NO.

167   Other published observational data of diurnal variation of O_3 in Beijing in April are available by

168   Xu et al. (2011) at four sites, two urban (Fengtai and Baolian), one suburban (Shunyi), and one

169   rural (Shangdianzi) in summer (21 June-12 September) in 2007. Since the diurnal variation of

170   the urban and suburban sites is consistent, the average of these three sites is plotted in Fig. 2(b),

171   marked by a dashed line with triangles. No monthly average diurnal variation of O_3 is available

172   for April in Beijing in the literature. Chen et al (2015) reported the monthly averaged daily

173   maximum mixing ratio of O_3 to be ca. 60 ppbv at an urban site (Dongsi), and ca. 75 and ca. 65

174   ppbv at two suburban sites (Daxing and Shunyi, respectively) within the selected grids in this

175   study. If we simply take the average of these three values, the daily maximum mixing ratio is ca.

176   65 ppbv (not shown in Fig. 2(a)). Only the IAP data are plotted for NO with solid lines in Figs.

177   2(c) and (d).

178   As can be seen in Figs. 2(a), (b), and Figs. 3(a), (b), the diurnal pattern of the simulated

179   surface ozone shows a maximum in the late afternoon around 14-16 o'clock local time in both

180   Beijing and Tokyo, agreeing well with the observations. The simulated mixing ratios of O_3 by

181   CMAQ 4.7.1 are the highest, and those simulated by NAQM are the lowest both in Beijing and

182   in Tokyo in both April and July. The diurnal variations of O_3 simulated by CMAQ 4.7.1 are in

183   parallel with the NAQM values for whole days in all cases, but the predicted mixing ratios by

184   CMAQ 4.7.1 are by ca. 20 ppbv and ca. 40 ppbv higher than those predicted by NAQM in April

185   and July, respectively, both in Beijing and in Tokyo. The O_3 mixing ratios predicted by CMAQ

186   5.0.2 have a peculiar seasonal characteristics, i.e., the mixing ratio is slightly higher but close to

187   that predicted by NAQM within 10 ppbv both in Beijing and in Tokyo in April, whereas in July

188   the daytime O_3 maximum predicted by CMAQ 5.0.2 is very close to that predicted by CMAQ

189   4.7.1, much higher than the value by NAQM. In Tokyo, the simulated mixing ratios of CMAQ

190   5.0.2 and NAQM are closer to the observations in April, and NAQM gives a closer matching

191   with observations in July, while CMAQ 4.7.1 overestimates the values in both months as shown

192   in Figs. 2 (b) and 3(b). A comparison with the observations will be discussed later including the

193   uncertainty of the observational data in Beijing.

194   The observed mixing ratios of NO show a peak value at around 7 AM, a decrease during

195   morning followed by a slow decay in the afternoon, and they start to build up during nighttime

196   both in April and in July, in both Beijing and Tokyo. The peak values of the mixing ratios in the

197   morning are ca. 13-14 and 6 ppbv in April and ca. 11 and 5-6 ppbv in July in Beijing and Tokyo,

198   respectively. The minimum mixing ratios in the evening are ca. 1.7 and 1.4 ppbv in April and

199   2.3 and 1.3 ppbv in July in Beijing and Tokyo, respectively. Thus, it can be noted that the NO

200   mixing ratios in Beijing are nearly the double of those in Tokyo.

201   The simulated mixing ratios of NO are generally in the order of NAQM > CMAQ 5.0.2 >

202   CMAQ 4.7.1., but they vary considerably among the models. In April, CMAQ 5.0.2 gives

203   morning peak values of 13-14ppbv in Beijing and ca. 5 ppbv in Tokyo, which agrees well with

204   the observations. NAQM overpredicts the NO mixing ratio in April in Beijing but gives a

205   reasonable agreement with the observations in Tokyo as shown in Figs 2(c) and 3(c). In contrast,

206   CMAQ 4.7.1 gives a broad daytime peak of only ca. 2 ppbv in Beijing and ca. 1 ppbv in Tokyo

207   in April, which is quite different from other models, and it underpredicts considerably the

208   observational data. In July, only NAQM gives a morning peak mixing ratio of ca. 8 ppbv in

209   Beijing and 5.5 ppbv in Tokyo, agreeing fairly well with the observations including diurnal

210   variation (Figs. 2(d) and 3(d)). In contrast, both CMAQ 5.0.2 and 4.7.1 give morning peaks as

211   low as 1-2 ppbv and nearly zero mixing ratio during nighttime, which are significantly lower

212   than the observational values.

