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Synergistic impacts of anthropogenic and biogenic emissions on summer surface O_3 in East Asia

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Abstract

A factor separation technique and an improved regional air quality model (RAQM) were applied to calculate synergistic contributions of anthropogenic volatile organic compounds (AVOCs), biogenic volatile organic compounds (BVOCs) and nitrogen oxides (NO*x*) to daily maximum surface O_3 (O_{3DM}) concentrations in East Asia in summer (June to August 2000). The summer averaged synergistic impacts of AVOCs and NO*x* are dominant in most areas of North China, with a maximum of 60 ppbv, while those of BVOCs and NO*x* are notable only in some limited areas with high BVOC emissions in South China, with a maximum of 25 ppbv. This result implies that BVOCs contribute much less to summer averaged O_{3DM} concentrations than AVOCs in most areas of East Asia at a coarse spatial resolution (1°×1°) although global emissions of BVOCs are much greater than those of AVOCs. Daily maximum total contributions of BVOCs can approach 20 ppbv in North China, but they can reach 40 ppbv in South China, approaching or exceeding those in some developed countries in Europe and North America. BVOC emissions in such special areas should be considered when O_3 control measures are taken. Synergistic contributions among AVOCs, BVOCs and NO*x* significantly enhance O_3 concentrations in the Beijing-Tianjin-Tangshan region and decrease them in some areas in South China. Thus, the total contributions of BVOCs to O_{3DM} vary significantly from day to day and from location to location. This result suggests that O_3 control measures obtained from episodic studies could be limited for long-term applications.

Key words: regional air quality model; volatile organic compounds; O_3; factor separation technique; synergistic contribution

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Introduction

Surface ozone (O_3) is a secondary chemical species in the atmosphere. High surface O_3 may affect human health, cause damage to forests and crops and severely threaten the balance of the ecosystem (Lippmann, 1991). East Asia has experienced rapid economic growth and industrial expansion in the past several decades. Elevated surface O_3 concentrations are frequently observed over vast areas in East Asia, especially in several large city clusters of China, e.g., the Beijing-Tianjin-Tangshan (BTT) region, the Yangtze River Delta, and the Pearl River Delta (Zhang et al., 1998, 2008; Song et al., 2002; Shao et al., 2006). The O_3 increasing trend is expected to continue (Kato and Akimoto, 1992; McElroy, 1998).

Volatile organic compounds (VOCs) (anthropogenic VOCs (AVOCs) + biogenic VOCs (BVOCs)) are critical in tropospheric O_3 formation. Most studies have emphasized the effect of AVOC emissions from industry and transportation. Recent studies indicate that BVOC emissions are significant compared with anthropogenic emissions at a global scale (Guenther et al., 1993, 1995, 2000). Many scientists in North America and Europe have investigated the impacts of BVOCs on surface O_3 (Chameides et al., 1988; Sillman et al., 1990; Simpson 1995; Thunis and Cuvelier 2000; Tao et al., 2003; Castell et al., 2010), and all show significant effects on surface O_3 formation. However, the related work in Asia is still limited (Shao et al., 2000; Peng et al., 2000; Han et al., 2005; Xie et al., 2007) and generally focuses on episodic (several days or weeks) O_3 studies. Control strategies obtained from episodic studies could be different from those from long-term (e.g., a seasonal) studies, and the importance of BVOCs may be variable in different areas.

O_3 formation is a complex nonlinear process resulting from VOCs and nitrogen oxides (NO*x*) known as primary precursors. The O_3 production rate and efficiency depend on concentrations of both VOCs and NO*x* and on VOC/NO*x* ratios. Many studies have revealed that at a

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given level of VOCs, there is an optimum VOC/NOx ratio at which a maximum amount of O_3 is produced. For the ratio in a VOC-limited regime, an increase in NOx can lead to a reduction in O_3 concentrations while an increase in VOCs leads to a rise in O_3 concentrations; conversely, for the ratio in a NOx-limited regime, a NOx increase leads to O_3 increase, and VOCs have a nearly insensitive effect on O_3 (Sillman et al., 1990; Solomon et al., 2000; Zhu et al., 2006). An O_3 isopleth is an empirical kinetic modeling approach that is frequently used to analyze O_3 reduction scenarios (Dodge, 1977), but it is not able to reflect impacts due to the changes in meteorological fields. Additionally, we have noted that most studies on source contributions to surface O_3 have been conducted using Eq. (1):

$$G_i = C_0 - C_i \tag{1}$$

where, C_0 and C_i represents simulations with and without emission source i, respectively. G_i is the expected contribution of source i. In fact, G_i only reflects the total contribution of the concerned source and cannot distinguish its pure impact from its synergistic impact with other emission sources.

This work uses an improved regional air quality model (RAQM) and the factor separation technique (Stein and Alpert, 1993), which can separate the sole impact of one species from the mutual impacts with other species, to quantify the synergistic and total contributions of AVOCs, BVOCs and NOx to O_3 formation in East Asia in the summer of 2000. The paper then discusses the relative importance of AVOCs and BVOCs in East Asia and the limitations on control measures obtained from episodic studies.

1 Model description

1.1 RAQM modeling system

RAQM is a three-dimensional Eulerian model utilizing a spherical terrain-following coordinate (An et al., 2002, 2003; Han et al., 2006). The model covers most of East Asia (75–155°E, 0–55°N) with horizontal grids of 1°×1° and 12 vertically unequal layers from 50 m to the top of the troposphere. The major processes, i.e., source emissions, advection, diffusion, deposition and chemistry are included. A modified Wesely's parameterization was applied to update the dry deposition module (Wesely, 1989; Walmsley and Wesely, 1996). The wet removal processes of pollutants were calculated using scavenging ratios (Brodzinsky et al., 1984; Okita et al., 1996). The vertical eddy diffusivity was parameterized according to the approach of Byun and Dennis (1995) used in the regional acid deposition model version 2.6. The RAQM has been used to study important issues in atmospheric environments. For example, An et al. (2002) simulated nitrate concentrations in rainwater over East Asia; An et al. (2003) and Kajino et al. (2004) simulated the impacts of volcanic emissions on the air quality of Japan; Han et al. (2004) studied a dust event coupled with an aerosol model in Asia; Han et al. (2006) investigated characteristics of wet deposition in East Asia, and Han et al. (2007) simulated O_3 and relevant gaseous species in East Asia. All the above works show that the RAQM can reproduce well the spatial and temporal distributions and long-range transport of major air pollutants in East Asia.

In this study, the RAQM was driven by a non-hydrostatic, fifth-generation mesoscale model (Grell et al., 1995) with a horizontal resolution of 81 km and a vertical extent consisting of 23 layers. The following solution schemes for the main physical processes were chosen: the Anthes-Kuo scheme for cumulus parameterizations, Medium-Range Forecasts for the atmospheric boundary layer, the mixed-phase for an explicit moisture scheme and the cloud cooling for radiation. Data from the European Center for Medium-range Weather Forecast were used for every six hours.

The uncertainty in long-term (e.g., monthly, seasonal and annual) simulations of rainfall within a large domain is very large (Seaman, 2000; Russell and Dennis, 2000). To reflect the temporal inhomogeneity in rainfall, the hourly gridded rainfall R is revised as:

$$R = (R_{\mathrm{hr}}/R_{\mathrm{mon}}) \times R_{\mathrm{obs}} \tag{2}$$

where, R_{hr} and R_{mon} denote hourly and monthly simulations of rainfall from fifth-generation mesoscale model, respectively. R_{obs} is the monthly observation of rainfall, which is not difficult to obtain by comparison with hourly observed data in a large area. R_{obs} was obtained by interpolating the observed rainwater from monitoring sites (i.e., 700 sites in mainland China) and was replaced by the National Center for Environmental Protections reanalysis data in areas without observations (e.g., oceans).

