Modeling study on the air quality impacts from emission reductions and atypical meteorological conditions during the 2008 Beijing Olympics

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\textbf{ABSTRACT}

Understanding of the relative impacts of emission reductions and meteorological variations on air quality during the 2008 Beijing Olympics has an important policy implication. In this work, detailed process analyses and sensitivity simulations under different emission and meteorology scenarios were conducted using CMAQ and the Process Analysis tool to quantify the air quality benefits from emission reductions and meteorological variations in August 2008. The results indicate that emission-driven changes dominate surface concentration reductions of SO\textsubscript{2}, NO\textsubscript{x}, VOCs, daily maxima O\textsubscript{3} and PM\textsubscript{2.5} by \(\frac{1}{C_0}\) 11\% to \(\frac{1}{C_0}\) 83\%. The effect of meteorology-driven changes on species concentrations can be either ways (by \(\frac{1}{C_0}\) 46\% to \(\frac{1}{C_0}\) 105\%) at different locations. The dominant processes contributing to O\textsubscript{3}, PM\textsubscript{2.5}, SO\textsubscript{4}\textsuperscript{2−}, NO\textsubscript{3}−, and secondary organic aerosol (SOA) are identified. Gas-phase chemistry is a major process for O\textsubscript{3} production, and PM processes are dominant sources for PM\textsubscript{2.5} in the planetary boundary layer (PBL). The reduced emissions weaken the source contributions of gas-phase chemistry to O\textsubscript{3} and those of PM processes to PM\textsubscript{2.5}, with weaker vertical mixing processes and horizontal transport in the PBL. Compared with 2007, 2008 has a higher humidity, lower temperature and more precipitation that benefits O\textsubscript{3} reduction within the PBL, and a weaker vertical mixing that disbenefits reductions of all pollutants concentrations. Stronger process contributions of cloud processes (e.g., below- and in-cloud scavenging, and wet deposition) in 2008 help reduce concentrations of PM\textsubscript{2.5}, NO\textsubscript{3}−, and SOA, but they (e.g., aqueous-phase chemistry) enhance surface SO\textsubscript{4}\textsuperscript{2−} concentrations. Smaller process contributions of aerosol processes help reduce the concentrations of SOA and SO\textsubscript{4}\textsuperscript{2−} but enhance NO\textsubscript{3}− and PM\textsubscript{2.5} in lower layers (1–6) due to the evaporation of NO\textsubscript{3}. The ratios of \(P_{\text{HNO}_3}/P_{\text{VOC}}\) increase under the controlled simulation, indicating that the emission control actions enforced during the 2008 Olympics weakened the sensitivity of O\textsubscript{3} chemistry to VOC emissions in urban areas.

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1. Introduction

As the capital, the political, economic and cultural center of China, and one of the megacities in the world, Beijing suffers severe deterioration of urban air quality since 1980s, due to the rapid increases of fossil fuel consumptions, active constructions, and vehicle population, as well as human population. The annual average concentrations of SO\textsubscript{2}, NO\textsubscript{x}, and PM\textsubscript{10} were 55, 71, and 149 \(\mu\)g m\textsuperscript{-3} in 2004, respectively, which are much higher than those in the western countries (Hao et al., 2007). High concentrations of PM\textsubscript{2.5} and O\textsubscript{3} in Beijing were frequently reported during past decades (He et al., 2001; Sun et al., 2004; Zheng et al., 2005; Duan et al., 2006; Wang et al., 2006; Fu et al., 2009; Tang et al., 2009; Zhao et al., 2009).

In order to keep the promise of Green Olympic Principle and ensure air quality at a healthy level during 2008 Beijing Olympic Games, the Chinese government enforced a series of aggressive measures, starting two-month in advance, to maximally reduce the emissions of key pollutants in Beijing and surrounding areas. The daily emissions of SO\textsubscript{2}, NO\textsubscript{x}, PM\textsubscript{10}, and anthropogenic non-methane...
volatile organic compounds (NMVOC) were reduced by 41%, 47%, 55%, and 57%, respectively, during the Olympic Games (Wang et al., 2010a). These emission control efforts resulted in a significant improvement in air quality during 2008 Beijing Olympic Games. For example, both aerosol optical depths (AOD) and column mass concentrations of NO\textsubscript{2}, SO\textsubscript{2}, and CO from satellite-retrievals showed a noticeable reduction over Beijing and surrounding areas during the Olympic period (Cermak and Knutti, 2009; Mijling et al., 2009; Wittie et al., 2009; Wu et al., 2010). The concentrations of O\textsubscript{3}, CO, NO\textsubscript{2}, SO\textsubscript{2} and particulate matter (PM) from ground-level monitoring sites also showed large decreases (Wang and Xie, 2009; Wang et al., 2009b; Braniš and Vetvicka, 2010). Wang et al. (2009d) reported that the reduction in the emissions of ozone precursors accounted for 80% of the decrease in O\textsubscript{3} mixing ratios at the Miyun rural site compared with the same period in 2006 and 2007. Wang et al. (2010a) also reported that more than 60% of PM\textsubscript{2.5} concentration decreases can be attributed to emission reductions compared to one month ahead of Olympic Games (i.e., July 2008).