213   It can be noted that the simulated and observed levels of O_3 are highly anti-correlated with

214   those of NO. For example, the reasonably good agreements of O_3 simulated by CMAQ 5.0.2

215   and NAQM in April, and by NAQM in July in Tokyo correspond to the reasonably good

216   agreement of NO in each case. Much higher overestimates of O_3 by CMAQ 4.7.1 in April and

217   by both CMAQ 5.0.2 and 4.7.1 in July correspond to the substantial underestimates of NO.

218   Figures 4(a) and (b) show the monthly averaged diurnal variation of O_3 mixing ratios at Oki

219   in April and July, respectively. As shown in Fig. 4(a), all the three models give consistent

Fig. 4

220   mixing ratios of O_3 at 60-65 ppbv in April, agreeing well with observations within 10 ppbv. In

221   July, although the simulated mixing ratios of O_3 agree well with each other within 10 ppbv, they

222   are in the range of 50-70 ppbv as compared to the observational level of 35-45 ppbv. Thus, all

223   the three models overestimate the O_3 mixing ratio by nearly 20 ppbv. Although the

224   characteristics of remote sites showing only a slight daytime build-up of O_3 is well reproduced

225   by the models, the substantial overestimate of the simulated O_3 mixing ratio in July compared to

226   the observational values should be of concern.

227

228   **Discussion**

229   The causes of the differences in the simulated results among the three models mentioned

230   above must be due to either chemical or transport processes incorporated in the models. Here,

231   possible causes of differences of those processes are discussed individually.

232   **Comparison of Chemical Mechanism Sub-Modules**

233   One of the differences in the three models in this study is the chemical reaction mechanism

234   sub-module. CMAQ 5.0.2 and 4.7.1 incorporate SAPRC99 while NAQM employs CBM-Z. It

235   has been well known that different photochemical mechanisms used in the regional chemical

236   transport models produce different results in the prediction of O_3. Jimenez et al. (2003)

237   compared seven photochemical mechanisms including CBM-IV (Gery et al., 1989) and

238   SAPRC99 using a box model. Comparisons of CBM-IV, CBM-V (Sarwar et al., 2008) and

239   SAPRC99 incorporated into regional chemical transport models have been made by Faraji et al.

240   (2007) and Luecken et al. (2008). The main differences among these mechanisms have been

241   noted to be the lumping technique describing organic compounds into surrogate groups

242   (Jimenez et al., 2003), the differences in the products of the reaction of aromatics with OH

243   radical, and the overall branching ratio of radical generation and termination reactions (Faraji et

244   al., 2007). The results of these studies gave a consistent picture that SAPRC99 gives higher

245   concentrations of O_3 than CBM-IV both in the box model calculation and in regional model

246   simulation over the United States. The O_3 concentration obtained by CBM-V is reported to be

247   between the CBM-IV and SAPRC99 values (Luecken et al., 2008). The reason for the higher

248   concentration of O_3 by SAPRC99 has been deduced to be due to the more efficient peroxy

249   radical production in the photochemical reaction scheme of SAPR99 compared to those of the

250   CBM modules.

251   Figures 5 (a)-(d) show the net chemical production of O_3 in Beijing and Tokyo in April and

252   July calculated in this study. Here, the net chemical production, $N(O_3)$, was calculated by the

253   equation, $N(O_3) = F(O_3)-D(O_3)=\{k_1[HO_2][NO]+ k_2[RO_2][NO]\}-\{k_3[O(^1D)][H_2O]+k_4[OH][O_3]+$

254    $k_4[HO_2][O_3]+ k_5[O_3][olefin]\}$ in NAQM. The CMAQ models give the net chemical production

255   as the difference in the O_3 mixing ratio between the calculation steps of the chemistry module

256   with a process analysis package. The net chemical production was calculated in each grid and

257   then the average was taken for all the grids. As revealed in Figure 5, the CMAQ models gave

258   higher net ozone productions than the NAQM models did, which is consistent with the results of

259   earlier studies, showing that the photochemical reaction scheme of SAPRC99 gives a higher O_3

260   production than do the CBM modules. The reaction scheme of CBM-Z is the revision of

Fig. 5

261   CBM-IV, and the major revision is described as (1) inclusion of revised inorganic chemistry, (2)

262   explicit treatment of lesser reactive paraffins, (3) revised parameterization for reactive paraffin,

263   olefin, and aromatic reactions, (4) inclusion of alkyl and acyl peroxy radical interactions and

264   their reaction with NO_3, (5) inclusion of organic nitrates and hydroperoxides, and (6) refined

265   isoprene chemistry. Although any intercomparison including CBM-Z has not been reported, the

266   overall photochemical reactivity would be assumed to be similar to CBM-V, which gives a

267   higher O_3 value than CBM-IV and a lower value than SAPRC99. Thus, the maximum values of

268   daytime net O_3 production in CMAQ 5.0.2 and 4.7.1 in July are ca.10 and 7-9 ppbv hr^{-1} as

269   compared to ca. 6 and ca. 2 ppbv hr^{-1} in NAQM in Beijing and Tokyo, respectively, showing

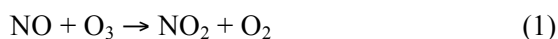270   substantially larger values for CMAQ than for NAQM.