The gas chemistry was the Lurmann-Lloyd-Atkinson mechanism (Lurmann et al., 1986; Carmichael et al., 1991; Zhu et al., 2002), which is widely used in East Asia instead of the condensed Carbon-Bond IV mechanism (An et al., 2002). The Lurmann-Lloyd-Atkinson mechanism contains 84 species and 178 chemical reactions, also including reactions of BVOCs and those between organic compounds and radicals.

The simulation period was from June 1 to August 31 2000. An initialization run was started three days prior to the simulation period. The O_3 concentrations from the surface to the top layer were set from 15 to 45 ppbv at the north boundaries and from 10 to 30 ppbv at the south boundaries. The boundary conditions for the other species, including VOCs and NOx, were taken as a vertically varying clean background (An et al., 2002).

The anthropogenic emission inventories of CO, SO_2, NH_3, NOx and VOCs in 2000 were obtained from Streets et al. (2003). The VOCs were divided into seven chemical species (i.e., C_2H_6, C_3H_8, C_2H_4, alkanes, alkenes, aromatics, oxygenates) and their mass splitting factors were

estimated in terms of the source intensity and national economic conditions in East Asia (Carmichael et al., 1998). The BVOC emissions, exhibiting significant variations in daytime and nighttime, were taken from the Acid Deposition and Oxidant Research Center (Tonooka, 2001). Isoprene and monoterpene were the major components of the BVOCs.

1.2 Simulation scenarios

The factor separation technique is an effective tool for performing model sensitivity analysis and for identifying factors that contribute significantly to model outputs. It is highlighted that the factor separation technique is able to decompose contributions from one factor alone and contributions from interactions with other factors by performing several case studies, especially when two or more factors are considered. This method has been widely applied to modeling studies in the meteorological and environmental sciences (Alpert et al., 1999; Romero et al., 2000; Thunis and Cuvelier, 2000; Tao et al., 2003, 2005). O_3 formation, which has two main precursors (VOCs and NOx), can be a good application for studying the interactions among different emission species.

In this work, the contributions of AVOCs (factor A), BVOCs (factor B) and NOx (factor N) emissions to O_3 were evaluated using a series of simulations with and without them. According to the factor separation rule, 2^3 simulations are required to quantify the contributions of A, B and N, which can be mathematically formulated as follows:

$$f_0 = f'_0 + 0 \quad (3)$$

$$f_N = f'_N + f_0 \quad (4)$$

$$f_A = f'_A + f_0 \quad (5)$$

$$f_B = f'_B + f_0 \quad (6)$$

$$f_{NA} = f'_N + f'_A + f'_{NA} + f_0 \quad (7)$$

$$f_{NB} = f'_N + f'_B + f'_{NB} + f_0 \quad (8)$$

$$f_{AB} = f'_A + f'_B + f'_{AB} + f_0 \quad (9)$$

$$f_{NAB} = f'_N + f'_A + f'_B + f'_{NA} + f'_{NB} + f'_{AB} + f'_{NAB} + f_0 \quad (10)$$

where, f is the model simulation result, while f' denotes the solution of equations for pure or synergistic contributions. f_0 is the background simulation with exclusion of factor A, B and N, and it represents physical and chemical situations isolated from the three factors. Thus, according to Stein and Alpert (1993), each simulation f can be split into a constant item (f_0) and items dependent on the three factors. Specifically, f_{NAB} represents the reference simulation with the inclusion of all three factors. f_A, f_B, f_N denote simulations with the inclusion of factor A alone, factor B alone and factor N alone, respectively. f_{NA}, f_{NB}, f_{AB} denote the result with the exclusion of factor B, factor A and factor N, respectively. f'_A, f'_B, f'_N denote the equation solution to the pure contribution of factors A, B and N, while f'_{NA}, f'_{NB}, f'_{AB}, f'_{NAB} represent the mutual interactions among factors N, A and B, respectively.

The daily maximum surface ozone (O_{3DM}) concentration at each grid from the reference simulation f_{NAB} was picked and the time to reach the peak was recorded. Correspondingly, simulated surface O_3 concentrations at the peak time of each day for the other seven simulated cases were selected to calculate the pure (f'_A, f'_B, f'_N) and synergistic (f'_{NA}, f'_{NB}, f'_{AB}, f'_{NAB}) contributions of emissions from Eqs. (3) to (10). The results were finally averaged over the whole summertime.

2 Results and discussion

2.1 Impacts of anthropogenic and biogenic emissions on O_3

2.1.1 Total contributions of AVOCs, BVOCs and NOx emissions

The surface O_3 formation from AVOCs or BVOCs and NOx emissions can be expressed by the sum of pure and synergistic impacts according to the factor separation technique. Use F_E to represent the ratio of total contributions of AVOCs, BVOCs and NOx to O_{3DM} concentrations:

$$F_E = \frac{f'_N + f'_A + f'_B + f'_{NA} + f'_{NB} + f'_{AB} + f'_{NAB}}{f_{NAB}} \times 100\% \quad (11)$$

High total contribution ratios (F_E) are found in the BTT region, the Henan, Anhui, Jiangsu provinces, some areas in the northern Korean Peninsula and in southern Japan, with a peak of approximately 50% (**Fig. 1a**). These ratios are high because the strong sunlight and high temperature in summer are favorable for photochemical reactions. In contrast, low contribution ratios are found in South China (< 30°N), especially in the southeastern coastal area with high VOCs and NOx emissions (**Fig. 2**). The abundant summer rainfall (**Fig. 1b**) caused by the Asian monsoon system brings much marine air from the lower latitudes and dilutes local high O_3 concentrations (Whelpdale and Moody, 1990; Chan et al., 1998). This effect is also the reason for the low O_3 concentrations usually observed at most monitoring sites in the East Asia Pacific rim regions (Wang et al., 1998; Monks, 2000; Pochanart et al., 2002, 2003).

The model simulations in this study used invariable boundary conditions which resulting in some uncertainties in long-term O_3 simulations (Khiem et al., 2011). However, the factor separation technique isolates the impact of boundary conditions by the term f_0, and therefore, the combination of pure and synergistic factors could reasonably reflect contributions of emissions.

