

ENVIRONMENTAL STUDIES

Global warming makes nitrogen oxide abatement key to ozone pollution mitigation

Wenjie Wang^{1,2}, Hang Su^{3*}, David D. Parrish⁴, Ruijing Ni¹, Xin Li⁵, Fengxia Bao^{1†}, Hongli Wang⁶, Cheng Huang⁶, Jonathan Williams^{1,7}, Hong Liao⁸, Keding Lu⁵, Yuanhang Zhang⁵, Yafang Cheng^{1*}

Global warming has become a critical factor affecting surface ozone (O₃) pollution. The effectiveness of emission reductions for O₃ pollution mitigation largely relies on the sensitivity of O₃ production to its precursors. However, how global warming affects the O₃ sensitivity remains unclear, posing a grand challenge in developing effective strategies for O₃ pollution mitigation. Here, by using comprehensive ambient observations to constrain model simulations, we show a strong temperature dependence of O₃ sensitivity over a large temperature range (−5° to 37°C) in Chinese cities. O₃ sensitivity shifts toward the nitrogen oxide–limited regime at higher temperatures. Temperature change alters the reaction regime by primarily modulating the rate coefficient of radical termination, rather than that of radical cycling, and by altering emissions of biogenic volatile organic compounds. Overall, future global warming will accelerate the transition of O₃ sensitivity toward the nitrogen oxide–limited regime, amplifying the benefits of nitrogen oxide emission abatement in mitigating O₃ pollution in urban areas worldwide.

INTRODUCTION

Near-ground ozone (O₃) is a major air pollutant that is harmful to human health, vegetation, and ecosystem productivity (1–3). Global warming affects the photochemical production and ambient concentrations of O₃ by altering biogenic emissions, chemical reaction rates, water vapor (thereby HO_x chemistry), and physical dilution in the atmosphere (4, 5). Under the warming climate, more frequent occurrence of extremely high temperatures exacerbates O₃ pollution (6).

Volatile organic compounds (VOCs) and nitrogen oxides (NO_x ≡ NO + NO₂) are important precursors of O₃ pollution (3). The O₃ sensitivity regime, i.e., whether O₃ production is NO_x limited or VOC limited (i.e., NO_x saturated), largely regulates the effectiveness of emission reductions for O₃ mitigation (7–9). In the NO_x-limited regime, controlling NO_x is more effective in reducing O₃ than controlling VOCs, whereas, in the VOC-limited regime, controlling VOCs is more effective than controlling NO_x. Regions worldwide affected by O₃ pollution have implemented ongoing reductions in O₃ precursor emissions, resulting in notable changes in O₃ sensitivity across many cities. As a result, for many cities in North America and Europe, summertime O₃ sensitivity has changed from a VOC-limited regime to a NO_x-limited regime over the past three decades (10, 11). In contrast, many cities in developing countries such as China and

India are still in a VOC-limited regime (8, 12, 13). Previous studies have shown that heat-wave events increased O₃ production by boosting anthropogenic and biogenic emissions (4, 14–18), whereas the temperature-driven change of the O₃ sensitivity regime and its impact on the effectiveness of emission reductions remain elusive, posing a grand challenge in designing effective strategies for O₃ pollution mitigation.

Here, by applying ambient observations combined with an observation-based box model and a chemical transport model (GEOS-Chem), we comprehensively investigate the impact of temperature on O₃ sensitivity in real atmospheric environments and then explore its implications for O₃ pollution mitigation under warming climate. A critically important aspect of this study is the availability of measurements of VOCs and major oxidants including hydroxyl radicals (OH) and peroxy radicals (HO₂ and RO₂), which provide strong constraints on the model simulation results.

RESULTS

The temperature dependence of O₃ sensitivity between seasons

To depict a clear framework of the relationship between temperature and O₃ sensitivity over a large temperature range, we investigate the difference in O₃ sensitivity between a wintertime month (February, on average of 3°C) and a summertime month (July, on average of 28.5°C) in 2019 at the Peking University Urban Atmospheric Environment Monitoring Station (PKUERS) site in Beijing. The comparison between the two time periods accounts for seasonal differences in temperature, water vapor, solar radiation, and concentrations of O₃ precursors. Beijing is one of China's megacities and suffers from severe O₃ pollution. Its experience in the control of O₃ pollution can serve as a useful reference for other Chinese cities that are still experiencing rapidly increasing O₃ concentrations. The PKUERS site is a representative urban site in Beijing, where the concentrations of O₃ and its precursors are comparable to citywide averages (12).