271   It can be noted that the net O_3 production in NAQM shows a peak in the early morning after

272   breaking of dawn in both Beijing and Tokyo, which could be a cause of overestimation or

273   earlier rise of O_3 in the morning by the NAQM simulation as seen in Figs. 2(a), (b) and Figs.

274   3(a), (b) although the effect is marginal in the case of Beijing in April. The cause of the early

275   morning peak of net O_3 production in NAQM might be due to the photolysis of higher HONO

276   that is produced by the heterogeneous reaction of NO_2. More quantitative sensitivity analyses

277   should be performed to confirm these effects.

278   In April, the net chemical production of O_3 is, in general, negative in all the models for both

279   Beijing and Tokyo, except for that in CMAQ 4.7.1 around midday and that in NAQM in early

280   morning, showing slightly positive values. A tendency of higher net O_3 production is seen

281   particularly for CMAQ 4.7.1, which may be the main cause of higher O_3 by this model both in

282   Beijing and in Tokyo in April (Fig. 2(a) and Fig. 3(a)). The daytime net O_3 production

283   simulated by CMAQ 5.0.2 is similar to that simulated by CMAQ 4.7.1 in July but is

284   substantially lower in April. Since the chemistry mechanism of SAPRC99 is used in both

285   CMAQ versions, the difference may be related to the vertical transport of some relevant species.

286   **Effects of heterogeneous "renoxification" reaction of HNO_3**

287   Figures 2 and 3 show the common feature of anti-correlation of O_3 and NO concentrations

288   as noted above. This feature is most clearly seen for the comparison of O_3 and NO

289   concentrations in July in both cities, demonstrating a large overestimation of O_3 and a large

290   underestimation of NO by CMAQ 4.7.1 and 5.0.2, while much lower O_3 and much higher NO

291   are estimated by NAQM. The situation in April also confirms this finding.

292   It should be noted that the rate constants of the most sensitive gas-phase reactions affecting

293   the balance of O_3 and NO (Finlayson-Pitts and Pitts, 2000; Akimoto, 2016) such as,

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

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

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

297   have been well established (Burkholder et al., 2015 and earlier evaluations of the series) and

298   more or less the same reaction rates are employed in both of SAPRC99 and CBM-Z. As for the

299   heterogeneous processes affecting NO_x, the reaction,

300                $N_2O_5 + H_2O$ (on particle) $\rightarrow 2\ HNO_3$ (4)

301   is included in common in the heterogeneous inorganic chemistry sub-module, ISORROPIA and

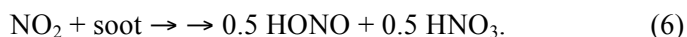302   employed in the CMAQ and NAQM models.

303   It has been noted that the simulated gaseous HNO_3 concentration and HNO_3/NO_x ratio were

304   found to be 2-10 times higher when using global and regional chemical transport models than

305   the observational data during the PEM-West (Singh et al., 1996), TRACE-P (Talbot et al.,

306   2003), and PEM-Tropics A and SONEX (Brunner et al., 2005) aircraft campaigns over the

307   Pacific and Atlantic Ocean. The same result has also been reported by ground observations in

308   the remote troposphere at Mauna Loa (Hauglustaine et al., 1996) and in the polluted boundary

309   layer of Beijing-Tianjin-Hebei region (Li, Y. et al., 2015).

310   Another concern regarding recent NO_x chemistry has been focused on the high

311   concentration of HONO in the urban atmosphere, which is thought to be produced by the

312   heterogeneous reaction of NO_2 and H_2O on the aerosol and ground surface (for example, Li, Y.

313   et al., 2011; Gonçalves et al., 2012; Wong et al., 2013). Inclusion of the additional

314   heterogeneous source of HONO not only affects the photochemical O_3 formation due to the

315   increase of OH radicals but also increases HNO_3 due to the increase of the reaction, $OH + NO_2$

316    $+ M \rightarrow HNO_3 + M$. Li, Y. et al. (2015) have shown that the inclusion of the heterogeneous

317   formation of HONO gives more HNO_3, which tends to give a larger overestimation of gaseous

318   HNO_3 in the Beijing-Tianjin-Hebei region.

319   In order to solve the problem of overestimation of HNO_3, the heterogeneous reaction of

320   HNO_3 on soot surface to reproduce NO and NO_2 has been proposed as "renoxification" process

321   early by Lary et al. (1997) in the analysis of the above aircraft observation data. The

322   heterogeneous reaction of HNO_3 on soot surface to produce NO/NO_2 has been confirmed

323   experimentally in laboratory studies (Disselkamp et al., 2000; Muñoz and Rossi, 2002),

324   although the product ratio and reaction mechanism are not well established yet. The steady state

325 uptake coefficient γ_{ss} of this reaction has been reported to be $(4.6 \pm 1,6) \times 10^{-3}$ for black soot

326 using geometric surface area (Muñoz and Rossi, 2002).