2.1.2 Synergistic contributions

Large synergistic contributions between AVOC and NOx (f'_{NA} > 10 ppbv) are found in some areas of Heilongjiang

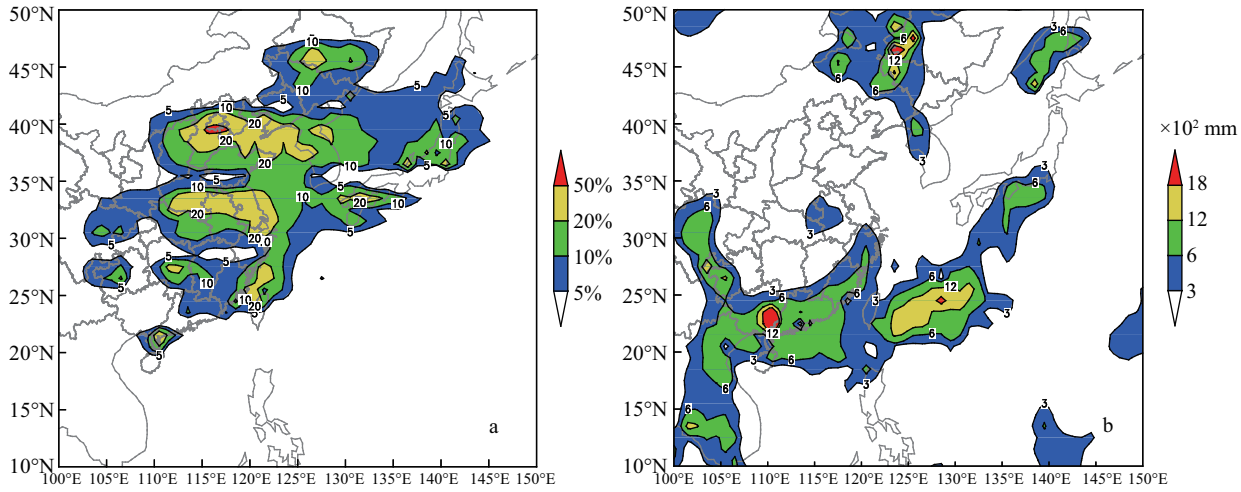

Fig. 1 (a) Fractions of total contributions of AVOCs, BVOCs and NOx to O_{3DM} concentrations in summer, (b) rainfall in summer.

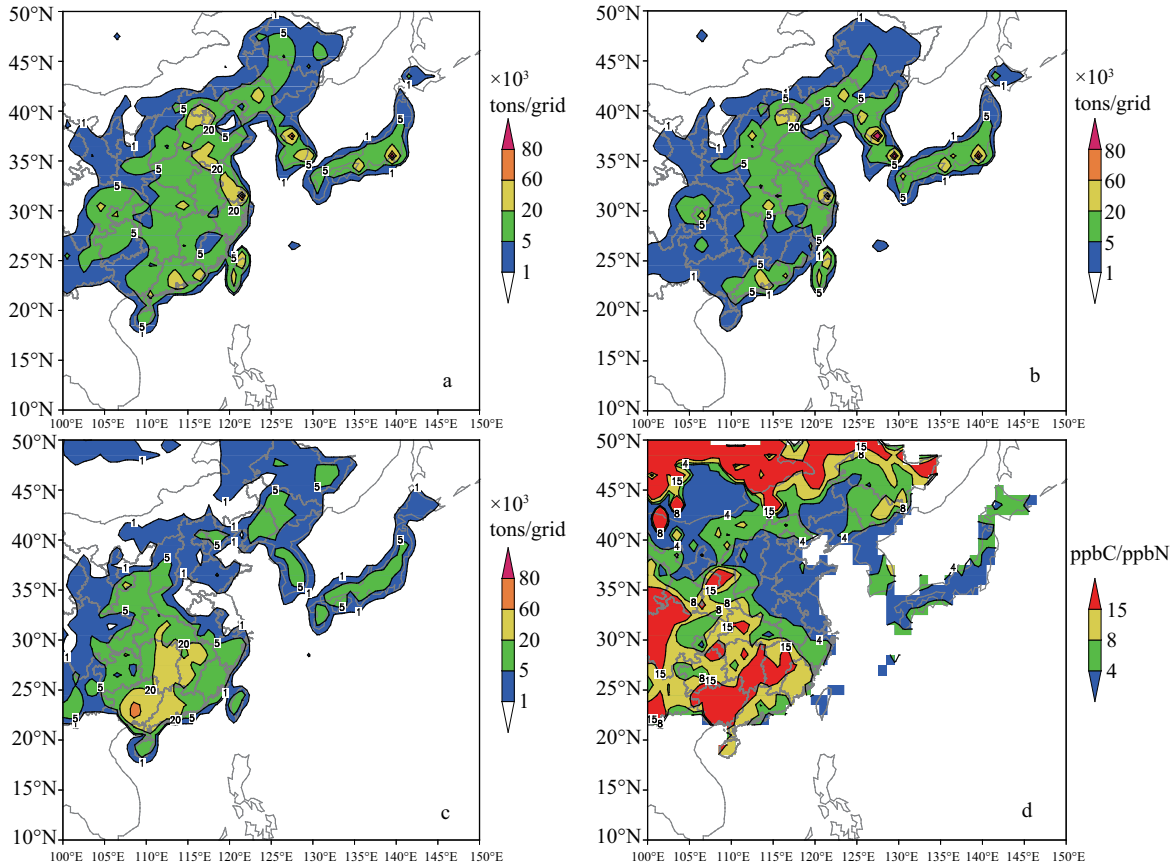

Fig. 2 Emissions of AVOCs, BVOCs and NOx in summer of 2000 and emission fractions. (a) AVOCs; (b) NOx; (c) BVOCs; (d) emission fractions of AVOCs and BVOCs to NOx.

Province, the BTT region, some areas of the Henan, Anhui and Jiangsu provinces, the central Korean Peninsula, and some areas in southern Japan, and the highest contributions are above 60 ppbv (**Fig. 3a**). This result coincides with high emission areas of AVOCs and NOx (**Figs. 2a** and **2b**). It is also noted that the values of f'_{NA} in China below 30°N are much lower than those in North China due to the influence of the Asian monsoon systems mentioned above (**Fig. 1b**).

Large synergistic contributions between BVOC and NOx (f'_{NB} > 5 ppbv) are found in North and South China, North Korea and central and southern Japan (**Fig. 3b**). It is interesting to see that the synergistic impacts of BVOC and NOx are prominent in some areas of South China, e.g., f'_{NB} reaches 25 ppbv near Zhanjiang in Guangdong provinces (**Fig. 3b**). This result suggests that BVOCs

