



Worsening urban ozone pollution in China from 2013 to 2017 – Part 2: The effects of emission changes and implications for multi-pollutant control

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Abstract. The Chinese government launched the Air Pollution Prevention and Control Action Plan in 2013, and various stringent measures have since been implemented, which have resulted in significant decreases in emissions and ambient concentrations of primary pollutants such as SO₂, NO_x, and particulate matter (PM). However, surface ozone (O₃) concentrations have still been increasing in urban areas across the country. In a previous analysis, we examined in detail the roles of meteorological variation during 2013–2017 in the summertime surface O₃ trend in various regions of China. In this study, we evaluated the effect of changes in multi-pollutant emissions from anthropogenic activities on O₃ levels during the same period by using an up-to-date regional chemical transport model (WRF-CMAQ) driven by an interannual anthropogenic emission inventory. The Community Multiscale Air Quality (CMAQ) model was improved with regard to heterogeneous reactions of reactive gases on aerosol surfaces, which led to better model performance in reproducing the ambient concentrations of those gases. The model simulations showed that the maximum daily 8 h average (MDA8) O₃ mixing ratio in urban areas increased by 0.46 ppbv per year (ppbv a⁻¹) ($p = 0.001$) from 2013 to 2017. In contrast, a slight decrease in MDA8 O₃ by 0.17 ppbv a⁻¹ ($p = 0.005$) in rural areas was predicted, mainly attributable to the NO_x emission reduction. The effects of changes in individual pollutant emissions on O₃ were also simulated. The reduction of NO_x emission increased the O₃ levels in urban areas due to the nonlinear NO_x and volatile organic compound (VOC) chemistry and decreasing aerosol effects; the slight increase in VOC emissions enhanced the O₃ levels; the reduction of PM emissions increased the O₃ levels by enhancing the photolysis rates

and reducing the loss of reactive gases on aerosol surfaces; and the reduction of SO₂ emissions resulted in a drastic decrease in sulfate concentrations, which increased O₃ through aerosol effects. In contrast to the unfavorable effect of the above changes in pollutant emissions on efforts to reduce surface O₃, the reduction of CO emissions did help to decrease the O₃ level in recent years. The dominant cause of increasing O₃ due to changes in anthropogenic emissions varied geographically. In Beijing, NO_x and PM emission reductions were the two largest causes of the O₃ increase; in Shanghai, the reduction of NO_x and increase in VOC emissions were the two major causes; in Guangzhou, NO_x reduction was the primary cause; in Chengdu, the PM and SO₂ emission decreases contributed most to the O₃ increase. Regarding the effects of decreasing concentrations of aerosols, the drop in heterogeneous uptake of reactive gases – mainly HO₂ and O₃ – was found to be more important than the increase in photolysis rates. The adverse effect of the reductions of NO_x, SO₂, and PM emissions on O₃ abatement in Beijing, Shanghai, Guangzhou, and Chengdu would have been avoided if the anthropogenic VOCs emission had been reduced by 24 %, 23 %, 20 %, and 16 %, respectively, from 2013 to 2017. Our analysis revealed that the NO_x reduction in recent years has helped to contain the total O₃ production in China. However, to reduce O₃ levels in major urban and industrial areas, VOC emission controls should be added to the current NO_x-SO₂-PM policy.

1 Introduction

China has experienced severe haze pollution due to high concentrations of particulate matter (PM) in the past decade (e.g., Guo et al., 2014; Huang et al., 2014). To alleviate this air-quality problem, the Chinese government launched the Air Pollution Prevention and Control Action Plan in 2013 and has since implemented various emission-control measures (Zhang et al., 2019). Anthropogenic emissions of sulfur dioxide (SO₂), nitrogen oxides (NO_x), carbon monoxide (CO), and PM_{2.5} (PM with an aerodynamic diameter less than 2.5 μm) in China were reduced by 59 %, 21 %, 23 %, and 33 % from 2013 to 2017, respectively, while the emission of volatile organic compounds (VOCs) increased slightly (Zheng et al., 2018). As a result, ambient concentrations of SO₂, NO₂, CO, PM_{2.5}, and PM₁₀ (PM with an aerodynamic diameter less than 10 μm) have declined, according to data from national environmental monitoring stations (<http://www.mee.gov.cn>, last access: 18 January 2020; Fig. S1 in the Supplement). However, surface ozone (O₃) concentrations in urban and surrounding areas increased from 2013 to 2017 (Lu et al., 2018). It is of critical importance to evaluate the effects of the existing control policies on atmospheric O₃ and refine these, if necessary, to improve overall air quality.

Ground-level O₃ is produced by chemical reactions involving NO_x, CO, and VOCs in the presence of sunlight. The key step in O₃ formation is the oxidation of nitric oxide (NO) by hydroperoxyl (HO₂) and alkylperoxyl (RO₂) to form NO₂, with subsequent photolysis of NO₂. It is well known that the relationship between O₃ and its precursors is nonlinear and that NO_x can either suppress or increase O₃ formation depending on its abundance relative to VOCs (and CO) (e.g., Atkinson, 2000; T. Wang et al., 2017). A large body of literature has established that O₃ formation in urban centers is generally VOCs limited; that is, reducing VOC emissions leads to a decrease in O₃ concentrations, but reducing NO_x emissions has the opposite result; in contrast, O₃ formation above rural areas is typically in the NO_x-limited or transitional regime, in which reducing NO_x emissions results in decreased O₃ (NRC, 1991; Atkinson, 2000; T. Wang et al., 2017). Any process that perturbs HO₂ and RO₂ radicals will also affect O₃ production (e.g., J. Li et al., 2018). Therefore, elucidating the chemical drivers of O₃ changes requires understanding the abundance and proportions of O₃ precursors and the radicals involved in O₃ formation. Aerosols in the atmosphere can affect O₃ concentrations via altering the solar actinic flux, which photolyzes gases to initiate oxidation (Li et al., 2011; Xing et al., 2017) and via heterogeneous reactions of reactive gases on aerosol surfaces (J. Li et al., 2018; Stadler et al., 2018; Lou et al., 2014).

Several studies have attempted to uncover the chemical drivers of the recent O₃ increase in China. Using a regional chemical transport model (WRF-CMAQ), P. F. Wang et al. (2019) derived the variation of maximum daily 8 h average (MDA8) O₃ due to emission changes during 2013–2015

by subtracting the simulated changes due to meteorological variations from the total observed changes. They found that the increase in O₃ concentrations in 2014–2015 relative to 2013 was mainly due to the emission changes, and they speculated that the decrease in PM_{2.5} concentrations and the reduction of NO_x emission in VOC-limited regions could be the causes. In their study, however, the effects of emission changes during the study period were not explicitly simulated with interannual emissions. Li et al. (2019) utilized a global model (GEOS-Chem) to simulate the MDA8 O₃ in 2013 and 2017 and conducted sensitivity experiments for the effects of changes in PM_{2.5} concentrations and anthropogenic emissions of O₃ precursors (NO_x and VOCs). Their results indicated that the drastic decrease in the PM_{2.5} concentrations (~ 40 %) during the period, which reduced the uptake of HO₂ on aerosol surfaces, was the main reason for the O₃ increase in the North China Plain (NCP). N. Wang et al. (2019) simulated the effect of NO_x emission reduction during 2012–2016 with the WRF-CMAQ model in eastern China, which indicated increasing surface O₃ in urban areas due to the reduction of NO_x emissions. Yu et al. (2019) applied the Kolmogorov–Zurbenko filtering technique to the observed MDA8 O₃ during 2013–2017 in the Yangtze River Delta region and concluded that the changes in O₃ precursor emissions contributed 76.7 % to the O₃ increase, compared with 22 % due to the decrease in PM_{2.5} concentration.