We investigate the O₃ sensitivity change by applying a box model with the detailed Master Chemical Mechanism (MCM) v3.3.1 chemistry scheme (19) (see the “Observation-based photochemical box

¹Max Planck Institute for Chemistry, Mainz 55128, Germany. ²Nanjing-Helsinki Institute in Atmospheric and Earth System Sciences, Nanjing University, Suzhou 215163, China. ³State Key Laboratory of Atmospheric Environment and Extreme Meteorology, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China. ⁴David D. Parrish, LLC, Boulder, CO 80303, USA. ⁵State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China. ⁶State Environmental Protection Key Laboratory of Formation and Prevention of Urban Air Pollution Complex, Shanghai Academy of Environmental Sciences, Shanghai 200233, China. ⁷Climate and Atmosphere Research Center, The Cyprus Institute, Nicosia, Cyprus. ⁸Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, Jiangsu Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, School of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing 210044, China.

*Corresponding author. Email: yafang.cheng@mpic.de (Y.C.); suhang@mail.iap.ac.cn (H.S.)

†Present address: Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen PSI CH-5232, Switzerland.

model" section). The inputs of the box model include comprehensive observations of C₂-C₁₀ nonmethane hydrocarbons (NMHCs), inorganic gases (NO_x, carbon monoxide, and sulfur dioxide), aerosol surface-area concentrations, and meteorological factors, such as temperature, relative humidity, air pressure, and photolysis frequencies. The model simulation accounts for the diurnal evolution of the planetary boundary layer, the exchange of O₃ between near surface air and the residual layer and the heterogeneous uptake of HO₂ radicals and reactive nitrogen species onto aerosols (12). Previous studies have demonstrated its good performance in the diagnosis of O₃ sensitivity given that O₃ sensitivity primarily depends on local photochemistry (12, 20). In addition, the model well simulates key photochemical products and RO_x radicals with biases of less than 25% (figs. S1 and S2). Figure 1 (A and B) shows the simulated isopleth diagrams for O₃ as a function of NO_x and OH reactivity of VOCs (VOC^R) in summer and winter. Although O₃ sensitivity falls into a VOC-limited regime in both winter and summer, the O₃ sensitivity in summer is closer to the transitional region between the two regimes (dashed lines in Fig. 1, A and B) than in winter. Shanghai, another megacity in southern China, exhibits a similar seasonal contrast in O₃ sensitivity to Beijing (fig. S3). The contrasting O₃ sensitivity between summer and winter has been supported by satellite measurements of the formaldehyde

to NO₂ ratio, a known metric of O₃ sensitivity (13), and by regional air-quality model simulations for Chinese urban areas (21).

Essentially, O₃ sensitivity depends on the dominant loss pathways of RO_x (RO_x ≡ OH + HO₂ + RO₂) radicals. O₃ production is NO_x limited if the self-reaction of peroxy radicals dominates the RO_x sink and VOC limited if the reaction of NO₂ with OH dominates (8, 22). Accordingly, the ratio of OH + NO₂ reaction rate to the total rate of the two RO_x sinks, defined as ϕ , is used to identify O₃ sensitivity regimes, as shown in Eq. 1 (text S1). O₃ production is NO_x limited if ϕ is lower than 0.5; otherwise, it is VOC limited. A lower ϕ value indicates a higher degree of NO_x-limited regime

$$\phi = \frac{k_{\text{OH}+\text{NO}_2} [\text{OH}] [\text{NO}_2]}{k_{\text{HO}_2+\text{RO}_2} [\text{HO}_2] [\text{RO}_2] + k_{\text{HO}_2+\text{HO}_2} [\text{HO}_2] [\text{HO}_2] + k_{\text{OH}+\text{NO}_2} [\text{OH}] [\text{NO}_2]} \quad (1)$$

where $k_{\text{OH}+\text{NO}_2}$, $k_{\text{HO}_2+\text{RO}_2}$, and $k_{\text{HO}_2+\text{HO}_2}$ are reaction rate constants of reactions OH + NO₂, HO₂ + RO₂, and HO₂ + HO₂, respectively. We calculate ϕ using the box model simulation constrained by comprehensive observations in winter and summer in Beijing. For this calculation, OH, HO₂, and RO₂ are simulated by the box model. The daytime (08:00 to 18:00) average of ϕ is used in this study as photochemical O₃ production primarily occurs during daylight hours.