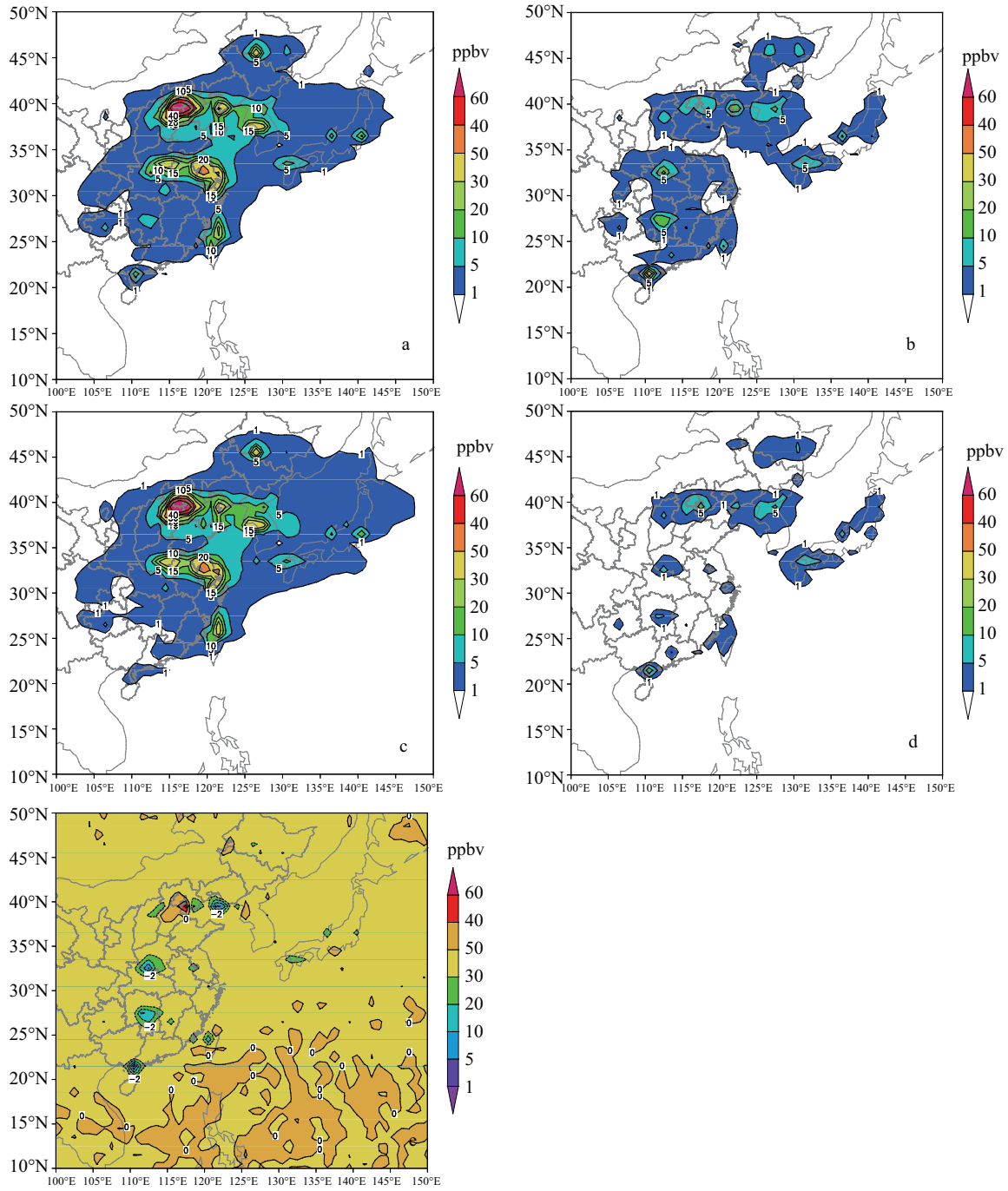

Fig. 3 Contributions of AVOCs, BVOCs and NOx to O_{3DM} in summer. (a) synergistic impacts between AVOCs and NOx; (b) synergistic impacts between BVOCs and NOx; (c) total contributions of AVOCs; (d) total contributions of BVOCs; (e) synergistic impacts among AVOCs, BVOCs and NOx.

mainly resulting from broad-leaf forests and shrubs play a major role in O_3 formation in a few small areas of South China.

By comparing of **Fig. 3a** and **b** we can see that f'_{NA} is over 10 ppbv in many areas above 30°N, especially in the BTT region, with a maximum of 60 ppbv. This result shows that synergistic impacts of AVOCs and NOx are dominant in most areas of North China. In contrast, f'_{NB} is generally lower than 10 ppbv in the studied domain, except for a few small areas in South China, e.g., Zhanjiang, where the monsoon system lowers the concentrations of O_3 precursors to a large extent in summer, while the O_3 formation through NOx and BVOCs reactions remains at a relatively high level.

The difference in synergistic contributions (f'_{NA} and f'_{NB}) between North and South China is evident and is similar to that for the spring in previous work (Qu et al., 2009). **Figure 4** shows the differences in the synergistic impacts

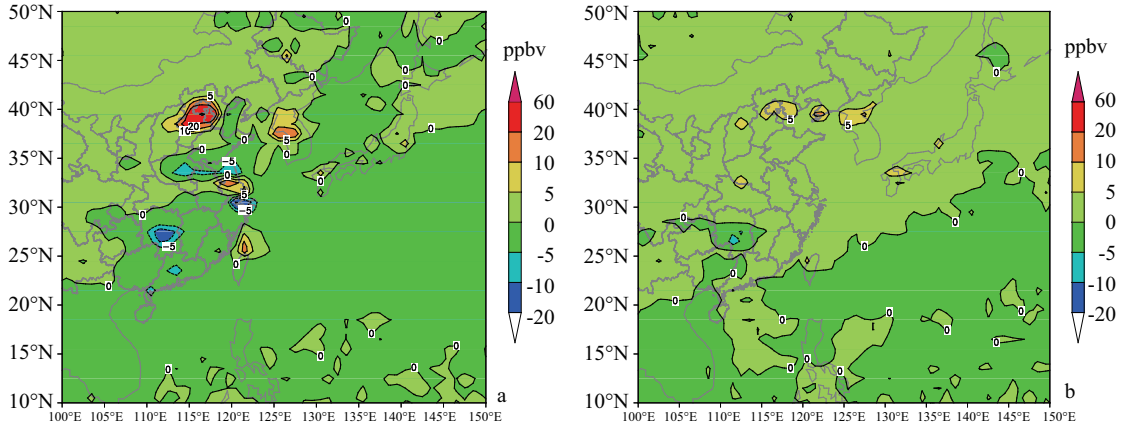

Fig. 4 Differences of synergistic impacts of AVOCs and NOx between summer and spring (a); differences of synergistic impacts of BVOCs and NOx between summer and spring (b).

between summer and spring. The f'_{NA} in the BTT and its surrounding areas in summer is generally larger by 10 ppbv than that in spring, with the largest differences approaching 60 ppbv. The increase of f'_{NB} in the BTT area in summer is only ~ 5 ppbv due to the low BVOC emissions compared with AVOC emissions. This illustrates that the high temperatures and radiation in summer significantly enhance the O_3 formation in those areas above 30°N with high NOx and VOC emissions. In most areas below 30°N, the f'_{NA} in summer is lower than that in spring due mainly to the monsoon systems. Moreover, in the central area of Hunan Province, the difference of f'_{NA} is large within the range of –10 ppbv to –20 ppbv. Another reason for these results is that excessive AVOC emissions suppress O_3 formation in the NOx-limited areas. The difference of f'_{NB} in the areas below 30°N ranges from –5 ppbv to 5 ppbv and is dissimilar to f'_{NA}; this is because the f'_{NB} is large in the high BVOC emission areas in summer and the influence of the monsoon systems on f'_{NB} is limited.

The total impact of AVOCs and BVOCs can be expressed by Eqs. (12) and (13):

$$T_A = f'_A + f'_{NA} + f'_{AB} + f'_{NAB} \quad (12)$$

$$T_B = f'_B + f'_{NB} + f'_{AB} + f'_{NAB} \quad (13)$$

T_A and T_B are the differences in the simulated results with and without AVOCs or BVOCs, respectively, as defined in Eq. (1). By the decomposition of the factor separation technique, it is seen that the total impacts of AVOCs or BVOCs actually include synergistic contributions with other emissions. Similar distribution patterns between **Fig. 3a, c** suggest that the synergistic contributions of AVOCs and NOx (f'_{NA}) are dominant in those areas where the emissions of AVOCs are much higher than those of BVOCs. From **Fig. 3d**, we can see that the T_B values do not exceed 10 ppbv in almost the entire studied domain, except Zhanjiang, with a peak of 15 ppbv, which is much lower than the synergistic contribution. This result can be explained by negative synergistic contributions of f'_{NAB} (**Fig. 3e**) among AVOCs, BVOCs and NOx, leading to O_3 decreases. The f'_{NAB} reduces O_3 concentrations in the southwestern areas of Henan Province and some areas of Hunan Province by 4–8 ppbv and by 10 ppbv in areas around Zhanjiang. Such is the case when O_3 decreases as VOCs (both AVOCs and BVOCs) continue increasing in the NOx-sensitive regimes (An et al., 1999; Zhu et al., 2006). The BVOC emissions are even larger than those of AVOCs in these areas (**Fig. 2**), revealing that reducing AVOCs alone can not effectively suppress O_3 formation (Chameides et al., 1988; Simpson, 1995; Thunis and Cuvelier, 2000; Tao et al., 2003). On the contrary, the f'_{NAB} enhances O_3 concentrations in the BTT region by 2–4 ppbv. The results indicate that the addition of BVOCs leads to an increase of O_3 concentrations in the VOC-sensitive regimes, but the O_3 formation from BVOC emissions is limited compared with that from AVOC emissions.