We have been further investigating the meteorological and chemical driver(s) of the increasing summer surface O₃ in urban areas of China during 2013–2017 using an improved regional chemical transport model (WRF-CMAQ) driven by interannual meteorological data and anthropogenic emission inventories. The role of meteorological variation and total emission changes, the effect of changes in individual meteorological factors, and the impact of changes in long-range transport of O₃ and its precursors from outside the modeling domain are discussed in a companion paper (Part 1; Liu and Wang, 2020). The goal of the present work is to quantify (1) the effect of the changes in anthropogenic emissions of individual pollutants (NO_x, VOCs, CO, PM, SO₂, and NH₃) on urban O₃, which has not been addressed in the aforementioned studies but is important for further development of mitigation policy and (2) the effects of changes in aerosol concentrations on O₃ using a regional model with up-to-date radical sources and heterogeneous reactions. The improved model should give a more realistic account of gas–particle interactions crucial to O₃ formation, compared with its earlier version. In Sect. 2, we briefly introduce the model system and experiment settings; Sect. 3 first compares the simulated reactive gases that are subject to significant heterogeneous reactions with the observations reported in the literature. We then quantify the simulated trends of MDA8 O₃ in urban and rural areas during 2013–2017. We further investigate the response of MDA8 O₃ to the changes in individual pollutant emissions from anthropogenic activities from 2013 to 2017. We then examine the effect of aerosols on the O₃ changes

by altering the photolysis rates and heterogeneous reactions. Lastly, we conduct numerical sensitivity experiments to calculate the magnitude of VOCs emission reductions needed to overcome the adverse effect of other pollutant reductions on the goal of O₃ mitigation. Section 4 gives the conclusions.

2 Methods

2.1 Model settings and emission inputs

The CMAQ model (Community Multiscale Air Quality model, version 5.2.1) driven by the Weather Research and Forecasting (WRF) model and the interannual Multi-resolution Emission Inventory for China (MEIC; <http://www.meicmodel.org>, last access: 18 January 2020) was applied to conduct the simulations in this study. The model settings and emission inputs are described in the companion paper (Liu and Wang, 2020). The CMAQ model is an offline chemical transport model (Byun and Schere, 2006) that does not consider the effect of pollutants on meteorology but applies an in-line method (Binkowski et al., 2007) that uses the aerosol and O₃ concentrations predicted within a simulation to calculate the solar radiation and photolysis rates. As a result, the model takes into consideration the effect of aerosols on O₃ formation via altering the photolysis rates.

2.2 Updating heterogeneous reactions

The heterogeneous reactions in the original CMAQ model (version 5.2.1) include only the absorptions of NO₂, NO₃, and N₂O₅ on aerosol surfaces. To faithfully reproduce the effect of aerosols on O₃ via scavenging gaseous pollutants, we updated the heterogeneous reaction rate of NO₂ and NO₃ on the aerosol surface and incorporated additional heterogeneous reactions of gases into the CMAQ model, namely those of HO₂, O₃, OH, and H₂O₂ (refer to Table S2 in the companion paper (Liu and Wang, 2020) for the detailed heterogeneous reactions in the original and updated CMAQ models). The uptake coefficients (γ) of gases are the key parameters of heterogeneous reactions, but they vary according to factors such as aerosol water content and aerosol composition. In this study, we selected the “best guess” uptake coefficients for the gases, which have been widely used in chemical transport models in previous studies.

The uptake coefficient of N₂O₅ in the original CMAQ model was incorporated by Sarwar et al. (2012), based on the parameterization developed by Bertram and Thornton (2009) that considered its dependence on particle liquid water, particulate nitrate, and chloride.

The heterogeneous reaction rate of NO₂ in the original CMAQ model was suggested by Kurtenbach et al. (2001), based on the measurements at a relative humidity of 50 % under dark conditions. Field and laboratory studies found that the rate not only depends on the relative humidity (Qin et al., 2009; Stutz et al., 2004) but also on sunlight intensity (Ndour

et al., 2008; Stemmler et al., 2007). Fu et al. (2019) developed a new parameterization for the NO₂ heterogeneous reaction rate that considered both these factors, which has improved the simulation of the reaction product, i.e., nitrous acid (HONO). This parameterization was adopted in the updated CMAQ model.

Several laboratory studies have shown that the measured γ_{NO_3} ranges from 10⁻⁴ to 10⁻² (Rudich et al., 1996; Exner et al., 1992; Moise et al., 2002). In the original CMAQ model, 10⁻⁴ was adopted as the value for γ_{NO_3} (Mao et al., 2013). A higher value (10⁻³) was recommended by Jacob (2000) and was subsequently widely adopted in chemical transport models to investigate the effect of heterogeneous reactions on O₃ concentrations (Stadtler et al., 2018; Lou et al., 2014). This value was adopted in the updated CMAQ model.

The uptake coefficients of HO₂ vary widely, depending on the transition metal ions contained in aerosols (George et al., 2013; Huijnen et al., 2014). The heterogeneous reaction of HO₂ can produce either H₂O₂ or H₂O, depending on the particulate compounds in the aqueous phase. Li et al. (2019) conducted sensitivity experiments for the products of this reaction using the GEOS-Chem model, finding little dependence on the reaction products when assessing the effect of aerosol on O₃ concentrations. Here, we let the heterogeneous reaction of HO₂ produce only H₂O₂, and adopt 0.2 for γ_{HO_2} , as recommended by Jacob (2000).

We used the value of 0.1 for the uptake coefficient of OH, based on the laboratory studies of DeMore et al. (1997). This value was also adopted by Zhang and Carmichael (1999) and Zhu et al. (2010) to explore heterogeneous reactions in a chemical transport model.

Previous laboratory and field studies of the heterogeneous reaction of O₃ have given a wide range of γ_{O_3} : from 10⁻⁶ to 10⁻⁴ on dust (Michel et al., 2002, 2003; Hanisch and Crowley, 2003), up to 10⁻⁴ on sodium chloride aerosol (Abbatt and Waschewsky, 1998), and from 10⁻⁵ to 10⁻³ on soot particles (Longfellow et al., 2000). Most previous modeling studies adopted 1 × 10⁻⁵ (Liao et al., 2004; Liao and Seinfeld, 2005; Pozzoli et al., 2008), while one recommended a lower value (3 × 10⁻⁶) for dust particles (Bauer et al., 2004). We applied 10⁻⁵ to the uptake of O₃ on all the aerosols in our simulation.

DeMore et al. (1997) reported that the uptake coefficient of H₂O₂ on sulfuric acid and water surfaces ranged from 8 × 10⁻⁴ to 0.18. De Reus et al. (2005) found that using accommodation coefficients of 0.2 and 2 × 10⁻³ for HO₂ and H₂O₂, respectively, ensured agreement between simulated and observed values, under the assumption that H₂O₂ was produced in the heterogeneous reaction of HO₂. Thus, 2 × 10⁻³ was adopted for the uptake coefficient of H₂O₂ in this study.

The companion paper (Part 1; Liu and Wang, 2020) presented validation results of the updated CMAQ model against the observations of SO₂, NO₂, CO, O₃, and PM_{2.5} from national environmental monitoring stations. In this study, we

used the updated and original CMAQ models to simulate the concentrations of gases lost or produced on aerosol surfaces for the summer of 2013 and compared the simulated results with the observations reported in the literature (Table S1 in the Supplement).