327 Only NAQM among the three models studied here incorporates the following heterogeneous

328 non-stoichiometric reactions on the surface of soot (Li, J. et al., 2015).

329 $\qquad$ $HNO_3 + soot \rightarrow \rightarrow NO + NO_2$ $\qquad$ (5)

330 $\qquad$ $NO_2 + soot \rightarrow \rightarrow 0.5\ HONO + 0.5\ HNO_3.$ $\qquad$ (6)

331 with $\gamma_{HNO3} = 3.0 \times 10^{-3}$ for Reaction (5) and $\gamma_{HONO} = 1.0 \times 10^{-4}$ for Reaction (6). The

332 "renoxification" by Reaction (5) could have contributed to the increase of NO in Figs. 2(c) and

333 (d) and Figs. 3(c) and (d) resulting in a better agreement with the observation. The increase of

334 NO could decrease O_3 by the titration reaction (Reaction (1)), which may also give a better

335 agreement for O_3 with the observation, particularly during nighttime. However, no quantitative

336 sensitivity analysis has been made in the present study, and it is highly recommended that

337 verification of the importance of such heterogeneous renoxification reaction in model

338 simulation be made against accurate measurements of gaseous HNO_3 together with other NO_y in

339 the polluted urban atmosphere.

340 **Effects of Vertical Transport**

341 Other than the difference in chemical reaction mechanisms, the difference in transport

342 module could give rise to differences in the output of O_3 concentrations. In order to analyze the

343 effects of transport, process analysis of horizontal and vertical transport of O_3 has been

344 conducted. Since it has been found that there is not much difference in horizontal transport and

345 surface deposition, and the chemical mechanisms of CMAQ 5.0.2 and CMAQ 4.7.1 are the

346 same, the difference in model performance must be ascribed to the difference in vertical

347 transport processes.

348 Figures 6(a) and (b) show the comparison of vertical O_3 transport among the three models in

349 Beijing in April and July, respectively, and Figs. 6(c) and (d) show similar plots for Tokyo. The

Fig. 6

350 daytime downward vertical flux of O_3 for both CMAQ models in Beijing are nearly the same

351 (22-25 ppbv hr^{-1}) in July, and much larger than the values (ca. 6 ppbv hr^{-1}) in April. In contrast,

352 the values of NAQM are ca. 10 ppbv hr^{-1} both in April and in July, which is larger than the

353 values of CMAQ in April, but smaller than those of CMAQ by a factor of two in July. The

354 diurnal variation of vertical O_3 flux in Tokyo is quite different from that in Beijing in July;

355 downward O_3 flux is positive only in the morning till noon and nearly zero or negative in the

356 afternoon. Such characteristics is common for all the three models. The maximum downward

11

357   fluxes of O_3 in the morning in Tokyo in CMAQ 5.0.2 (ca. 17 ppbv hr^{-1}) and CMAQ 4.7.1 (ca.

358   13 ppbv hr^{-1}) are much higher than those in NAQM (< 5 ppbv hr^{-1}). Thus, it is concluded that at

359   least a part of much higher O_3 concentrations estimated by CMAQ 5.0.2 and 4.7.1 as compared

360   to NAQM shown in Fig. 2(b) and Fig. 3(b) in Beijing and Tokyo in July can be ascribed to the

361   higher downward O_3 flux estimated by the CMAQ models compared to NAQM.

362   A peculiar feature of vertical O_3 flux in the CMAQ 5.0.2 shown in Fig. 6 is the strong

363   positive morning peak at around 7 and 6 am in Beijing in April and July, respectively, and also

364   at 6-7 am in Tokyo in April. Here, it should be noted that the vertical transport was computed in

365   the PPM scheme in CMAQ 5.0.2 instead of the direct extraction from WRF in CMAQ 4.7.1 as

366   described in the method section. The PPM method has been known to introduce more

367   downward flux of O_3 from higher layers to the surface layer. Another point to be noted is the

368   delayed rise of vertical downward O_3 flux by nearly 2 hours in NAQM both in April and July in

369   Beijing and Tokyo. Although this feature is not scrutinized in this study, it should be noted here

370   that the vertical transport treatment affects significantly the simulated results of O_3 in regional

371   chemical transport models.