2.1.3 Daily mean contributions

The former section shows seasonal mean impacts of emissions of AVOCs or BVOCs with NOx on O_3 concentrations. This section will focus on the daily mean contributions of emissions of AVOCs or BVOCs with NOx by analyzing the simulations of four typical sites from northern to southern China, i.e., Beijing, Zhanjiang, Shuangfeng, and Guangzhou (**Fig. 5**), representing a northern economically developed city (Zhang et al., 2011), a southern ecological area, a southern forest (the Heng Mountains) and a southern economically developed city (Zhou et al., 2007), respectively.

T_A plays a dominant role in the formation of O_3 at Site Beijing in North China, with comparatively low BVOCs emissions. f'_{NA} is the main contributor to T_A, and both have nearly identical time variations. Although the daily peak value of T_B at Beijing can exceed 20 ppbv with an increase in BVOC emissions in summer, it only contributes approximately 13% to O_{3DM} concentrations and has relatively low impacts on O_3 formation. Except for a few days, f'_{NAB} is generally positive, indicating that mutual impacts among AVOCs, BVOCs and NOx enhance O_3 concentrations. AVOCs emissions should be reduced for

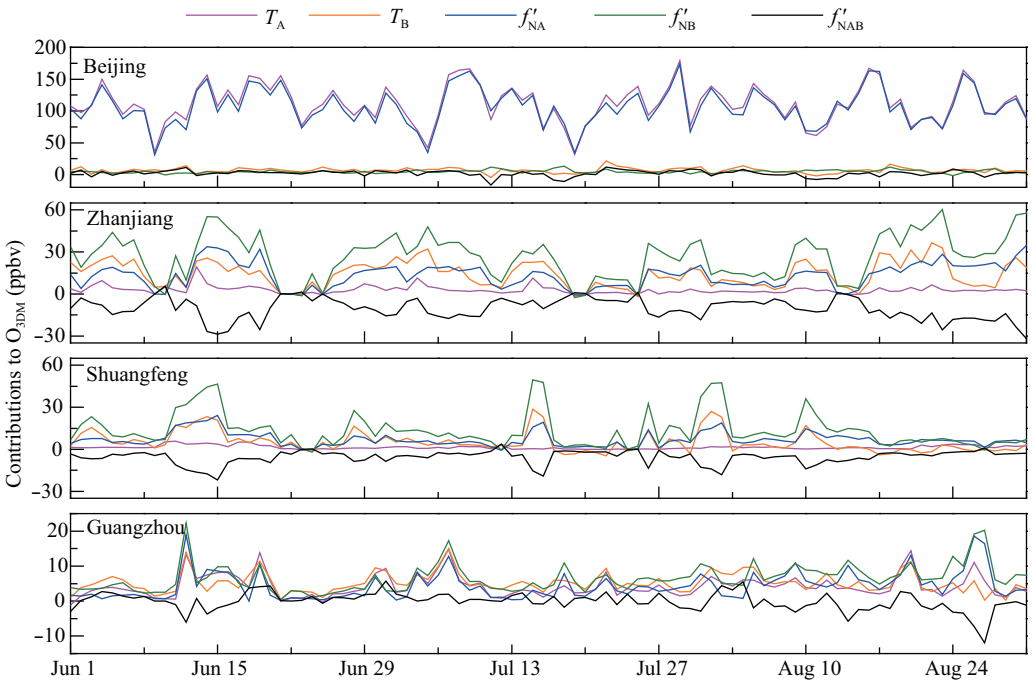

Fig. 5 Daily contributions of synergistic and total contributions to O_{3DM} at four sites from June to August 2000. T_A: total contributions of AVOCs; T_B: total contributions of BVOCs; f'_{NA}: synergistic contributions of AVOCs and NOx; f'_{NB}: synergistic contributions of BVOCs and NOx; f'_{NAB}: synergistic contributions among AVOCs, BVOCs and NOx.

effective O_3 controls.

Compared with Beijing, the T_A at Site Guangzhou, which also has high anthropogenic emissions (AVOCs and NOx), shows no large fluctuations during the whole summer, and the T_A at this site stays below 15 ppbv. The summer monsoon system significantly dilutes O_3 precursors and then decreases O_3 concentrations. T_B has similar daily variations with T_A because the BVOC emissions are comparable to those of the AVOCs at Guangzhou, where BVOCs and AVOCs play a competitive role in the reaction with NOx. The synergistic impact of f'_{NAB} appears positive in some days and negative in other days, depending on meteorological conditions and BVOC emissions. Guangzhou is located in a transition regime for O_3 formation according to the VOCs/NOx ratios (**Fig. 2d**), and f'_{NAB} shows an increasing or a decreasing function to O_{3DM} from day to day. Therefore, both AVOCs and BVOCs should be considered in O_3 control measures. It is also notable that T_B is greater than T_A in the first week of August, while T_B is less than T_A in the last week, showing that control strategies from case studies can be infeasible for a long-term applications (e.g., seasonal).

Large BVOC emissions lead to a large T_B at Site Shuangfeng, accounting for approximately 30 ppbv. Among these four sites, BVOCs have the largest impact on O_3 formation at Site Zhanjiang, where the daily peak of T_B is ca. 40 ppbv (nearly 40% of O_{3DM} concentrations), approaching or exceeding those in some developed countries in Europe and North America (Thunis and Cuvelier, 2000; Tao et al., 2003). Most T_B is from the synergistic contributions of BVOCs and NOx (f'_{NB}) at Sites Shuangfeng and Zhanjiang, and f'_{NB} is considerably greater than T_B in many days; this is because f'_{NAB} always remains below zero and has large negative values in some days. This result displays a mitigated effect when emissions of AVOCs and BVOCs are larger than those of NOx and O_3 formation is restricted with the availability of VOCs. Thus, remarkable negative values of T_B can be seen at Sites Shuangfeng and Zhanjiang when the negative f'_{NAB} shows typical daily changes. This effect is also why the total contributions of BVOCs can be less than the synergistic contributions of BVOCs and NOx, as mentioned above. Comparably, T_A has low contributions to O_{3DM} due to large negative f'_{NAB} values. BVOCs emissions are the main contributor to O_3 formation in the forest and ecological zones.

It is notable that Sites Zhanjiang and Guangzhou have similar large biogenic emissions (**Fig. 2c**), but the total contributions of BVOCs are completely different. The BVOC emissions at Zhanjiang are larger than those at Guangzhou, whereas Guangzhou has higher NOx emissions than Zhanjiang (**Fig. 2b**). The relatively low NOx emissions at Zhanjiang lead to a weak depletion of O_3. The combined result produces high T_B at Site Zhanjiang.