2.3 Experiment settings

We applied the updated WRF-CMAQ model to conduct simulations for the summer months (June, July, and August) from 2013 to 2017 with anthropogenic emissions. The shipping emissions were kept unchanged in the 5-year simulation, due to a lack of data for recent years. In Part 1 of our work (Liu and Wang, 2020), we showed the effect of changes in total anthropogenic emissions on O₃ changes by comparing the O₃ levels in 2013 simulated using anthropogenic emissions from different years. In this study, three additional sets of modeling experiments were established. The first was designed to quantify the responses of O₃ to changes in individual pollutant emissions from 2013 to 2017, with the simulation in 2013 being regarded as the baseline experiment. The anthropogenic emissions of NO_x, VOCs, SO₂, CO, NH₃, PM (comprising PM₁₀, PM_{2.5}, and its components), black carbon (BC), organic carbon (OC), and combined NO_x and VOCs in 2013 were changed individually to those for 2017 in each sensitivity experiment (total number of experiments is 10), and the results were compared with those in the baseline experiment (Table S2). The second set of experiments was designed to investigate the effect of changes in aerosols on O₃ levels via altering the photolysis rates and heterogeneous reactions (Table S3). The individual effects of aerosols were deleted in each sensitivity experiment, and the results were compared with those in the baseline simulation. The corresponding differences showed the effects of aerosols on O₃ in 2013 in terms of photolysis rates or with respect to each heterogeneous reaction. A similar method was applied to the simulation of 2013 but with the 2017 anthropogenic emissions, and the difference was the effect of aerosols on the O₃ levels when the anthropogenic emissions of 2017 were applied in 2013. Finally, by comparing the results before and after the change in emissions from 2013 to 2017, the responses of O₃ to changes in aerosols via altering the photolysis rates and each heterogeneous reaction were quantified. Nineteen sensitivity experiments were performed. The third set of experiments was designed to calculate the magnitude that the VOC emissions in 2017 would have had to be reduced by from 2013 to overcome the adverse effect of the changes in other pollutant emissions on O₃ reduction during this period. Based on the simulation of 2013 incorporating the 2017 anthropogenic emissions of all pollutants except VOCs, the VOC emissions were reduced by 10 %, 20 %, 30 %, 40 %, and 50 % in the sensitivity runs and the results were compared with those in the baseline experiment (Table S4). By comparing the response of the 2013 O₃ level to various VOC

emission reductions, the required reduction of VOC emissions was quantified.

3 Results

3.1 Comparison of the simulated and observed reactive gases

The simulated mixing ratios of reactive gases that are subject to significant heterogeneous reactions were compared with the observed values for the gases O₃, NO₂, NO₃, N₂O₅, HONO, ClNO₂, HO₂, OH, and H₂O₂ (Table S1). Except for O₃ and NO₂, which are measured by the regular national air monitoring network, the other gases were measured only in research-focused field campaigns. We compiled literature-reported summer concentrations of these gases for various years and compared these with the model-simulated values for 2013.

The uptake of NO₂ on wet aerosol surfaces can produce HONO in the atmosphere, which is an important source of OH radicals via photolysis. After the update of the CMAQ model, the predicted average NO₂ mixing ratio in China decreased from 19.2 to 16.6 ppbv, which came close to the observed value (15.1 ppbv). As a product of NO₂ uptake, the HONO mixing ratios increased significantly and approached the observed values in Beijing (J. Q. Wang et al., 2017) and Guangzhou (Qin et al., 2009; X. Li et al., 2012). The decrease in NO₂ and increase in HONO were attributed to the increase in heterogeneous reaction rates of NO₂ due to the effects of relative humidity and sunlight intensity in the updated CMAQ model (Fu et al., 2019). Table S1 also presents the observed HONO mixing ratios at two coastal sites in Hong Kong (Z. Y. Li et al., 2018; Xu et al., 2015), but their levels were substantially underpredicted because capturing such coastal characteristics is challenging for the model, due to its low horizontal resolution (36 km).

The simulated NO₃ mixing ratio decreased slightly (~ 1 pptv) due to the decrease in NO₂ and O₃ mixing ratios and the increase in γ_{NO_3} (from 10⁻⁴ to 10⁻³). This decrease in NO₃ value was much smaller than the differences between the simulated and observed values in Shanghai (Wang et al., 2013) and Guangzhou (S. W. Li et al., 2012). Nevertheless, the simulated NO₃ value moved closer to the observed value in Shanghai (Wang et al., 2013) after the heterogeneous reactions in the model were updated.

The parameterization of $\gamma_{\text{N}_2\text{O}_5}$ remains unchanged in the revised model. However, the decrease in NO₂ and O₃ levels resulted in a decrease in N₂O₅ and thus a decrease in ClNO₂. The simulated maximum N₂O₅ mixing ratio at the Wangdu site decreased by ~ 50 % and thus agreed much better with the observed value (Tham et al., 2016). The simulated maximum ClNO₂ mixing ratio decreased slightly, by a margin much smaller than the biases between the simulation and observation. Table S1 presents the observed N₂O₅ and ClNO₂

values at a high-altitude site on Mount Tai (Z. Wang et al., 2017) and a coastal site in Hong Kong (Yan et al., 2019; Tham et al., 2014). Large differences between simulations and observations were found due to the complex terrains at these two sites, which are difficult for our model to simulate.

The CMAQ model predicted the mixing ratios of HO₂ and OH radicals to be slightly lower after the incorporation of their heterogeneous reactions. The changes were small, probably due to the scavenging effects of aerosols being counteracted by the increase in radical sources generated by HONO photolysis. The measured value for HO₂ contains an uncorrected contribution from RO₂ (Fuchs et al., 2011), which could explain in part the underestimation of HO₂ that occurred when using the updated and original models. For OH radicals, the mixing ratios simulated by both the original and updated models were comparable with the observed value in Wangdu (Tan et al., 2017), Beijing (Lu et al., 2013), and Guangzhou (Lu et al., 2012). The slight decrease in the OH mixing ratio after the update helped bring the simulation closer to the observations.

In the original CMAQ model, the MDA8 O₃ mixing ratio was overestimated by 11.4 ppbv. The bias was reduced to 6.8 ppbv with the updated heterogeneous reactions. In addition to the greater uptake of O₃ on aerosol surfaces, the updated model also includes other heterogeneous gas–aerosol reactions, weakening the atmospheric oxidation capacity and thus inhibiting O₃ formation.

The H₂O₂ mixing ratio decreased substantially from ~ 0.8 to ~ 0.2 ppbv, and the simulated value agreed well with the values recorded in Wangdu (Wang et al., 2016) and Beijing (Qin et al., 2018; Liang et al., 2013) after updating the model. Our results suggest that the chemical transport models are likely to substantially overestimate the H₂O₂ concentration if they do not include the sink of H₂O₂ on aerosol surfaces.

In summary, after updating the heterogeneous reactions in the CMAQ model, the simulations agreed better with the observations, especially for NO₂, HONO, O₃, and H₂O₂.

3.2 Variations in the urban and rural O₃

As most of the 493 air-quality monitoring sites established in 2013 are located in urban areas (refer to Fig. S1 in Part 1, Liu and Wang, 2020), the data from these stations mainly reflect the O₃ concentration changes in urban areas. The model simulations for the summer months from 2013 to 2017 over China give a comprehensive picture of the O₃ variations over the entire land areas of the country. Our previous analysis based on model simulations revealed that different trends in O₃ concentrations existed in urban and rural areas (Liu and Wang, 2020). In this study, we further quantified the O₃ trends in urban and rural areas over China using the nighttime light data from the Visible Infrared Imaging Radiometer Suite (VIIRS) Day/Night Band (DNB) (Fig. S2). We allocated the nighttime light data to the CMAQ modeling domain and averaged the values in each modeling grid cell. An urban

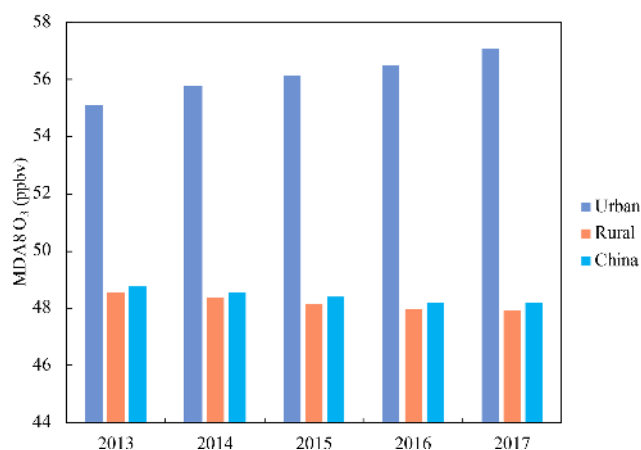


Figure 1. Trends of simulated MDA8 O₃ mixing ratios averaged in urban and rural areas and all land areas of China in summer (June–August) from 2013 to 2017. See Fig. S3 for the locations of urban and rural areas.