372   **Comparison of the Transport Process in CMAQ v. 5.0.2 and v. 4.7.1**

373   As seen in Fig. 2 and Fig. 3, CMAQ 5.0.2 gives relatively low O_3 and relatively high NO

374   mixing ratios, closer to the values in NAQM in April, but relatively high O_3 and low NO closer

375   to those in CMAQ 4.7.1 in July both in Beijing and in Tokyo. Since the chemical mechanisms

376   of CMAQ 5.0.2 and CMAQ 4.7.1 are the same, the difference in the model performance must

377   be ascribed to the difference in transport processes. Figures 7(a) and (b) show the comparison of   Fig. 7

378   O_3 mixing ratios and the change in hourly O_3 mixing ratios between CMAQ 5.0.2 and the

379   observations in Beijing in April, and similar plots for July are shown in Figs. 7(c) and (d). As

380   for the observational values, data provided by IAP are used for the plots. The large rise in the

381   change of O_3 concentrations at 7-8 am shown in Figs. 7(b) and (d) clearly correspond to the

382   early morning peak of downward transport flux of O_3 at 6-7 am in Figs. 6(a) and (b). Such a

383   sharp rise at 7 am is not seen in CMAQ 4.7.1 although a small peak is discernable in April. This

384   implies that such a feature is due to the characteristics of the vertical transport module of

385   CMAQ 5.0.2. Similar plots for NO are shown in Figs. 8(a)-(d). In April, the NO mixing ratio by

386   CMAQ 5.0.2 rises in early morning, which corresponds well with the observation. The cause of

387   such an early morning rise of NO mixing ratio and change in hourly mixing ratio is assumed to

388   be the increase of traffic in the morning. In July however, although the observation of NO

Fig. 8

389 mixing ratio and hourly change shows a similar morning peak in April, the CMAQ 5.0.2

390 simulation doesn't give any such morning peak, which would correspond to a very low NO

391 mixing ratio simulated by CMAQ 5.0.2 together with CMAQ 4.7.1 as seen in Fig. 2(d).

392 Although the phenomena could be caused by rapid oxidation of NO to NO_2 in summer, the

393 reason is unknown at this stage.

394   It should be noted that after the large rise at 7-8 am, the hourly change of O_3 mixing ratio

395 simulated by CMAQ 5.0.2 agrees well with the observed O_3 change in the late morning and

396 afternoon as shown in Figs. 7(b) and (d). This implies that the large morning surge gives a much

397 earlier rise of O_3 compared to the observation. It can be noted, however, that the morning surge

398 at 7 am in July is ca. 15 ppbv, which is not much higher than the ca.10 ppbv in April. Thus,

399 although the morning surge is larger in July than in April, this would not be the main cause of

400 the much higher predicted O_3 concentration in the morning in July as compared to April. A

401 large difference in the simulated concentration of nighttime O_3 can be seen between April and

402 July in CMAQ 5.0.2, and also between CMAQ 5.0.2 and CMAQ 4.7.1 in April. The nighttime

403 O_3 is as low as 10-20 ppbv in Beijing, and 20-30 ppbv in Tokyo in both   CMAQ 5.0.2 and

404 NAQM in April, agreeing with observation. However, the nighttime O_3 simulated by CMAQ

405 4.7.1 is as high as 30 and 45 ppbv in April in Beijing and Tokyo, respectively. In July, the

406 nighttime O_3 is 20-30 ppbv in Beijing and ca. 20 ppbv in Tokyo in NAQM, which is close to the

407 observation, while both CMAQ models give 40-50 ppbv both in Beijing and in Tokyo, which is

408 substantially higher than the observation. The high nighttime O_3 simulated by the CMAQ

409 models would contribute at least partly to the high daytime O_3 in July. Although the coarse

410 resolution of 45 km grid tends to give a higher nighttime O_3 due to less effective NO titration, it

411 would not be enough to explain such a high nighttime O_3 in CMAQ 4.7.1 both for April and for

412 July, and CMAQ 5.0.2 for July, since the NAQM simulation with the same grid size reproduces

413 the nighttime O_3 as low as 20 ppb, agreeing better with the observation. It would be important to

414 quantify the effect of the heterogeneous production of nighttime NO from HNO_3 to evaluate its

415 impact on nighttime O_3.

416 **Comparison of simulations with the observational data of O_3 in Beijing and Tokyo**

417   Both CMAQ 5.0.2 and NAQM give reasonably good agreement of O_3 mixing ratios with the

418 observational data in April in Tokyo. It can be noted that both CMAQ 5.0.2 and NAQM give

419 higher mixing ratios by 10-15 ppb after dawn. For CMAQ 5.0.2, as mentioned above, the

420 overestimate could be caused by the peak of downward O_3 flux in the early morning. NAQM

13

421   gives a similar overestimate of the O_3 mixing ratio by ca. 10 ppbv in the early morning, but this

422   phenomenon could be caused by the peak of the net chemical ozone production (Fig. 5) rather

423   than the vertical transport. Although the cause of the early morning peak of the net O_3

424   production has not been elucidated in this study, it may be related to the photolysis of HONO

425   accumulated during nighttime, since the heterogeneous production of HONO (Eq. 6) is included

426   in NAQM.