2.2 Comparison of observations and simulations

All observed data were obtained from the Acid Deposition Monitoring Network in East Asia (EANET, http://www.adorc.gr.jp), which implements strict quality assurance and quality control in data management. Detailed EANET information can be found in previous publications (An et al., 2002; Han et al., 2006). Twenty monitoring sites from East Asian countries were selected

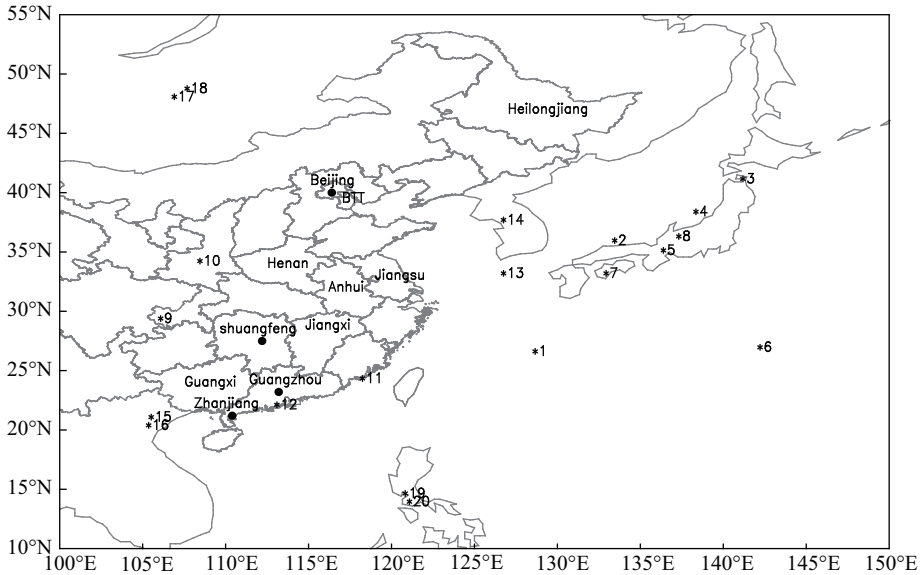

Fig. 6 Distribution of 20 EANET monitoring sites and specific locations mentioned in this work. (1) Hedo; (2) Oki; (3) Tappi; (4) Sado; (5) Ijira; (6) Ogasawa; (7) Yusuhara; (8) Happo; (9) Guanyinqiao; (10) Weishuiyuan; (11) Hongwen; (12) Xiangzhou; (13) Cheju; (14) Kanghwa; (15) Hanoi; (16) Hoa Binh; (17) Ulaanbaatar; (18) Terelj; (19) Metro Manila; (20) Los Banos.

due to their good regional representativeness and are marked in **Fig. 6**.

By comparing the observations and simulations at Sites Happo, Oki, Tappi, and Sado of Japan (**Fig. 7**), we can see that the RAQM well simulates the temporal variations of NOx and O_3. The temporal NOx variations are quite well reproduced. The O_3 concentrations in the period of July and August are generally overestimated; uncertainties in the initial and boundary O_3 concentrations are the main reasons for this result, as discussed by An et al. (2002).

The NO_3^- simulations in rainwater at most sites in Japan fit the observations, with discrepancy within a factor of 2 (**Fig. 8**). The simulations at Site Ijira are significantly underestimated, whereas those at Site Ogasawa are remarkably overestimated in Japan. The coarse spatial resolution ($1^\circ\times1^\circ$) may underestimate the emissions at Site Ijira, while the emissions at Site Ogasawa may be overestimated. The simulated NO_3^- concentrations at Sites Weishuiyuan, Hongwen, Ulaanbaatar, Terelj, and Metro Manila are significantly underestimated due to uncertainties in both the emissions and the coarse spatial resolution.

3 Conclusions

Synergistic contributions between AVOCs or BVOCs and NOx are always positive and favorable for O_3 formation. The maximum synergistic contributions of AVOCs and NOx reach 60 ppbv in the BTT region. BVOCs plays a relatively minor role in O_3 formation throughout the summer in most areas over East Asia, except some limited areas with elevated emissions of BVOCs, with the maximum synergistic contributions reaching 25 ppbv. This result suggests that BVOC emissions have a significant impact on O_{3DM} concentrations in such special areas in summer and should be considered when O_3 control measures are taken. The synergistic contributions among AVOCs, BVOCs and NOx show a remarkable spatial variation, increasing O_3 concentrations in the BTT region, where emissions of AVOCs are much higher than those of BVOCs, and decreasing O_3 concentrations in some NOx-limited areas in South China where BVOC emissions are high.

Compared with those in spring, the O_3 concentrations from synergistic contributions of AVOCs and NOx and BVOCs and NOx in summer are considerably increased in those areas above 30°N with high NOx and VOC emissions. f'_{NA} and f'_{NB} are lower than those in spring in some areas below 30°N as a combined result of the monsoon systems and the excessive emissions of AVOCs and BVOCs.

The total contributions of BVOCs to O_{3DM} vary significantly from day to day and from location to location. T_B only contributes approximately 13% to O_{3DM} concentrations in the northern sites such as Beijing, with a peak value of 20 ppbv, while it contributes nearly 40% of the O_{3DM} concentrations in the southern sites such as Zhanjiang, with a peak value of 40 ppbv. In some areas (e.g., Guangzhou) BVOCs make a greater total contribution than AVOCs to O_{3DM} concentrations on some days, while they make a lesser contribution than AVOCs on other days. This result implies that O_3 control measures obtained from episodic studies may be limited for long-term (e.g. seasonal) applications.

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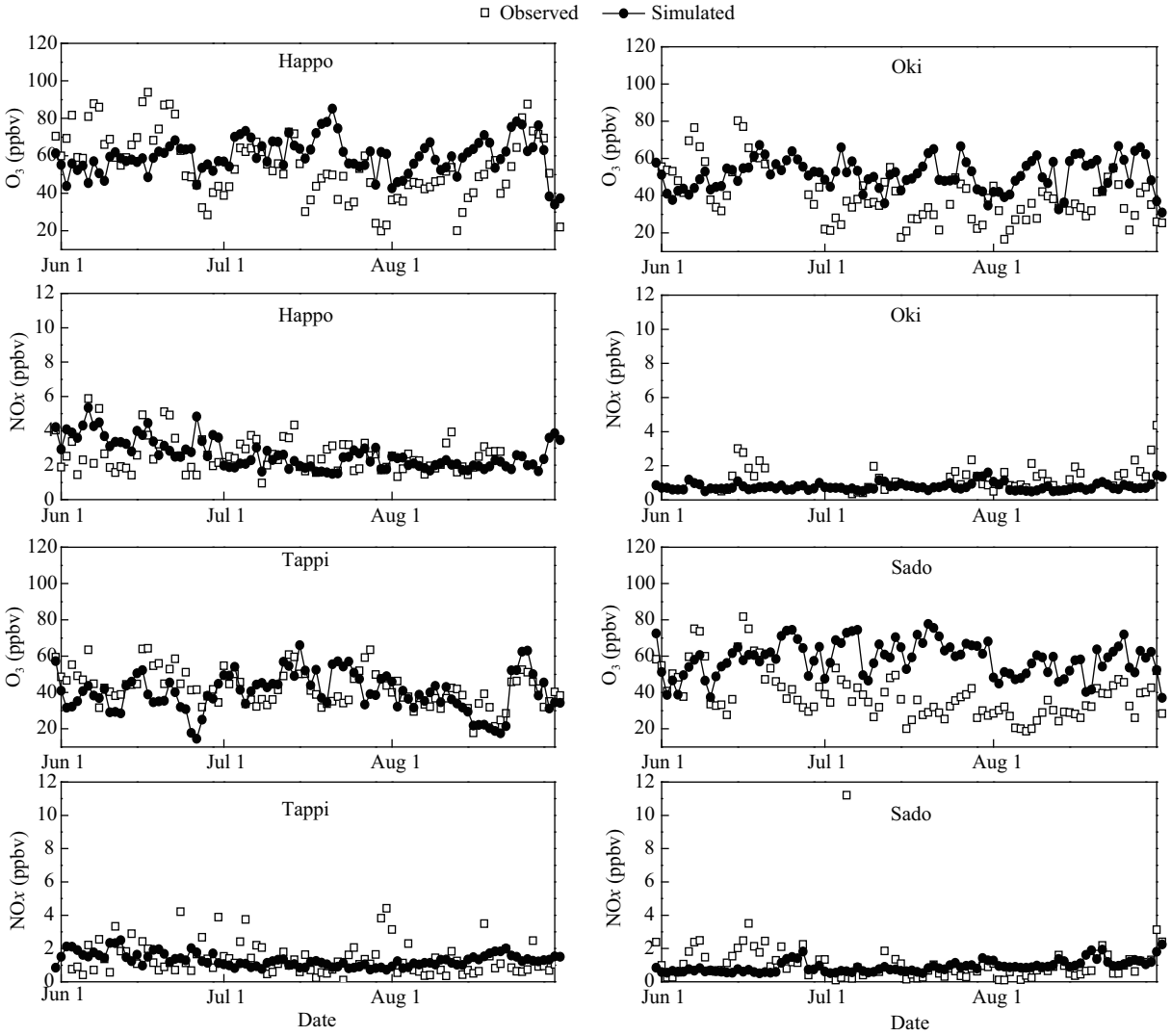