area (or rural area) was regarded as a grid point with an averaged light value $\geq 2 \text{ nW cm}^{-2} \text{ sr}^{-1}$ (or $< 2 \text{ nW cm}^{-2} \text{ sr}^{-1}$). Figure S3 shows the spatial distribution of the urban and rural areas in China. The rates of changes in the MDA8 O₃ mixing ratios in urban and rural areas from 2013 to 2017 were then quantified based on the simulation results (Fig. 1). The model predicted that the MDA8 O₃ mixing ratio in urban areas increased at a rate of 0.46 ppbv per year (ppbv a^{-1}) ($p = 0.001$). This simulated increase (~ 2 ppbv from 2013 to 2017) in the nighttime-classified urban areas is much lower than the average increase observed at 493 sites in 74 cities (~ 9 ppbv, Fig. S1d). The discrepancy can be explained as follows. The urban areas determined using the nighttime data are not exactly the same as those 493 sites and cover some rural areas (with decreasing ozone) and additional small townships (Fig. S3). When we matched the modeled locations to the 493 observation sites, the model captured 57 % of the rate of increase of MDA8 O₃ averaged at those sites (see Fig. S3 in Part 1, Liu and Wang, 2020). Part 1 also showed a large variability of meteorological impacts on O₃ in different regions (e.g., Beijing, Shanghai, Guangzhou, and Chengdu), and the simulated overall urban O₃ trend with a high confidence level ($p = 0.001$) suggests that this regional variability in meteorological impact can be “averaged out”, leading to a clearer urban O₃ trend driven by emission changes.

The simulated MDA8 O₃ mixing ratio in rural areas decreased at a rate of $-0.17 \text{ ppbv a}^{-1}$ ($p = 0.005$), which is supported by the recently reported rural ozone trends in China. T. Wang et al. (2019) revealed no significant change in O₃ levels observed at a coastal site (Hok Tsui) in South China in the outflow of air mass from eastern China during 2007–2018. More recently, Xu et al. (2020) reported decreasing O₃ mixing ratios from 2013 to 2016 at two rural sites in Beijing–Tianjin–Hebei (BTH) (Shangduanzi) and

Yangtze River Delta (YRD) (Linan). Overall, the MDA8 O₃ mixing ratio in China exhibited a slightly decreasing trend ($-0.15 \text{ ppbv a}^{-1}$, $p = 0.006$) due to the decrease in a large rural area, which suggested that the ozone concentration has leveled off in recent years.

3.3 Response of O₃ to changes in multi-pollutant emissions

Figure 2 presents the spatial distribution of changes in individual pollutant emissions in 2017 relative to 2013 (<http://www.meicmodel.org>, last access: 18 January 2020). Significant reductions in anthropogenic emissions of NO_x, CO, SO₂, NH₃, PM₁₀, PM_{2.5}, BC, and OC were found in eastern China, while the emissions in western China decreased slightly and even increased in some areas. NH₃ emission, which is primarily from agriculture (Fig. S4e), generally decreased across eastern China but increased in large areas in Neimenggu (Inner Mongolia Autonomous Region) and northwestern China and some scattered areas in eastern China. VOC emissions, which have not been subject to effective control measures, increased at scattered points (mostly industrial sites) over eastern China, except for Shandong province, where VOC emissions decreased across the region. In summary, the emissions of NO_x, CO, SO₂, PM₁₀, PM_{2.5}, BC, and OC over mainland China were reduced by 21 %, 24 %, 61 %, 38 %, 33 %, 29 %, and 34 % in summer from 2013 to 2017, respectively (Fig. S4). In contrast, NH₃ emissions only decreased by 4 %, and VOC emissions increased by 5 % during the same period.

Figure 3 shows the spatial distribution of the effect of changes in these pollutant emissions on the MDA8 O₃ levels over China between 2013 and 2017. The average changes in O₃ mixing ratios in urban and rural areas (see Fig. S3 for their locations) are shown in Fig. 4a and b, respectively. The decrease in NO_x emissions caused an increase in O₃ mixing ratios in urban and industrial hot spots but a decrease in O₃ concentrations across a large swathe of rural areas (Fig. 3a). Quantitatively, the MDA8 O₃ mixing ratio increased by 0.30 ppbv in urban areas and decreased by 1.08 ppbv in rural areas, due to the NO_x emission reductions (Fig. 4a and b). In view of the small effects of changes in other pollutant emissions on rural O₃ mixing ratios (Fig. 4b), the decreasing trend of O₃ levels from 2013 to 2017 in rural areas was mainly ascribed to the reduction of NO_x emissions, consistent with the fact that O₃ formation in rural areas in China is generally limited by NO_x (e.g., Xing et al., 2011; T. Wang et al., 2017). The increase in O₃ levels in urban areas due to NO_x reductions can be explained by two factors. First, most urban areas are in the VOCs-limited regime, where the reduction of NO_x emissions reduces the NO titration effect on O₃, resulting in increased O₃ concentrations. Second, the decrease in NO_x emissions can reduce the NO₃⁻ concentration and increase O₃ via weakening the aerosol effects.

In the simulation of VOCs emission changes, the spatial distribution of the O₃ levels closely tracked the changes in VOC emissions (Fig. 3b). Specifically, the increase in VOCs emission caused an increase in the MDA8 O₃ mixing ratios across eastern China, except for Shandong province, where O₃ levels decreased due to the substantial reduction of VOC emissions from the transportation sector according to the MEIC emission inventory (<http://www.meicmodel.org>, last access: 18 January 2020). The simulation predicted an increase of 0.41 ppbv in the MDA8 O₃ mixing ratios from 2013 to 2017 due to the increase in VOC emissions in urban areas (Fig. 4a). When changes in both the NO_x and VOC emissions were simulated, it was the changes in NO_x emissions that primarily contributed to the changes in O₃ mixing ratio (Fig. 3c). In the simulation of changing CO emissions, the reduction of CO emissions reduced the O₃ level across China (Fig. 3d). A particularly large decrease in the O₃ mixing ratio was found in the NCP region, where both the CO emissions and their corresponding reduction were large. The CO emission reductions led to a decrease of 0.41 ppbv in MDA8 O₃ in urban areas (Fig. 4a). CO is an important O₃ precursor and plays a similar role to VOCs in O₃ formation, but the changes in its emission have rarely been discussed in previous studies of the causes of variations in O₃ concentrations. In fact, our results indicated that the reduction of CO emissions was the only government-implemented measure that reduced O₃ levels in recent years.

In addition to the effects of O₃ precursors, the emissions of other pollutants can also affect O₃ concentrations by altering photolysis rates and the loss of reactive gases from heterogeneous reactions. The reduction of SO₂ emissions increased the O₃ levels across China, particularly in northern China and the Sichuan Basin (SCB) (Fig. 3e). Quantitatively, SO₂ emission reductions led to an increase of 0.75 ppbv in the MDA8 O₃ mixing ratios in urban areas (Fig. 4a), which was the largest cause of O₃ increases among all the pollutant emissions changes considered in this work. The SO₂ emission was reduced by more than 60 % from 2013 to 2017, which resulted in a significant decrease in ambient SO₄²⁻ concentrations and increased O₃ concentrations by increasing the photolysis rates and retarding the loss of reactive gases from heterogeneous reactions. The reduction of NH₃ emissions, an important precursor of ammonium, increased the O₃ mixing ratio across China in a similar way to the reduction in SO₂ emissions (Fig. 3f), but to a small extent, as the NH₃ emission was only reduced by 4 %. Specifically, the increase in the MDA8 O₃ mixing ratios in urban areas due to the reduction of NH₃ emissions was only 0.06 ppbv (Fig. 4a), which was an insignificant fraction of the total increases in O₃ mixing ratios.