427   In July, NAQM is the sole model giving a good agreement with the observation in Tokyo. It

428   can be noted, however, that the calculated concentration is higher than the observation by ca. 10

429   ppbv in early morning similar to April. Such a higher rise of the O_3 mixing ratio in the early

430   morning is discernible in July in Tokyo in CMAQ 5.0.2. The same phenomenon can also be

431   seen in July in Tokyo, and the cause is assumed to be the early morning peaks of downward

432   flux of O_3 and net O_3 production in CMAQ5.0.2 and NAQM, respectively. It should be noted

433   that the enhanced mixing ratios of O_3 in early morning are persistent at least till noon, giving

434   higher values of simulated mixing ratios.

435   Substantially higher simulated O_3 mixing ratios in CMAQ 4.7.1 than the observation both in

436   April and in July, and in CMAQ 5.0.2 in July in Tokyo (Figs. 3(a) and (b)), may at least

437   partially be caused by the higher nighttime mixing ratios of O_3, which would contribute to the

438   baseline mixing ratio for the whole day. It would be expected that if the nighttime O_3 could be

439   reduced to the observational level, a better agreement of O_3 with observation would be expected

440   for the whole day.

441   As for the observational data in Beijing, the daily maximum of O_3 mixing ratio in July is ca.

442   90 ppbv in Xu et al. (2011) and ca. 60 ppbv by the IAP data, while the nighttime minimums are

443   both 10-20 ppbv consistently. Since the maximum O_3 mixing ratio in summer is expected to be

444   higher in Beijing than in Tokyo (ca. 60 ppbv) due to higher NO (see Figs. 2(d) and 3(d)) and

445   NO_2 levels by a factor of ~2 (not shown), the higher observational data in Beijing than in

446   Tokyo in Fig. 2(c) could be more representative for the average of the calculated grids in

447   Beijing. Although there still is a large uncertainty in the monthly averaged observational data of

448   O_3 in Beijing in 2010, a tendency of overestimation by CMAQ 5.0.2 and 4.7.1, and

449   underestimation by NAQM in Beijing in July can be suggested.

450   In April in Beijing, Chen et al. (2015) reported the daily maximum mixing ratio of O_3 at ca.

451   65 ppbv in 2014-2015, which is substantially higher than the IAP data of ca. 40 ppbv in 2010.

452   An increase in surface ozone has been reported in Beijing at the rural sites of Shangdianzi

453   during the period of 2004-2015 with regard to the maximum daily average 8 hr mixing ratios

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454 (MDA8) (Ma et al., 2016). Although the long-term increasing trend indicates an average rate of

455 1.13 ± 0.01 ppb yr^{-1}, no monthly data was reported, and the year-by-year variability is

456 substantial. If we assume that the monthly averaged MDA8 values in April in 2010 are lower by

457 10 ppbv than those in 2015, the uncertainty of the daily maximum observational value in April

458 in Beijing would be in the range of 40-55 ppbv. Thus, within the uncertainty range, a tendency

459 of overestimation by CMAQ 4.7.1 and an underestimation by NAQM could be suggested.

460 As for the discussion of reproducibility of the model simulation, a comparison of three-year

461 averaged values in more recent years after 2013, when routine monitoring data at considerably

462 more sites within the targeted grids are available, would be highly desirable, particularly in

463 Beijing.

464 **Overestimation of O_3 at Oki, a remote oceanic site**

465 At the remote site of Oki, an overestimation by ca. 20 ppb for daytime O_3 has been seen in

466 July in Fig. 4(b) by all the three models with a spatial resolution of 45 km. Such an

467 overestimation of summertime O_3 at Oki by the CMAQ models has been reported by Lin et al.

468 (2009) with MM5-CMAQ v. 4.6 (27 km × 27 km), while a much better agreement with the

469 observation was previously reported by Yamaji et al. (2006) (80 km × 80 km) using

470 RAMS-CMAQ v. 4.4, and Li, J. et al. (2007) using NAQM (81 km × 81 km). The seasonal

471 variation of O_3 at remote sites around Japan has shown a springtime monthly maximum of ca.

472 60 ppb and a summertime monthly minimum of 35-40 ppb (Pochanart et al., 1999, 2002), which

473 is consistent with the observational data shown in Fig. 4. The summertime minimum at Oki and

474 other remote islands in this region are well established to be due to prevailing clean marine air

475 (Pochanart et al., 2002; Yamaji et al., 2006).