Fig. 7 Simulated and observed daily mean O_3 and NO*x* concentrations at the Happo, Oki, Tappi and Sado sites from June to August 2000.

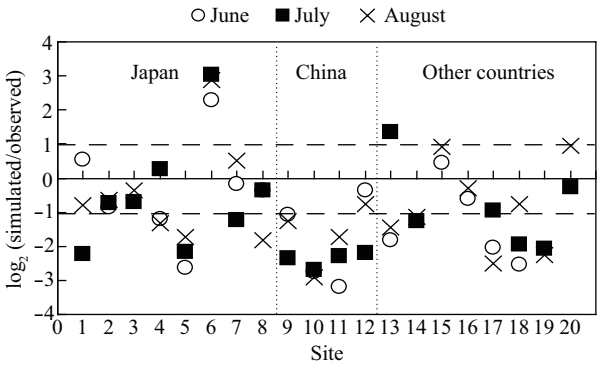

Fig. 8 Comparison of simulated and observed concentrations of NO_3^- in rainwater at 20 sites (Sites 1–20 are the same as that in **Fig. 6**).

References

Alpert P, Tsidulko M, Itzigsohn D, 1999. A shallow, short-lived meso-beta cyclone over the Gulf of Antalya, eastern Mediterranean. *Tellus*, 51(2): 249–262.

An J L, Han Z W, Wang Z F, 1999. Impacts of changes in the concentration of nonmethane hydrocarbon (NMHC) and NO*x* on amount of O_3 formation. *Chinese Journal of Atmospheric Sciences*, 23(6): 753–761.

An J L, Ueda H, Kazuhide M, Hasome H, Iwata M, 2003. Simulated impacts of SO_2 emissions from the Miyake volcano on concentration and deposition of sulfur oxides in September and October of 2000. *Atmospheric Environment*, 37(22): 3039–3046.

An J L, Ueda H, Wang Z F, Matsuda K, Kajino M, Cheng X J, 2002. Simulations of monthly mean nitrate concentrations in precipitation over East Asia. *Atmospheric Environment*, 36(26): 4159–4171.

Brodzinsky R, Cantrell B K, Endlich R M, Bhumralkar C M, 1984. A long-range air pollution transport model for Eastern North America-II. Nitrogen oxides. *Atmospheric Environment*, 18(11): 2361–2366.

Byun D W, Dennis R, 1995. Design artifacts in Eulerian air quality models: evaluation of the effects of layer thickness and vertical profile correction on surface O_3 concentrations. *Atmospheric Environment*, 29(1): 105–126.

Carmichael G R, Peters L K, Saylor R D, 1991. The STEM-II regional scale acid deposition and photochemical oxidant model: I. An overview of model development and applications. *Atmospheric Environment*, 25(10): 2077–2092.

Carmichael G R, Uno I, Phadnis M J, Zhang Y, Sunwoo Y, 1998. Tropospheric O_3 production and transport in the springtime in east Asia. *Journal of Geophysical Research*, 103(D9): 1649–1671.

Castell N, Mantilla E, Stein A F, Salvador R, Millan M, 2010. A modeling study of the impact of a power plant on ground-level O_3 in relation to its location: Southwestern spain as a case study. *Water Air and Soil Pollution*, 209(1-4): 61–79.

Chameides W L, Linsay R W, Richardson J, Kiang C S, 1988. The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. *Science*, 241(4872): 1473–1475.

Chan L Y, Liu H Y, Lam K S, Wang T, Oltmans S J, Harris J M, 1998. Analysis of the seasonal behavior of tropospheric O_3 at Hong Kong. *Atmospheric Environment*, 32(2): 159–168.

Dodge M C, 1977. Combined use of modeling techniques and smog chamber data to derive O_3 precursor relationships. In: Proceedings of the International Conference on Photochemical Oxidant Pollution and its Control (Dimitriades B). Vol II, EPA-600/3-77-0016, US EPA, RTP, NC. 881–889.

Grell G A, Dudhia J, Stauffer D R, 1995. A description of the fifth-generation Penn State/NCAR mesoscale model (MM5). NCAR Techinacal Note/NT-398+ STR. http://www.mmm.ucar.edu/mm5/documents/mm5-desc-doc.html.

Guenther A B, Geron C, Pierce T, Lamb B, Harley P, Fall R, 2000. Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America. *Atmospheric Environment*, 34(12-14): 2205–2230.

Guenther A B, Hewitt C N, Erickson D, Fall R, Geron C, Graedel T et al., 1995. A global model of natural volatile organic compound emissions. *Journal of Geophysical Research*, 100(D5): 8873–8892.

Guenther A B, Zimmerman P R, Harley P C, Monson R K, Fall R, 1993. Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses. *Journal of Geophysical Research*, 98(D7): 12609–12617.

Han Z W, 2007. A regional air quality model: Evaluation and simulation of O_3 and relevant gaseous species in East Asia during spring 2001. *Environmental Modelling & Software*, 22(9): 1328–1336.

Han Z W, Ueda H, Matsuda K, 2005. Model study of the impact of biogenic emission on regional O_3 and the effectiveness of emission reduction scenarios over eastern China. *Tellus*, 57(1): 12–27.

Han Z W, Ueda H, Matsuda K, Zhang R, Arao K, Kanai Y et al., 2004. Model study on particle size segregation and deposition during Asian dust events in March 2002. *Journal of Geophysical Research*, 109(D19). DOI: 10.1029/2004JD004920.

Han Z W, Ueda H, Tatsuya S, 2006. Model study on acidifying wet deposition in East Asia during wintertime. *Atmospheric Environment*, 40(13): 2360–2373.

Kajino M, Ueda H, Satsumabayashi H, An J L, 2004. Impacts of the eruption of Miyakejima volcano on air quality over far east Asia. *Journal of Geophysical Research*, 109. DOI: 10.1029/2004JD004762.

Kato N, Akimoto H, 1992. Anthropogenice missionso f SO_2 and NO*x* in Asia: Emission inventories. *Atmospheric Environment*, 26: 2997–3017.