The reduction of primary PM emissions also enhanced O₃ formation across China, especially in the NCP and SCB regions (Fig. 3g). The MDA8 O₃ mixing ratios increased by 0.72 ppbv due to the PM emission reduction in urban areas (Fig. 4a). The effect of the changes in PM emissions on

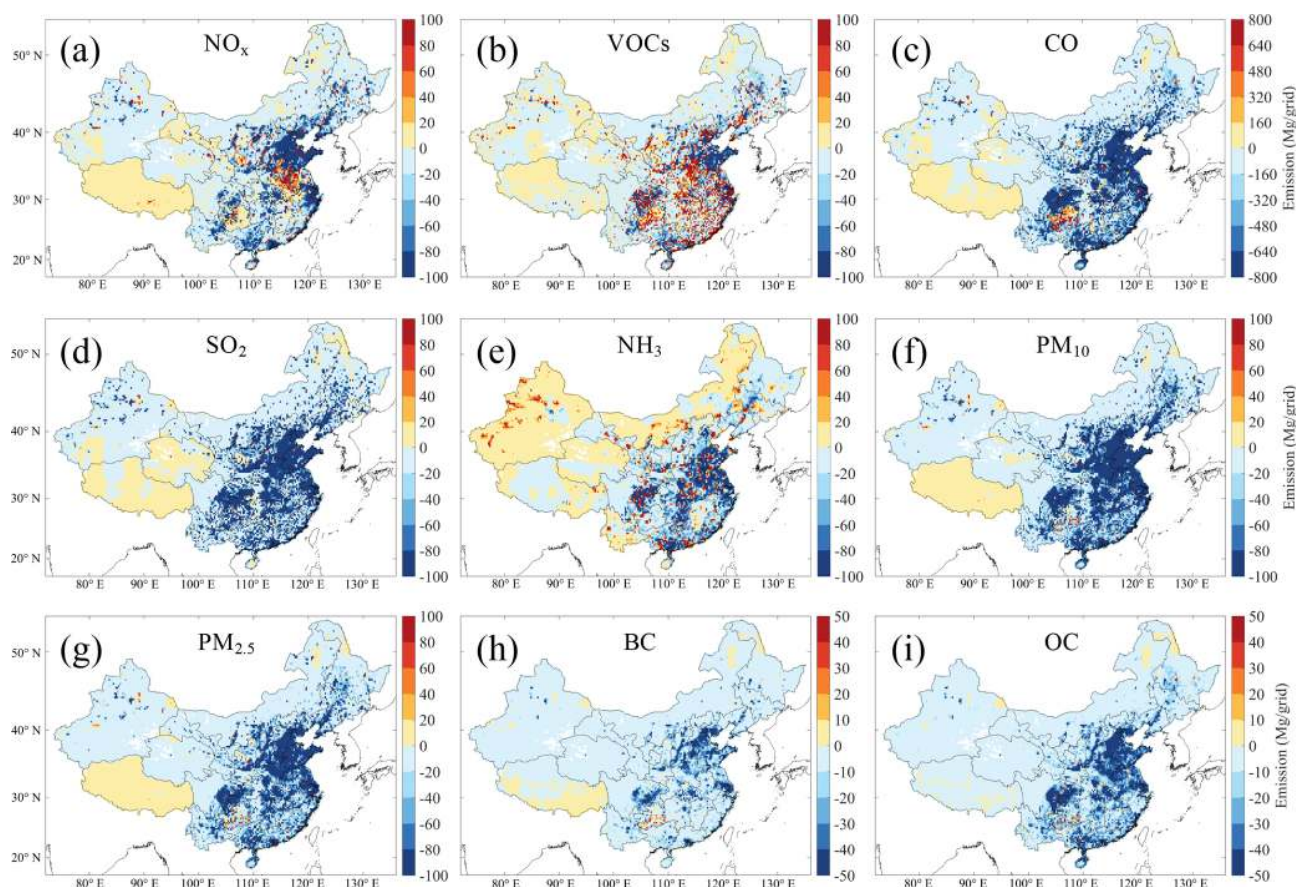


Figure 2. Spatial distributions of changes in anthropogenic pollutant emissions in the summer of 2017 relative to that of 2013, including (a) NO_x , (b) VOCs, (c) CO, (d) SO_2 , (e) NH_3 , (f) PM_{10} , (g) $\text{PM}_{2.5}$, (h) BC, and (i) OC. Emission data are obtained from the Multi-resolution Emission Inventory for China (MEIC; <http://www.meicmodel.org>, last access: 18 January 2020).

O_3 levels was comparable with that of the changes in SO_2 emissions, which indicated the significant O_3 -promoting role played by reductions in both primary and secondary aerosols. BC and OC are among the components of direct aerosol emissions, and reductions in both were found to increase the O_3 levels (Fig. 3h and i). Although the reduction of BC emissions was smaller than the reduction in OC emissions, the increase in MDA8 O_3 due to the former was more significant. BC is an especially strong absorber of visible solar radiation in the atmosphere (Ramanathan and Carmichael, 2008), and therefore greatly retards photolysis rates by reducing the solar radiation reaching the earth's surface.

The dominant cause of O_3 increases due to emission changes varied among regions. Figure 4 shows the average changes in O_3 mixing ratios due to changes in individual pollutant emissions in four megacities, i.e., Beijing, Shanghai, Guangzhou, and Chengdu (refer to Fig. S1 in Part 1 for their locations), which are the representative cities in the BTH, YRD, Pearl River Delta (PRD), and SCB regions, respectively. In Beijing, NO_x and PM emission reductions were the two largest causes of rising O_3 levels, followed by SO_2 emission reductions. Air quality in the BTH region is a ma-

ajor concern, and strict emission-control measures have been implemented since 2013. As a result, the emissions of NO_x , $\text{PM}_{2.5}$, and SO_2 in BTH were reduced by 25 %, 44 %, and 65 % from 2013 to 2017 (Fig. S5), respectively, which were generally larger reductions than occurred in other regions (Fig. 2). In Shanghai, the increase in the O_3 level was mainly due to the reduction of NO_x emissions and increase in VOC emissions. This result is consistent with the finding of Yu et al. (2019) using the Kolmogorov–Zurbenko filtering technique, who also suggested that the changes in O_3 precursor emissions in the YRD contributed more to O_3 increases than did the decrease in $\text{PM}_{2.5}$ concentrations. In the YRD, NO_x emissions decreased by 19 %, and that of VOCs increased by 10 % from 2013 to 2017 (Fig. S6). Meanwhile, the $\text{PM}_{2.5}$ concentration in Shanghai was relatively low in summer. As a result, the effects of the PM and SO_2 emission reductions were smaller than those due to the changes in NO_x and VOC emissions. In Guangzhou, the NO_x emission reduction was the dominant cause of the O_3 increase, while the effects of SO_2 and PM emission reductions on O_3 levels were insignificant. This result can likewise be ascribed to the low concentration of $\text{PM}_{2.5}$ in summer and relatively large reduc-