476 Since the overestimation does not depend on the spatial resolution of the model, as noted

477 above, and the daytime build-up of O_3 due to local photochemical activity is <10 ppbv in the

478 observation and 5-15 ppbv in the simulation as shown in Fig. 4(b), the overestimation of O_3

479 concentration in July by all the three models cannot be ascribed to the direct influence of nearby

480 terrestrial emissions of precursors in mainland Japan. The overestimation could be either due to

481 a more frequent influence of terrestrial air masses by WRF compared to the real meteorology, or

482 higher O_3 concentration in the oceanic air around this area affected by the influence of

483 non-episodic terrestrial emissions including long-range transport. The reproduction of observed

484 concentrations by models at Oki would be important for the analysis of air quality in Japan,

485 since air masses passing through Oki provide a flowing-in background mixing ratio to mainland

15

486 Japan.

487

488 **Summary**

489 In order to identify the causes of the substantial variability among the simulated modelling

490 results for surface ozone in MICS-Asia III even though using the same emissions,

491 meteorological field and boundary conditions, three regional models, namely CMAQ 5.0.2,

492 4.7.1 and NAQM were selected and a detailed comparison was made in the selected grids

493 covering the metropolitan areas in Beijing and Tokyo and at the remote oceanic site of Oki. The

494 analyses were made for the monthly averaged diurnal change of surface ozone in April and July

495 in 2010.

496 The simulated O_3 concentration was the highest in CMAQ 4.7.1, followed by those in

497 CMAQ 5.0.2 and NAQM both in Beijing and in Tokyo in April, while both CMAQ models

498 gave much higher O_3 values than NAQM did in July. At Oki, the simulations for O_3 by all the

499 three models agree well with each other and with the observation in April. In July, however, all

500 the models overestimated daytime O_3 by ca. 20 ppb compared to the observation.

501 Three causes for the difference among model outputs have been identified and discussed.

502 (1) The chemistry mechanism sub-module, SAPRC99 used in the CMAQ was found to give

503 higher net ozone production values than CBM-Z in NAQM, agreeing with previous studies.

504 (2) Higher NO concentrations have been predicted by NAQM than by CMAQ, possibly due to

505 the inclusion of a heterogeneous "renoxification" reaction of HNO_3 (on soot surface) $\rightarrow$ NO

506 + NO_2, which gave a better agreement with observational concentration particularly for

507 nighttime NO and O_3.

508 **(3)** A vertical downward O_3 flux was found to affect substantially the diurnal pattern and

509 mixing ratios of O_3.

510

511 **Acknowledgements**

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676

677   Figure Captions

678

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

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682   Fig. 2   Monthly averaged diurnal variation in Beijing, (a) O_3 in April, (b) O_3 in July , (c) NO in
683   April, and (d) NO in July.

684

685   Fig. 3   Monthly averaged diurnal variation in Tokyo, (a) O_3 in April, (b) O_3 in July , (c) NO in
686   April, and (d) NO in July.

687

688   Fig. 4   Monthly averaged diurnal variation of O_3 at Oki (a) in April, (b) in July.

689

690   Fig. 5   Comparison of net chemical O_3 production in   (a) Beijing in April, (b) Beijing in July,
691   (c) Tokyo in April, and (d) Tokyo in July.

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693   Fig. 6   Comparison of vertical transport of O_3 in (a) Beijing in April, (b) Beijing in July, (c)
694   Tokyo in April, and (d) Tokyo in July.

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696   Fig. 7   Monthly averaged diurnal variation of (a) O_3 concentration in April, (b) hourly O_3
697   concentration change in April,   (c) O_3 concentration in July and (d) hourly O_3 concentration
698   change in July in Beijing.

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700   Fig. 8   Monthly averaged diurnal variation of (a) NO concentration in April, (b) hourly NO
701   concentration change in April, (c) NO concentration in July and (d) hourly NO concentration
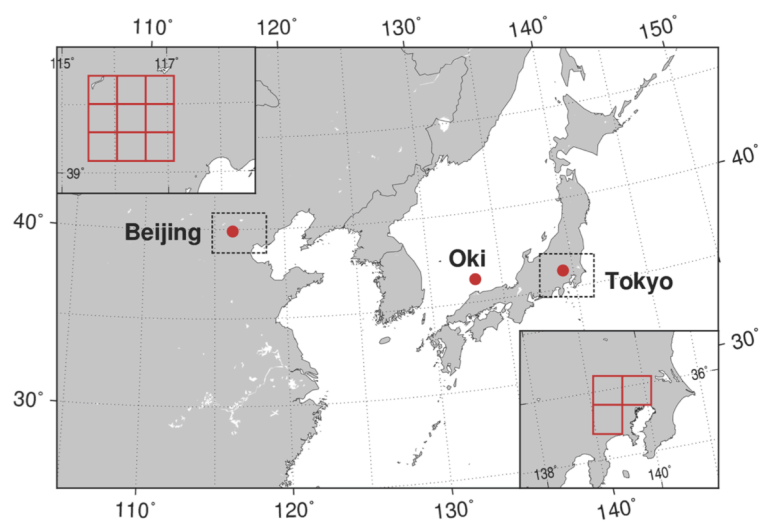702   change in July in Beijing.