On the other hand, some studies indicated that atypical meteorological conditions had a significant effect on air quality during the Olympic Games. Cermak and Knutti (2009) reported a statistically significant reduction in aerosol load in Beijing and the immediate surroundings by 11%, but attributed meteorological variability to be the main factor causing such a decrease. Wang et al. (2009b) reported that the atypical meteorological conditions accounted for 40% of the total variation in PM\textsubscript{10} concentrations, which is more than the contribution of source control measures (i.e., 16%). Wang et al. (2010b) reported that the improved air quality on most of the days during the Olympics had apparent relationship with weather changes, which warrants future modeling studies to quantify the relative importance of the emission reduction and meteorology variations in affecting air quality.

Understanding of the effects of emission reductions and meteorological variations on air quality, in particular, those on the successful air quality improvement during the Olympic Games, is crucial for future control policy design for Beijing and other cities in China. O\textsubscript{3} and PM\textsubscript{2.5}, as two major regional air pollutants, are affected by many factors including emissions of multi-pollutants (e.g., NO\textsubscript{x}, VOCs, SO\textsubscript{2}, NH\textsubscript{3}, and primary particles), meteorological processes (e.g., atmospheric transport and cloud scavenging), and chemical reactions (e.g., photochemistry and multi-phase reactions). The intricate interactions among these processes usually cause highly non-linear responses of chemical concentrations to the changes of emissions. Process analysis (PA), as one of advanced probing tools embedded in the U.S. Environmental Protection Agency (EPA) Model-3/Community Multi-scale Air Quality (CMAQ) modeling system (Binkowski and Roselle, 2003), enables quantitative assessment on integrated rates of various processes and reactions, thereby quantifying their relative influences on key pollutants. PA has been widely used to study the fate and formation mechanisms of regional O\textsubscript{3} and particles (e.g., Jang et al., 1995; Zhang et al., 2005, 2009, 2010; Tonse et al., 2008; Xu et al., 2008; Wang et al., 2009a; Liu et al., 2010a,b, 2011).

Beijing Olympic Games, as a successful example of emission reduction actions that involved the whole society in a short time period, provides a good opportunity for researchers to evaluate the effectiveness of mandatory emission restrictions. Following an evaluation of the emission reductions during the Beijing Olympic Games reported by Wang et al. (2010a), we applied CMAQ-PA tool for a detailed process analysis and conducted multi-scenarios analysis on the model responses to emission reductions and variations of meteorological conditions in this work. Our objectives were to examine the influential processes and their sensitivity to the variation of emissions and meteorological conditions and estimate the effects of emissions reductions and atypical meteorological conditions on air quality improvement. The most influential processes that lead to the formation and accumulation of O\textsubscript{3} and PM species (e.g., sulfate (SO\textsubscript{4}\textsuperscript{2-}), nitrate (NO\textsubscript{3}\textsuperscript{-}), and secondary organic aerosol (SOA)) are identified. The ratios of the production rates of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) and nitrate acid (HNO\textsubscript{3}) combined with several other photochemical indicators are used to indicate the NO\textsubscript{x} vs. VOC-limited O\textsubscript{3} chemistry in Beijing.

2. Methodology

2.1. Modeling system and process analysis

CMAQ version 4.7 with the 2005 Carbon Bond gas-phase mechanism (CB05) and the AEROS aerosol module was used in this study. The meteorological fields were obtained using the fifth-generation National Center for Atmospheric Research (NCAR)/Pennsylvania State University (PSU) Mesoscale Model (MM5), version 3.7. Triple-nested simulations at 36-km over China, 12-km over the eastern China, and 4-km over the Beijing area, as shown in Fig. 1, are conducted for both August 2007 and August 2008. The emissions we used in this study are described in Supplementary information. The model system was described in our previous paper (Wang et al., 2010a). The model performance for 2007/2008 baseline simulation has been thoroughly evaluated and discussed in Supplementary information. As shown in Table S2, the statistics

Fig. 1. Triple nesting simulation domains and locations of two observational sites: Tsinghua (THU) and Miyun (MIY) (Domain1: 36-km over China with 164 × 97 × 14 grids; Domain 2: 12-km over the eastern China with 214 × 136 × 14 grids; Domain 3: 4-km over Beijing with 54 × 60 × 14 grids. Simulation period is August 1–31, 2007 and August 1–31, 2008; THU is located in the north of metropolitan areas with millions of people and a busy on-road network. Few industry plants exist near THU. Its surrounding sources include on-road transportation and domestic emissions. It is under the influence of other sources of urban areas. MIY is a rural site, 100 km away from the Beijing urban center, and it is located in the north-west of Beijing as a direct downwind site in summer. The terrain elevation in MIY is higher than the urban area, and temperature is relative lower).
indicate that the model generally catch the meteorological conditions and pollution concentrations.