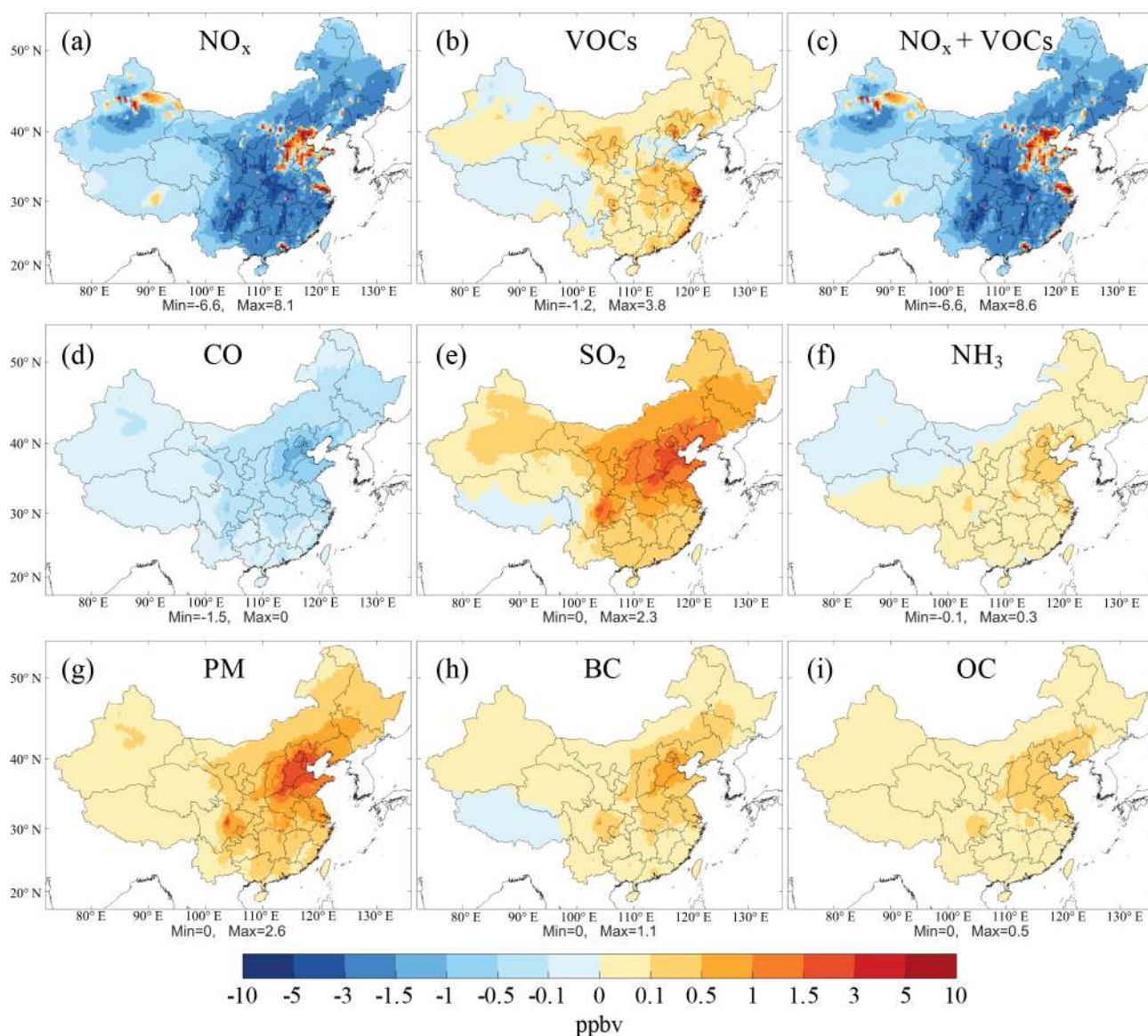


Figure 3. Spatial distribution of the simulated MDA8 O₃ mixing ratios responding to the changes in individual pollutant emissions in summer from 2013 to 2017, including (a) NO_x, (b) VOCs, (c) NO_x and VOCs, (d) CO, (e) SO₂, (f) NH₃, (g) PM, (h) BC, and (i) OC.

tion of NO_x emissions (Fig. S7) in the PRD. In Chengdu, the PM and SO₂ emission reductions contributed most to the increases in O₃ levels. The concentration of PM_{2.5} in the SCB was high due to the basin topography and high emissions of both PM and its precursors. The significant reductions of PM_{2.5} (35 %) and SO₂ (65 %) emissions in the SCB (Fig. S8) were thus the two major causes of the O₃ increase there. The intercity variations in the dominant causes of increases in O₃ concentrations suggest that if the government wishes to alleviate urban O₃ pollution, they can adopt additional, localized emission-reduction measures as part of policies (see Sect. 3.5).

3.4 The effects of aerosol on the O₃ variations

Aerosols in the atmosphere derived from direct emission and secondary formation can reduce photolysis rates and scavenge reactive gases from heterogeneous reactions, thereby inhibiting O₃ formation. Figure 5 shows the spatial distribution of changes in the MDA8 O₃ mixing ratios due to the changes in the radiative and heterogeneous chemical effects of aerosols from 2013 to 2017 (see Methods section). We isolated the effects of changes in seven heterogeneous reactions on the O₃ variations, and the average changes in O₃ levels in urban and rural areas are shown in Fig. 6a and b, respectively. As the PM_{2.5} concentrations decreased substantially due to the reduction of anthropogenic pollutant emis-

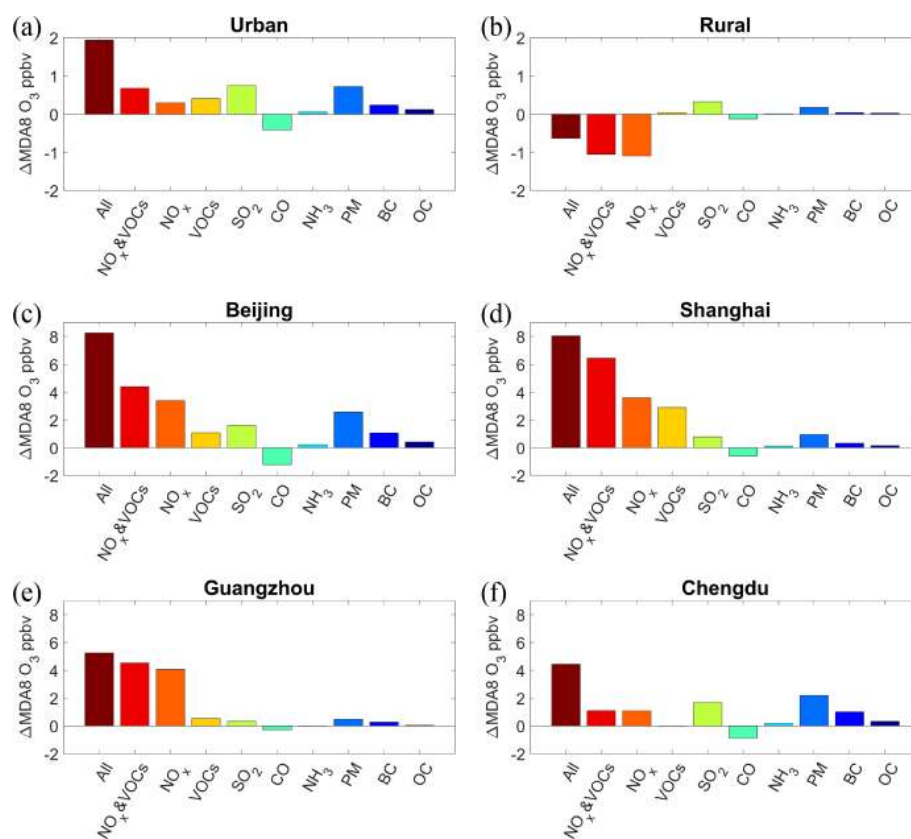


Figure 4. Response of the simulated MDA8 O₃ mixing ratios to the changes in individual pollutant emissions in summer from 2013 to 2017 in (a) the urban areas, (b) the rural areas, (c) Beijing, (d) Shanghai, (e) Guangzhou, and (f) Chengdu. See Fig. S1 in Part 1 (Liu and Wang, 2020) for the locations of the four megacities.

sions, the effects of aerosols on O₃ concentrations also decreased, which led to an increase in O₃ levels. The effects of the decrease in PM concentrations on O₃ were insignificant in western China. Significant increases in O₃ mixing ratios due to the decrease in various aerosol effects were found in urban and industrial areas of eastern China, particularly the NCP and SCB regions, where pollutant emissions were high and subject to a substantial reduction in the past few years. We found that the heterogeneous chemical effect, rather than the radiative effect, contributed most to the increase in O₃ levels driven by changes in PM concentrations. Quantitatively, the changes in photolysis rates and heterogeneous reactions increased the MDA8 O₃ mixing ratio by 0.30 and 2.12 ppbv in urban areas, respectively. In rural areas, the MDA8 O₃ mixing ratio increased by 0.87 ppbv via the heterogeneous chemical reactions on aerosols, while the effect of changes in photolysis rates was negligible. As for various heterogeneous reactions, the changes in individual reactions all increased MDA8 O₃ from 2013 to 2017. The decrease in the aerosol-sink effect of HO₂ contributed most to the O₃ increase due to changes in PM concentrations, followed by O₃, N₂O₅, and H₂O₂. The effects of changes in the hetero-

geneous reactions of NO₂, NO₃, and OH on the increase in O₃ levels were small.