Khiem M, Ooka R, Huang H, Hayami H, 2011. A numerical study of summer O_3 concentration over the Kanto area of Japan using the MM5/CMAQ model. *Journal of Environmental Sciences*, 23(2): 236–246.

Lippmann M, 1991. Health effects of tropospheric O_3. *Environmental Science and Technology*, 25(12): 1954–1962.

Lurmann F W, Lloyd A C, Atkinson R, 1986. A chemical mechanism for use in long-range transport/acid deposition computer modeling. *Journal of Geophysical Research*, 91(D10): 10905–10915.

McElroy M B, Nielsen C P, Lydon P, 1998. Industrial growth, air pollution, and environmental damage: Complex challenges for China. In: Energizing China: Reconciling Environmental Protection and Economic Growth. Harvard University Press, Harvard.

Monks P S, 2000. A review of the observations and origins of the spring O_3 maximum. *Atmospheric Environment*, 34(21): 3545–3561.

Okita T, Hara H, Fukuzaki N, 1996. Measurements of atmospheric SO_2 and SO_4^{2-}, and determination of the wet scavenging coefficient of sulfate aerosols for the winter monsoon season over the Sea of Japan. *Atmospheric Environment*, 30(22): 3733–3739.

Peng L X, Tang X Y, Bai Y H, Li J L, 2000. Effect of biogenic hydrocarbon to photochemical pollution in Guangzhou. *China Environmental Science*, 20(2): 132–135.

Pochanart P, Akimoto H, Kajii Y, Potemkin V M, Khodzher T V, 2003. Regional background O_3 and carbon monoxide variations in remote Siberia/East Asia. *Journal of Geophysical Research*, 108(D1): 4028. DOI: 10.1029/2001JD001412.

Pochanart P, Akimoto H, Kinjo Y, Tanimoto H, 2002. Surface O_3 at four remote island sites and the preliminary assessment of the exceedances of its critical level in Japan. *Atmospheric Environment*, 36(26): 4235–4250.

Qu Y, An J L, Zhou H, Ye X F, 2009. Synergistic impacts of anthropogenic and biogenic emissions on spring surface O_3 in East Asia. *Chinese Journal of Atmospheric Sciences*, 33(4): 670–680.

Romero R, Doswell C A, Ramis C, 2000. Mesoscale numerical study of two cases of long-lived quasi-stationary convective systems over eastern Spain. *Monthly Weather Review*, 128(11): 3731–3751.

Russell A, Dennis R, 2000. NARSTO critical review of photochemical models and modeling. *Atmospheric Environment*, 34(12-14): 2283–2324.

Seaman N L, 2000. Meteorological modeling for air quality assessments. *Atmospheric Environment*, 34(12-14): 2231–2259.

Shao M, Tang X Y, Zhang Y H, Li W J, 2006. City clusters in China: air and surface water pollution. *Frontiers in Ecological Environment*, 4(7): 353–361.

Shao M, Zhao M P, Zhang Y H, Peng L X, Li J L, 2000. Biogenic VOCs emissions and its impact on O_3 formation in major cities of China. *Journal of Environmental Science and Health*, 35(10): 1941–1950.

Sillman S, Logan J A, Wofsy S C, 1990. The sensitivity of O_3 to nitrogen oxides and hydrocarbons in regional O_3 episodes. *Journal of Geophysical Research*, 95(D2): 1837–1851.

Simpson D, 1995. Biogenic emissions in Europe. 2: Implications for O_3 control strategies. *Journal of Geophysical Research*, 100(D11): 22891–22906.

Solomon P, Cowling E, Hidy G, Furiness C, 2000. Comparison of scientific findings from major O_3 field studies in North America and Europe. *Atmospheric Environment*, 34(12-14): 1885–1920.

Song Y, Tang X Y, Zhang Y, Hu M, Fang C, Zen L et al., 2002. Effects on fine particles by the continued high temperature weather in Beijing. *Environmental Science*, 23(4): 33–36.

Stein U, Alpert P, 1993. Factor separation in numerical simulations. *Journal of the Atmospheric Sciences*, 50(14): 2107–2115.

Streets D G, Bond T C, Carmichael G R, Fernandes S D, Fu Q, He D et al., 2003. An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. *Journal of Geophysical Research*, 108. DOI: 10.1029/2002JD003093.

Tao Z N, Larson S M, Williams A, Caughey M, Wuebbles D J, 2005. Area, mobile, and point source contributions to ground level O_3: a summer simulation across the continental USA. *Atmospheric Environment*, 39(10): 1869–1877.

Tao Z N, Larson S M, Wuebbles D J, Williams A, Caughey M, 2003. A summer simulation of biogenic contributions to ground-level O_3 over the continental United States. *Journal of Geophysical Research*, 108(D14). DOI: 10.1029/2002JD002945.

Thunis P, Cuvelier C, 2000. Impact of biogenic emissions on O_3 formation in the Mediterranean area – A BEMA modeling study. *Atmospheric Environment*, 34(3): 467–481.

Tonooka Y, 2001. Emission inventory compilation for NMVOC and CO in East Asia. In: The 5th International Workshop on the Comparison of Trans-boundary Air Pollution Model and Harmonization of the Methodology of Emission Inventories of Air Pollutants in East Asia, Japan.

Walmsley J L, Wesely M L, 1996. Modification of coded parametrizations of surface resistances to gaseous dry deposition. *Atmospheric Environment*, 30(7): 1181–1188.

Wang Y H, Logan J A, Jacob D J, 1998. Global simulation of tropospheric O_3-NOx-hydrocarbon chemistry: 2. Model evaluation and global O_3 budget. *Journal of Geophysical Research*, 103(D9): 10727–10756.

Wesely M L, 1989. Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models. *Atmospheric Environment*, 23(6): 1293–1304.

Whelpdale D M, Moody J L, 1990. Large-scale meteorological regimes and transport processes. In: The Long Range Transport of Natural and Contaminant Substances. Kluwer, Dordrecht. 3–36.

Xie M, Wang T J, Jiang F, Yang X Q, 2007. Modeling of natural NOx and VOC emissions and their effects on tropospheric photochemistry in China. *Environmental Science*, 28(1): 32–40.

Zhang J, Ouyang Z Y, Miao H, Wang X K, 2011. Ambient air quality trends and driving factor analysis in Beijing, 1983–2007. *Journal of Environmental Sciences*, 23(12): 2019–2028.

Zhang Y H, Shao K S, Tang X Y, 1998. The study of urban photochemical smog pollution in China. *Acta Scientiarum Naturalium Universitatis Pekinensis*, 34(2-3): 392–400.

Zhang Y H, Su H, Zhong L J, Cheng Y F, Zeng L M, Wang X S et al., 2008. Regional O_3 pollution and observation-based approach for analyzing O_3-precursor relationship during the PRIDE-PRD2004 campaign. *Atmospheric Environment*, 42(25): 6203–6218.

Zhou K, Ye Y H, Liu Q, Liu A J, Peng S L, 2007. Evaluation of ambient air quality in Guangzhou, China. *Journal of Environmental Sciences*, 19(4): 432–437.

Zhu B, An J L, Wang Z F, Li Y, 2006. Relations of diurnal variations of photochemical O_3 to its precursors. *Journal of Nanjing Institute of Meteorology*, 29(6): 744–749.

Zhu B, Sun Z B, An J L, 2002. A research of photochemical transformation of NOx in troposphere. *Chinese Journal of Atmospheric Sciences*, 26(4): 487–495.

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