The PA in CMAQ includes the Integrated Process Rates (IPRs) and Integrated Reaction Rates (IRRs). IPRs provide hourly contributions to pollutant concentrations from seven major atmospheric processes including the emissions of primary species, horizontal transport (i.e., the sum of horizontal advection and diffusion), vertical transport (i.e., the sum of vertical advection and diffusion), gas-phase chemistry, dry deposition, cloud processes (i.e., the net effect of cloud attenuation of photolytic rates, aqueous-phase chemistry, below- and in-cloud scavenging, and wet deposition) and PM microphysical processes (i.e., the net effect of thermodynamic equilibrium and dynamics of PM species). These processes provide dominant sinks or sources of pollutants. They are identified through vertical profile analysis at various heights of PBL (defined to be the layer from the ground level to 2.9 km above the ground in this study, corresponding to the model layers of 1–10) and during different time frames (monthly-average diurnal variation analysis).

The net increase or decrease in the total process contribution, calculated by summing the contributions from those processes above, indicates a net production/accumulation or destruction/depletion, respectively, of pollutant concentrations.

IRRs provide rates of 187 gas-phase reactions in CB05, which are grouped into 34 categories according to the reactions for radical initiation, propagation, production, and termination, as shown in Table 1 of Zhang et al. (2009), following the grouping approach of Liu et al. (2010b). Variables reflecting the overall tropospheric oxidation capacity include chemical production of total odd oxygen (Total_OxProd) $O_3$, the sum of $O_3$ and reactive nitrogen, as defined in Zhang et al. (2009) and the chain length of hydroxyl radical (OH) (OH_CL). From IRRs results, the ratio of $P_{NOx}/P_{SO2}$ is used as an indicator to determine $NOx$- or VOC-limited conditions for $O_3$ chemistry, and comparison of the amount of $O_3$ reacted with anthropogenic ($OH_{AVOC}$) and biogenic VOC ($OH_{BVOC}$) reflects the percentage of contributions from human activities and natural sources, respectively.

2.2. Simulation design and evaluation/methodology

Table 1 summarizes all CMAQ-PA simulations conducted at 4-km under different emission scenarios and meteorological conditions. In addition to the 2007 baseline simulation (2007ACT) and the 2008 baseline simulation (2008ACT) for August 2007 and August 2008, respectively, two hypothetical simulations were conducted to identify the influences of emissions and meteorological conditions. Hypothetical simulation in August 2008 (2008HYP) was simulated with the 2008 meteorological conditions but the 2007 emissions that did not include mandatory emission reductions. The differences between 2008ACT and 2008HYP can provide an estimate of the effectiveness of the mandatory emission reductions during August 2008 Olympics (i.e., Emis-driven changes). Hypothetical simulation in August 2007 (2007HYP) is simulated using the 2007 meteorological conditions but the 2008 emission that considered the emission reductions. The differences between 2008ACT and 2007HYP reflect the influences from meteorological conditions (i.e., Met-driven changes). Detailed analysis was performed at THU and MIY, which represents urban and rural conditions, respectively, as shown in Fig. 1.

3. Results and discussions

3.1. Air quality responses to changes in emission and meteorology

In August 2008, it presents some atypical meteorological conditions compared to 2007. Fig. 2 compares simulated meteorological conditions in 2007 and 2008 in terms of 2-m temperature (T2), 2-m relative humidity (RH2), wind speed at 10-m (WSP10), wind direction at 10-m (WDR10), precipitation (Precip.), and PBL height (PBLH). August 2008 had higher RH (by 17.3% domainwide mean), slightly lower T (by $-1.5 \,^\circ C$), heavier Precip. (by 12 mm month$^{-1}$), and lower PBLH (by 80 m). The monthly average WSP around urban areas was similar in both months, varying within 0.2 m s$^{-1}$ in urban area. The dominant WDR was from south to the north in both months. Those comparisons indicate the possible impacts of meteorological changes in 2008 relative to 2007 on air quality. Higher RH, slightly lower T as well as heavier Precip. in 2008 will favor a cleaner air, while lower PBLH in 2008 will exaggerate air pollution. The net meteorological impacts on air quality depend on the magnitude of these competing effects.