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Figures

Fig. 1

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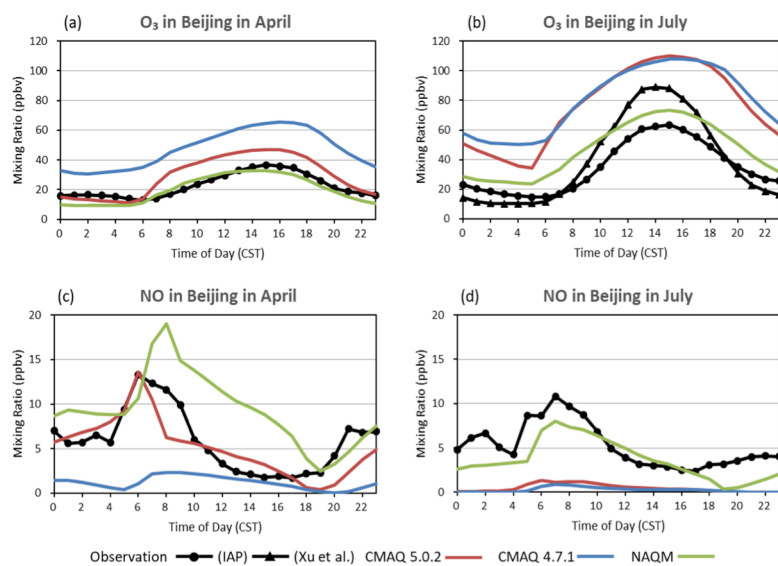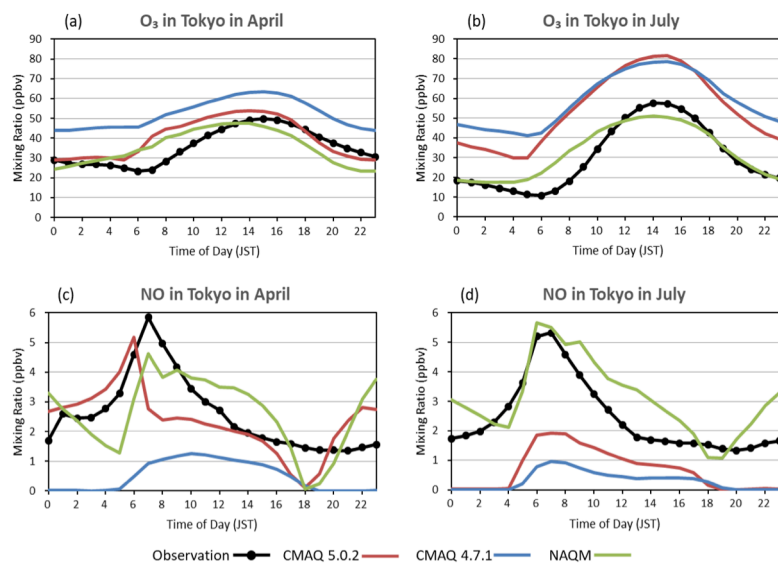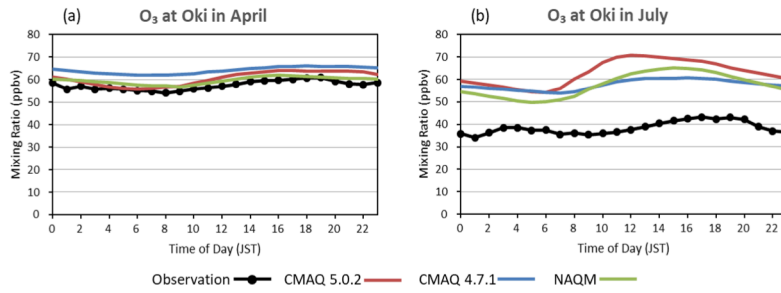716
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Fig. 2

Fig. 3

Fig. 4

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Fig. 5

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(a) O₃ concentration in Beijing in April
(b) O₃ concentratioin change in Beijing in April
(c) O₃ concentration in Beijing in July
(d) O₃ concentratioin change in Beijing in July

Observation   CMAQ 5.0.2

Fig. 7

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(a) NO concentration in Beijing in April
(b) NO concentratioin change in Beijing in April
(c) NO concentration in Beijing in July
(d) NO concentratioin change in Beijing in July

Observation   CMAQ 5.0.2

Fig. 8

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