The effect of the decrease in aerosol concentrations on O₃ levels varied by city. Significant effects were found in Beijing and Chengdu, where the PM_{2.5} concentration was high and was subject to a large reduction by the implementation of emission-control measures. In contrast, the PM_{2.5} concentration was lower in Shanghai and Guangzhou, and their O₃ levels were less affected by the decrease in aerosol concentrations.

Li et al. (2019) also investigated the effects of changes in photolysis rates and heterogeneous reactions on O₃ levels, using the GEOS-Chem model incorporating heterogeneous reactions of nitrogen oxides and HO₂. They quantified the effect of changes in photolysis rates by scaling the aerosol-extinction rate using the satellite-based aerosol optical depth changes and the effect of changes in heterogeneous reactions by scaling the aerosol surface area using the measurement-based PM_{2.5} changes from 2013 to 2017. They concluded that the increase in O₃ mixing ratios due to changes in PM concentrations could be largely ascribed to the decrease in the effect of HO₂ heterogeneous reaction. Using a regional model and adopting different experimental settings, our work

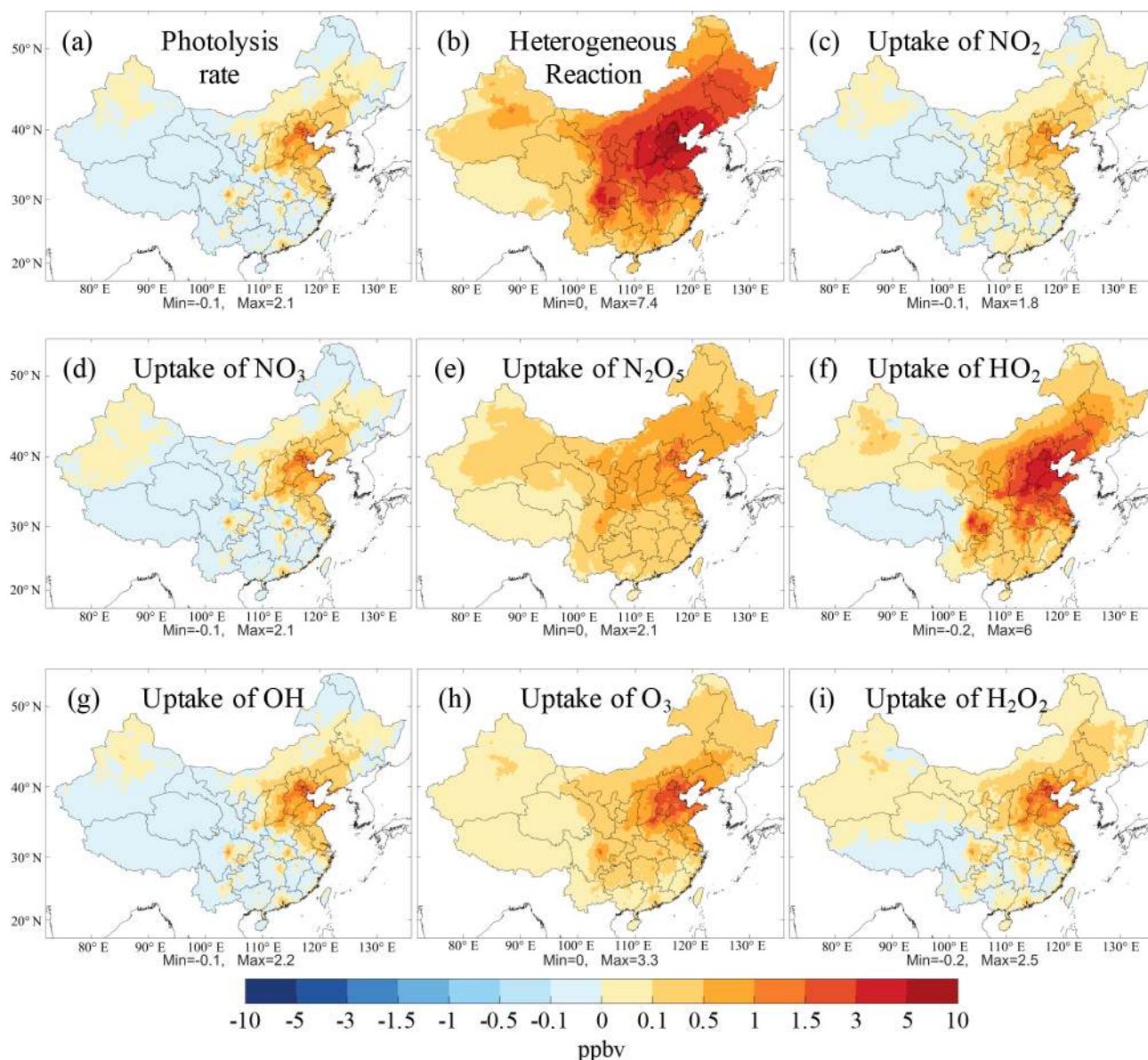


Figure 5. Spatial distribution of the simulated MDA8 O₃ mixing ratios responding to the changes in the effects of aerosol in summer from 2013 to 2017 (see Methods section). The aerosol affects O₃ via altering (a) photolysis rates, (b) all heterogeneous reactions, and individual heterogeneous reactions, namely the uptake of (c) NO₂, (d) NO₃, (e) N₂O₅, (f) HO₂, (g) OH, (h) O₃, and (i) H₂O₂.

uncovered a similar and substantial effect of HO₂ uptake on increases in O₃ levels due to changes in PM concentrations. In addition, with more heterogeneous reactions implemented in the CMAQ model, we found that the uptake of O₃ on aerosol surfaces was also important, following HO₂.

3.5 The anthropogenic VOCs emission controls to reduce O₃

The results in the preceding sections show that although the CO emission reductions contributed to a decrease in O₃ levels, the reductions of SO₂, NO_x, and PM emissions had a

counterproductive effect on O₃ reductions, resulting in a substantial increase in urban O₃ concentrations due to the non-linear NO_x and VOC chemistry and the weakening of aerosol effects. To alleviate these negative effects of PM-targeted control policies and thereby reduce ambient O₃ concentrations, we found that anthropogenic VOC emissions must also be reduced alongside reductions in emissions of other pollutants.

Figure 7 presents the changes in the MDA8 O₃ mixing ratios from its 2013 value, where the 2013 VOC emissions were decreased from 0 % to 50 %, while the 2017 emissions of other pollutants were retained (see Methods section). The