The changes in simulated air quality in 2008, relative to those in 2007, can be attributed to both emission reductions (Emis-driven) and variations in meteorological conditions (Met-driven). As shown in Figs. 3 and 4, positive effects on pollutant concentrations reduction by Emis-driven changes are dominant for $SO_2$, $NO_2$, VOCs, $O_3$, and SOA domainwide. However, the extent of effectiveness of emission reductions varies spatially, due to the non-linear responses of the model predictions to complicated atmospheric physical and chemical processes. For gaseous species (see Fig. 3), the Emis-driven changes of $SO_2$, $NO_2$ and VOCs could vary from little (i.e., $-0.14\%$, $-0.15\%$ and $-0.93\%$, respectively) to strong impacts (i.e., $-70.4\%$, $-82.7\%$, and $-56.3\%$, respectively) over the whole domain. The location of maximum reduction in $SO_2$ and $NO_2$ that occurs in the southwest of Beijing (where small boilers and cement plants used to locate before their relocations) and the reduction of VOCs is maximum over central Beijing. They are different from $O_3$ reduction maximum area. Monthly-averaged $O_3$ reduction by Emis-driven changes is more concentrated in the north of Beijing (up to $-10.8\%$) which is located in the downwind direction of urban areas. For particles (see Fig. 4), $PM_{2.5}$ and $SO_4^{2-}$ concentrations were reduced more by Emis-driven effects in the south (by 0 to $-55\%$ and 0 to $-25\%$, respectively). The reduction in the concentrations of $NO_3$ and SOA occurred over much larger areas, particularly in the north of Beijing following the downwind direction, which are similar to $O_3$. Their Emis-driven effects can

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<thead>
<tr>
<th>Simulation short name</th>
<th>Model setup</th>
<th>Simulation description</th>
<th>Emission scenario</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008ACT</td>
<td>August 2008 at 4 km, with PA</td>
<td>August 2008 simulation with actual meteorology and emissions</td>
<td>&quot;Actual&quot; emissions with the reductions enforced during Olympics, considered to be 2008 baseline</td>
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<tr>
<td>2008HYP</td>
<td>August 2008 at 4 km, with PA</td>
<td>August 2008 simulation with meteorology but hypothetical emissions</td>
<td>&quot;Hypothetic&quot; emissions without reduction, the same as 2007 actual emissions</td>
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Fig. 2. Simulated meteorological conditions in August 2007 and August 2008, as well as their differences (Abs: 2008 minus 2007). Note that all variables are monthly-mean except for precipitation which is the total amount in the whole month. T2 – Temperature at 2-m; RH2 – Relative humidity at 2-m; Precip. – Precipitation; PBLH – PBL height; WSP10 – wind speed at 10-m; WDR10 – wind direction at 10-m.
cause concentration reductions by up to −28% and −11%, respectively.

The effect of Met-driven changes on species concentrations can be either ways at different locations. For SO$_2$, NO$_2$, and VOCs (see Fig. 3), positive impacts on pollutant concentration reduction (up to −30%) from MET-driven changes occurred in rural area of Beijing and negative impacts (up to −20%) occurred around or near urban areas. Relatively lower PBLH, slightly lower WSP in 2008 (see Fig. 2d,e) inhibit dispersion of primary pollutants. This exaggerated local air pollution in urban area, and benefitted air quality in downwind rural areas. Obvious negative impacts (up to −100%) occurred in the northeast corner of the simulated domain, caused by the stronger southwest and south to northeast flow from the polluted southeast areas in August 2008 (see Fig. 2f). Positive impact on reductions in O$_3$ mixing ratios was more concentrated in the southwest area (up to −13%). Lower temperature and higher RH favor such reductions. Dominant negative impacts are found in all PM species over most area of Beijing (except for NO$_3$ and SOA in some areas in the west and east portions of the domain). Impacts from Met-driven changes on PM$_{2.5}$, SO$_4^{2-}$, NO$_3$, and SOA are up to −30%, −60%, −60% and 8% in Beijing area, respectively. Domainwide higher RH in August 2008 (see Fig. 2b) favors SO$_4^{2-}$ formation in aqueous phase. Domainwide lower T and higher RRs (see Fig. 2a) in August 2008 inhibited the evaporation of NO$_3$ during afternoon time in polluted areas, which may dominate over a stronger scavenging effect by more frequent precipitation domainwide (see Fig. 2c), leading to a net increase in NO$_3$ concentrations in polluted areas. Therefore, the impacts from Met-driven changes are negative on NO$_3$ reduction in polluted area and positive in the rural area, except in the northeast corner. Met-driven changes of SOA reductions are influenced by changes in its precursor as VOC responses to changes in meteorology. Similarly, strong negative impacts are found in polluted area, and positive impacts in rural areas except the northeast corner. In addition, domainwide lower T (see Fig. 2a) favors SOA formation from semi-volatile oxidation products.

3.2. Analyses of Integrated Process Rates (IPRs)

The IPR analysis can identify the dominant processes and mechanisms underlying the model responses to changes in emissions and meteorology. The responses of process contributions to such changes along with baseline IPR results are provided below.

3.2.1. IPR analysis on O$_3$ in August, 2008

Figs. 5 and 6a, b, c, d show the results of IPR from the baseline simulation 2008ACT for O$_3$ and PM$_{2.5}$, respectively, at two sites (THU and MIY). Figs. 5 and 6e, g, h compare IPR results of 2008HYP and 2008ACT. Figs. 5 and 6f show the responses of process contributions to the changes of emissions, which are obtained by taking differences in IPR results between simulations 2008HYP and
As shown in Fig. 5a, for selected afternoon hours (12:00–17:00 local time (LT)) in 2008 in the PBL, gas-phase chemistry contributes to O3 production at both THU and MIY sites. Horizontal transport is the major sink of O3 at THU. Horizontal and vertical transport can be either a sink or a source of O3 at MIY, indicating the relative importance of regional transport and vertical mixing in O3 production and accumulation at this site. Vertical profile of process contributions shown in Fig. 5b indicates that gas-phase chemistry contributes to O3 production above the surface layer (layers 2–9) at THU. Gas-phase chemistry contributes little during afternoon time (see Fig. 5c-1) in the surface layer at THU due to sink processes including titration of O3 by NO and termination of OH by excessive NO2. But significant contributions from gas-phase chemistry are shown in upper layers as 2–9, during afternoon time (see Figs. 5d-1). Dry deposition acts as a major sink during afternoon when O3 mixing ratios are high at THU. Vertical transport through mixing (by turbulence) brings high O3 from upper layers to surface layer, contributing to the accumulation of surface O3 mixing ratios. Controlled by dominant vertical wind direction (see the structure of vertical wind in Fig. 7, upward wind dominates in layers 1–6 and downward wind dominates in layers 7–8), the air mass in lower layers (layers 2–6) and higher layers (9–10) are blown into mid-layers (7–8) at THU, therefore the vertical transport in layers 2–6 and 9–10 acts as a major sink while in layer 7–8 acts as a major source but horizontal transport becomes a major sink. This suggests that the height of O3 export from urban area are in layers 8–9 (1.5–2 km above ground). At MIY, downward wind dominates in layers 3–10 (the strongest downward wind speed occurs in layer 7); dominant vertical wind blows the air mass in upper layers to lower layers. Therefore, the vertical transport in layers 1–6 acts as a major source and in layers 8–10 acts as a major sink and horizontal transport becomes a major source instead. Little contributions from gas-phase chemistry are found in layers 1–7 during afternoon time (see Fig. 5b-2, c-2 and d-2). As shown in Fig. 5c-1, gas-phase chemistry acts as the major sink in urban areas during nighttime due to titration of O3 by NO and no photochemical reactions to generate O3. The major sink is dry deposition during the daytime for both THU and MIY sites.

Comparing the uncontrolled level during the same period (i.e., 2008HYP) to the 2008 baseline (i.e., 2008ACT), the responses of IPRs in the PBL show larger contributions of gas-phase chemistry and a stronger removal of horizontal transport at both sites (Fig. 5e). While higher precursor emissions enhance the negative impacts of gas-phase chemistry on O3 at the urban site in lower layers (layers 1–3), they increase the source contributions of gas-phase chemistry in upper layers at the urban site and all layers at the rural site (Fig. 5f). As shown in the diurnal variations in the surface layer (Fig. 5g), the net-increase lines of O3 show an obvious
Fig. 5. Integrated processes contributions to O3 mixing ratios in August 2008 (afternoon time (12:00–17:00 Local Time (LT)) for contributions in the PBL (layers 1–10) and vertical profile analysis (i.e., Figures a, b, e, f); diurnal variations are monthly-average values over 1:00 to 24:00 LT (i.e., Figures c, d, g, h); NET Incr. is calculated by summing the contributions from all processes; M. avg. = monthly-average value; D. avg. = daily average value. The height of layers 1–10 above ground are 36, 72, 145, 294, 444, 674, 1070, 1568, 2093, and 2940 m, respectively.)
Fig. 6. Integrated processes contributions to PM$_{2.5}$ mass concentrations in August 2008 (diurnal variations are based on monthly-average values over 1:00 to 24:00 Local Time (LT); NET. Incr. is calculated by summing the contributions from all processes; M. avg. = monthly-average value; D. avg. = daily average value; The height of layers 1–10 above ground are 36, 72, 145, 294, 444, 674, 1070, 1568, 2093, 2940 m, respectively).
peak around 9–10 am at both sites, which indicates the breaking of an inversion layer with an enhanced vertical mixing. The second O₃ peak appeared at 1–2 pm at THU and at 3–4 pm at MIY, which is due to photochemical production. Obvious enhancement of net-increase lines can be found after 9–10 am (when the inversion layer breaks down) at surface and during the peak O₃ time (1–2 pm at THU and 4 pm at MIY) in layer 7 (Fig. 5g and h). Little increase in the O₃ mixing ratios at surface at THU due to changes in NO emissions (though a slight increase appeared in upper layers,) but the O₃ reduction during nighttime is much larger, due to a stronger