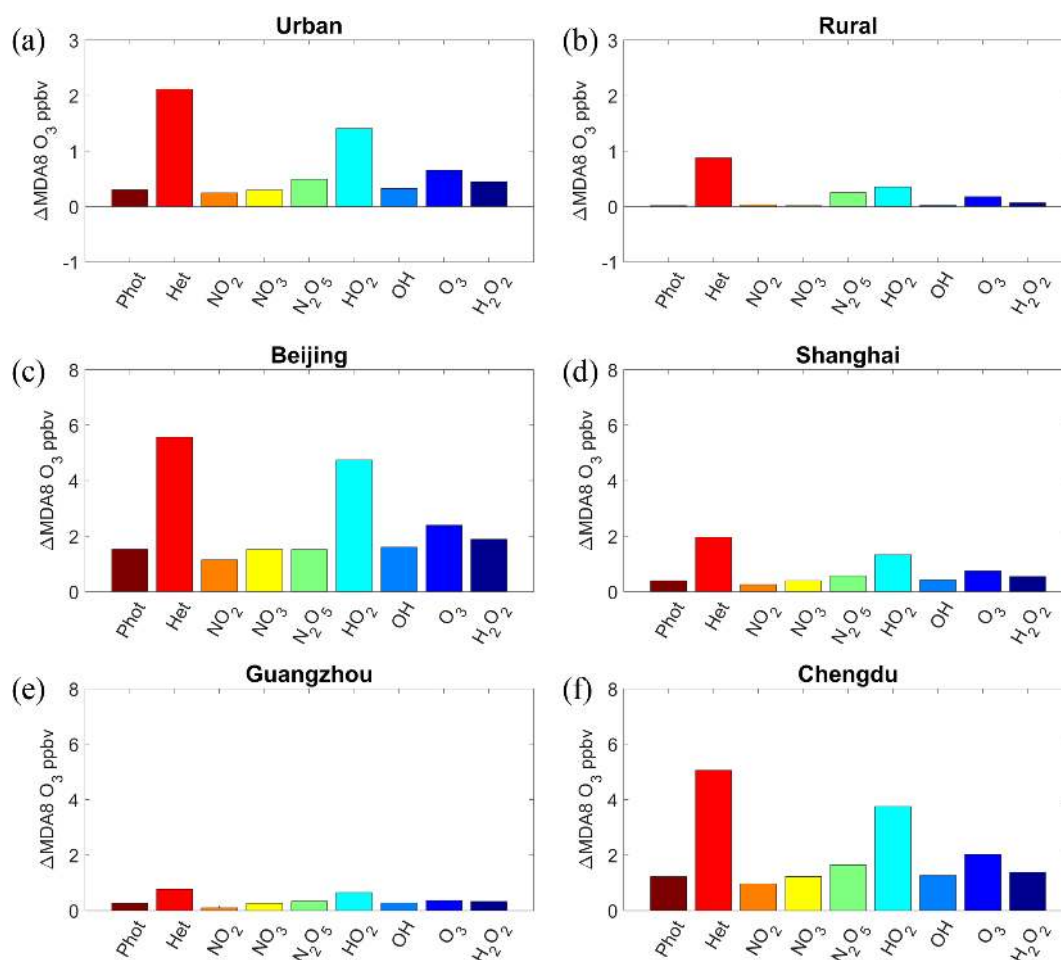


Figure 6. Response of the simulated MDA8 O₃ mixing ratios to the changes in the effects of aerosols in summer from 2013 to 2017 in (a) the urban area, (b) the rural area, (c) Beijing, (d) Shanghai, (e) Guangzhou, and (f) Chengdu. The aerosol affects O₃ via altering the photolysis rates (Phot), all heterogeneous reactions (Het), and individual heterogeneous reactions, namely the uptake of NO₂, NO₃, N₂O₅, HO₂, OH, O₃, and H₂O₂.

MDA8 O₃ mixing ratios in the four studied megacities decrease linearly with the reduction of VOC emissions, reflecting that O₃ formation in these cities is VOCs limited. Compared with the O₃ level in 2013, the VOC emissions would have needed to be reduced by approximately 20% to prevent increases in MDA8 O₃ from 2013 to 2017. This suggests that the adverse effects of the reductions of NO_x, SO₂, and PM emissions on urban O₃ could have been avoided with a ~20% reduction of VOC emissions from 2013 to 2017. The exact reductions of VOC emissions required vary among the four megacities: Beijing (24%), Shanghai (23%), Guangzhou (20%), and Chengdu (16%). In Beijing (BTH region), the drastic reductions of NO_x, SO₂, and PM emissions would have necessitated a more substantial reduction of VOC emissions to counteract the O₃ increase. In Shanghai (YRD region) and Guangzhou (PRD region), the increase in O₃ concentrations due to the reductions in NO_x emissions also calls for a significant reduction in VOC emissions. In

Chengdu (SCB region), a smaller VOCs emission reduction is needed because of the relatively small increase in O₃ concentrations due to changes in other emissions. We also found that the required percentage reductions of VOC emissions in each city were comparable with the actual percentage reductions in NO_x emissions (25%, 19%, 18%, and 14% for Beijing, Shanghai, Guangzhou, and Chengdu, respectively), suggesting that similar percentage reductions of VOCs and NO_x would have prevented the increase in O₃ levels from 2013 to 2017.

Our results have important implications for air-pollution control policy in the coming years. In 2018, the Chinese government issued a Three-Year Action Plan (2018–2020) mandating further reductions of national SO₂ and NO_x emissions by at least 15% by the year 2020 compared with those in the year 2015 and an 18% reduction in ambient PM_{2.5} concentrations in cities currently not compliant with China's PM_{2.5} standards (<http://www.gov.cn/>

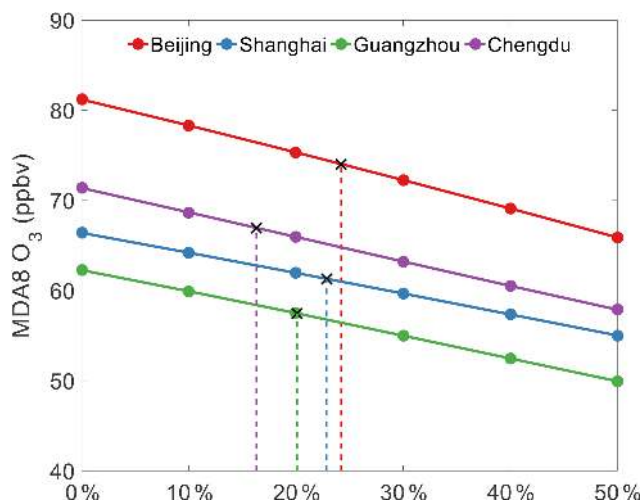


Figure 7. Response of simulated MDA8 O₃ mixing ratios with 2017 emissions (except for VOCs) to the reductions of anthropogenic VOCs from the 2013 level in summer in Beijing, Shanghai, Guangzhou, and Chengdu. The black crosses depict the MDA8 values in 2013 and the required reduction of VOC emissions in 2017 to maintain the 2013 O₃ level in each city.

zhengce/content/2018-07/03/content_5303158.htm, last access: 18 January 2020). This implies that if VOC emissions are not reduced in the near future, the O₃ pollution in major cities will continue to worsen. Therefore, we suggest that VOC emission controls be implemented together with the PM-targeted measures in order to alleviate the urban O₃ pollution.

4 Conclusions

This study has quantified the effects of changes in pollutant emissions from anthropogenic activities on the summer surface O₃ concentrations over China from 2013 to 2017. The control measures, while successful in reducing the concentrations of primary pollutants and particulate matter, were found to increase urban O₃ but reduce rural O₃; overall, the NO_x emission reduction has helped to contain total ozone production in China. The reduction in NO_x emission and slight increase in VOC emissions led to ozone increase in urban areas due to the nonlinear chemistry of O₃, and the large reductions in PM and SO₂ emissions contributed to urban ozone increase resulting from the complex effects of aerosols on radiation and chemical reactions. Among the primary PM components, the emission decrease in BC increased O₃ more than that for OC despite its smaller reduction compared to OC, resulting from BC being a strong absorber of solar radiation. The dominant causes of the urban ozone increase due to emission change varied among different cities, and they were NO_x and PM in Beijing, NO_x and VOC in Shanghai, NO_x in Guangzhou, and PM and SO₂ in Chengdu. For the

aerosol effects, the decrease in heterogeneous uptake of reactive gases was more important than the increase in photolysis rates. Only the CO emission cut helped to decrease urban ozone. Our results show that comparable percentage reductions in anthropogenic VOCs to that achieved for NO_x could have prevented the increases in urban O₃ concentrations. We thus recommend that VOCs controls be implemented in current and future emission-reduction measures to improve the overall air quality. In view of the importance and complexity of the uptake of reactive gases on aerosol surfaces, more research should be conducted in this area.

Code and data availability. The code or data used in this study are available upon request from Yiming Liu (yming.liu@polyu.edu.hk) and Tao Wang (cetwang@polyu.edu.hk).

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Author contributions. TW initiated the research. YL and TW designed the research framework. YL modified the model and performed model simulations. TW and YL analyzed the results and wrote the paper.

Competing interests. The authors declare that they have no conflict of interest.

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