Fig. 7. Differences in vertical profiles of IPRs between two meteorological conditions (2007ACT minus 2008ACT, based on monthly average of values during selected afternoon time (12:00–17:00 Local time (LT)) for O₃, monthly-average values over 1:00 to 24:00 LT for other species. The heights of layers 1–10 above ground are 36, 72, 145, 294, 444, 674, 1070, 1568, 2093, 2940 m, respectively. * MIY is located at the edge of mountain areas where strongly affected by the mountain-valley wind; THU is located in the urban area, where the upward wind dominates caused by the urban heat island effect.
titration of O₃ by higher NO level. At the rural site, mixing ratios of O₃ in both surface and upper layers slightly increase during afternoon time.

3.2.2. IPR analysis on PM₂.₅ in August 2008

At both sites, PM processes are the dominant source for PM₂.₅ in the PBL, while horizontal transport and cloud processes act as sinks of PM₂.₅, as shown in Fig. 6a. Vertical profile of process contributions is shown in Fig. 6b. PM processes act as a source above layer 5 due to a dominance of the formation of SO₄²⁻, NO₃, and SOA over other PM processes, while in low layers (layers 1–3), they act as a sink due to a dominance of the evaporation of NO₃/C0 and SOA over other PM processes. In higher layers (layers 7–9), PM processes act as a major source due to local emissions in 2008HYP amplifying the magnitudes of peak and trough PM₂.₅, as shown in Fig. 6c and d). Besides the opposite roles of vertical and horizontal transport as discussed above, the diurnal contributions of PM processes are also different in surface and upper layers. PM processes act as a source throughout the day, especially during afternoon time when the atmospheric oxidation capacity is strong and favors SO₄²⁻, NO₃, and SOA formation. While in surface layers, PM processes act as a source in the night time but a sink in the afternoon time, since the evaporation of NO₃ over-whelms the contributions from the formation of SO₄²⁻ and SOA.

A detailed discussion on each PM component, as SO₄²⁻, NO₃, and SOA are provided in the Supplementary information.

In the PBL, contributions of emissions at THU and PM processes at both sites become larger in 2008HYP, along with stronger removal of horizontal transport (Fig. 6e). For PM₂.₅, at THU, larger contributions by emissions occur in layers 1–2, along with a stronger vertical transport to upper layers, and a stronger horizontal transport to export PM₂.₅ out of upper layers 7–9 (Fig. 6f-1). At MIY, the contribution from PM processes is increased in all layers within the PBL, along with a stronger horizontal and vertical transport (Fig. 6f-2). PM₂.₅ concentrations are increased appreciably at both sites, especially during nighttime in the surface layer at THU (Figs. 6g-1), because of the weaker vertical mixing during nighttime and increases in NO₃ and SOA formation at night. At both sites, the net increase results in one obvious trough during 8–10 am (when the inversion layer breaks down) and one obvious peak during 6–8 am (when the morning inversion layer is formed) at surface. One peak in layer 7 at both sites is at 10 am and another at MIY appears at 10–12 am (when the inversion layer breaks down) and one obvious peak during 6–8 am (when morning inversion layer is formed) at surface.

3.2.3. Comparison of IPRs under two meteorological conditions

As discussed in Section 3.1, the MET-driven changes in 2008 relative to 2007 have a positive impact on the reductions of O₃

Fig. 8. Monthly-average vertical profiles of total O₃ production, OH chain length and OH reacted with AVOCs and BVOCs and their responses to emission increases. (unit: ppm day⁻¹).

Fig. 9. Spatial distributions of total O₃ production, OH chain length and OH reacted with AVOCs and BVOCs at surface in different emission scenarios. (unit: ppm h⁻¹).
mixing ratios but a negative impact on reductions of PM$_{2.5}$ concentrations. The discrepancies of IPRs under the two meteorological conditions can help identify the dominant contributors provided by the meteorological influences. Fig. 7 shows the vertical profile of the responses of process contributions to different meteorological conditions which are obtained by taking differences in IPR results between simulations 2007HYP and 2008ACT at THU and MIY. A positive response indicates that such a process benefits for O$_3$ reduction (a weaker source or a stronger sink, depending on its role) in 2008, as compared with 2007, and a negative response indicates that such a process contributes more to O$_3$ in 2008. The differences in the vertical profiles of the vertical wind speed from both simulations at both sites are also shown to illustrate their impacts on dominant processes in each layer.

Compared to 2007ACT, weaker vertical winds from layers 1–7 at THU in 2008 indicate weaker vertical advection, which is the major sink in those layers for most of species, except in O$_3$ (in layer 1) and NO$_3$ where the vertical turbulence is more important than advection. Fewer pollutants are brought by weaker upward winds from lower layers (1–7) to upper layers (8–9) where they are exported by horizontal transport. Such weaker exports do not benefit reductions of all pollutants at THU. Vertical winds at MIY within the PBL are similar (slightly stronger in 2007) in the two simulations. For O$_3$ in August 2008, less intensive photochemical reactions (as a source) to produce O$_3$ within the PBL and stronger dry deposition (as a sink) to reduce O$_3$ at surface benefit O$_3$ reduction. For fine particles in August 2008, stronger process contributions of cloud processes benefit the reductions of PM$_{2.5}$, NO$_3$, and SOA (as a sink), but enhance surface SO$_4^{2-}$ concentrations (as a source). Slightly stronger dry deposition (as a sink) benefits SO$_4^{2-}$ reduction. Smaller process contributions of PM processes benefit SOA and SO$_4^{2-}$ reduction (as a source) but enhance NO$_3$ and PM$_{2.5}$ concentrations in lower layers (1–6) (as a sink due to the evaporation of NO$_3$).

3.3. Analyses of Integrated Reaction Rates (IRR)

3.3.1. Total Ox production and OH chain length

Vertical profile of total Ox production (Total$_{OxProd}$) is given in Fig. 8. At THU, a large amount of Ox exists in lower layers, and its amount declines as altitude increases. The surface OH chain (OH$_{CHL}$) is about 3 near surface, but decreases to <1 in upper layers till layer 11, then increase again to almost 6 in layers 12–14. Total Ox production at MIY is much smaller (by ~60%) than that at THU. The OH chain length is smaller than 1, with little changes aloft in layers 1–11, then increases to almost 6 in layers 12–14. The amount of OH reacted with anthropogenic VOCs (OH$_{AVOC}$) is larger than that with the biogenic VOCs (OH$_{BVOC}$), even at the rural site MIY, although the ratio of BVOC to total VOCs at MIY is larger than that at THU.

In the 2008HYP scenario, the total Ox production increases obviously by 30% in lower layers, the OH$_{AVOC}$ also increases by 40% due to increased atmospheric oxidation capacity and AVOC emissions. OH$_{BVOC}$ shows a slight increase at MIY due to increased atmospheric oxidation capacity.

Fig. 9 shows the spatial distributions of total Ox$_{prod}$, OH chain length and OH reacted with AVOCs and BVOCs at surface from simulations under the two different scenarios in 2008. Production of Total Ox and the amount of OH$_{AVOC}$ are higher and the OH chain length is longer in urban areas than in rural areas for both simulations. OH$_{BVOC}$ is generally higher in the north-west of Beijing areas than the remaining areas for both simulations, due to more forest there. Meteorological condition in 2008 benefits for the reduction of the overall tropospheric oxidation capacity, compared to that in 2007.

3.3.2. Indicators of NOx-/VOC-sensitive O$_3$ chemistry

Ratio of P$_{H_2O_2}$/P$_{HNO_3}$ is a useful indicator for NO$_x$- or VOC-limited O$_3$ photochemistry. Transition values of <0.2 and >0.2, correspond to VOC-limited, and NO$_x$-limited regimes, respectively (Sillman, 1995; Zhang et al., 2009). Daily variation of P$_{H_2O_2}$/P$_{HNO_3}$ in
different layers (layers 1, 3, 5, 7) is given in Fig. 10. Higher ratio of $P_{H_2O}/P_{HNO_3}$ is found during afternoon hours when the photochemical reaction rates are high. In 2008ACT, surface $P_{H_2O}/P_{HNO_3}$ ratios at THU are slightly below 0.2 in the afternoon, indicating a ridgeline (sensitive to both NOx and VOCs but more to NOx) regime, but the ratios in upper layers are higher than 0.2, indicating a transition from ridgeline to NOx-limited condition. O3 chemistry at MIY is strongly NOx-limited during the daytime.

Compared to 2008ACT, the ratios of $P_{H_2O}/P_{HNO_3}$ decrease at both sites from the simulation 2008HYP as shown in Fig. 10. THU site falls into the ridgeline (sensitive to both NOx and VOCs but more to VOCs) regime with the ratio less than 0.1 at surface and also in upper layers (e.g., layers 3 and 5) except for layer 7. This means, control actions enforced during the 2008 Olympics with ~50% reduction of local NOx and AVOCs emissions has changed O3 chemical regime from the near VOC-limited ridgeline to near NOx-limited ridgeline regime at surface and from ridgeline to NOx-limited at some layers (e.g., layers 3 and 5) at THU. The combined NOx and VOC emission control has not influenced surface O3 mixing ratios during afternoon at THU surface as shown in Fig. 5g-1. A possible reason may be that the control benefit from VOC reductions could be partially compensated by NOx reduction in such area where O3 chemistry is in the ridgeline regime, leading to nearly constant O3 mixing ratios. The negative effect of NOx emission control, however, has been compensated. Therefore, additional stronger NOx controls could be effective to O3 reduction. Compared to 2008HYP, obvious reductions of O3 mixing ratios in 2008ACT can be found at MIY (see Fig. 5-2), which are under dominant NOx-limited regime. Higher ratios of $P_{H_2O}/P_{HNO_3}$ in 2008ACT indicate a stronger NOx-limited O3 chemistry.

Fig. 11 shows the spatial distribution of the monthly-mean ratios of surface $P_{H_2O}/P_{HNO_3}$. The areas under obvious ridgeline (sensitive to both NOx and VOCs but more to VOCs, with ratio below 0.1) regime can be found in the center of Beijing in 2008HYP. Compared with 2008HYP, the VOC-limited area located in the center of Beijing becomes smaller in 2008ACT scenario with ~50% reduction of local NOx and AVOCs emissions. That suggests urban sites which are located in a stronger VOC-limited area are much harder to control O3 than rural sites. Partly controls on NOx without VOC emission reductions will leads to O3 enhancement. Therefore, a stronger NOx emission control with synergistic controls on VOC emission is necessary.

4. Conclusions

Based on the detailed emission control information during the 2008 Beijing Olympics period, this study simulated air quality under two emission scenarios and two meteorology scenarios. The air quality benefits from emission reductions and meteorological variations are assessed. The dominant processes contributing to O3, PM2.5, SO2, NO3, and SOA at one urban (THU) and one rural (MIY) site are identified. Indicator as $P_{H_2O}/P_{HNO_3}$ has been used to examine the NOx vs. VOC-limited O3 chemistry in Beijing.

There are several limitations in this study. First, we assume that the results from the two simulations (e.g., 2008ACT and 2008HYP) are additive which may not be valid for a highly non-linear system. The interaction between the two factors of emissions and meteorology or among more factors may contribute to some extent, e.g., the behavior of emission reductions effectiveness may change under different meteorological conditions. Second, the model biases and errors in meteorology and chemical predictions may affect process analysis results. For example, the simulated change of PM$_{2.5}$ (~4%) is not as much as the observed one (~19%). Slightly underestimated of RH (by 6–20%) may cause the underestimation (by 28%) of aqueous-phase oxidation of SO$_2$ to form SO$_4^{2-}$. Uncertainty of spatial distributions of NH3 emission may explain the moderately overestimation of ammonium (by 57%). Nevertheless, the results from this study provide useful insights into the estimation on the effects of emissions reductions and atypical meteorological conditions on air quality improvement and the governing processes, which reflect the impacts from variations of emissions and meteorological conditions. They indicate that the importance of emission controls despite of positive changes in meteorology. This is because emission controls benefit for all pollutants reductions, though the extent of effectiveness from emission reductions varies from locations to locations. By contrast, the effect of meteorology-driven changes on species concentrations can be either ways at different locations. In addition, the spatial and temporal distributions of the differences of O3 chemistry regimes should be considered in emission control policy-making process. A stronger NOx control with synergistic controls on VOCs is essential to reduce O3 concentrations in urban areas.

Acknowledgments

This work was financially supported by the U.S. EPA, the U.S. NSF Career Award No. ATM-0348819, and Natural Science Foundation of China (2011-140095). The authors also thank to Xinyu Wen, Kai Wang, and Ping Liu at North Carolina State University and Satoru Chatani from Toyota Central R&D Labs.

Appendix. Supplementary information

Supplementary information related to this article can be found at doi:10.1016/j.atmosenv.2011.01.025.

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