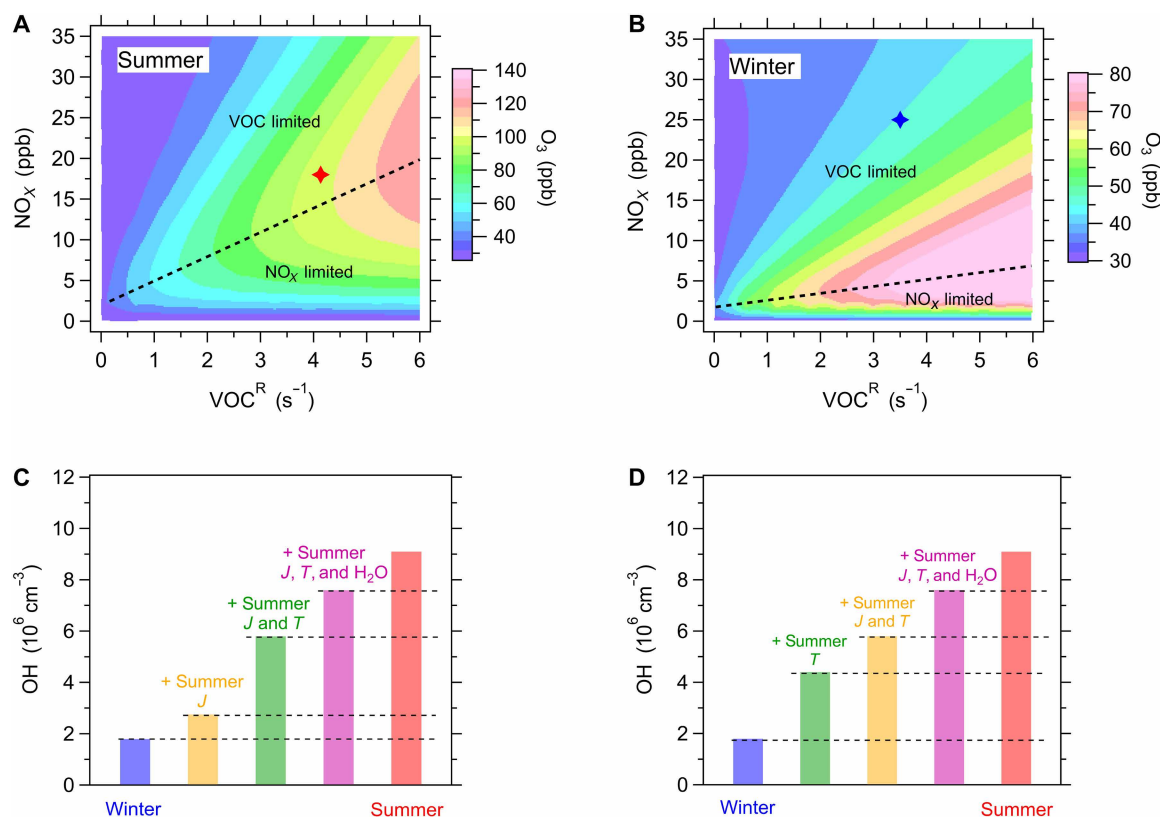


Fig. 1. The contrast of O₃ sensitivity between summer and winter in Beijing. (A and B) Box model–simulated isopleth diagrams for O₃ as a function of NO_x and VOCs in summer (A) and winter (B), respectively. VOCs are quantified by OH reactivity of VOCs (VOC^R) (see the “Measurement data” section). The averages of NO_x and VOC^R in summer (red symbol) and winter (blue symbol) are marked on the isopleth diagrams. The dashed lines indicate the ridge lines that distinguish between VOC-limited and NO_x-limited regimes. (C and D) Box model–simulated peak OH concentrations. In (C), five scenarios are simulated: winter (blue bar); summer (red bar); winter with summertime photolysis frequencies (J) (orange bar); winter with summertime photolysis frequencies and temperature (T) (green bar); and winter with summertime photolysis frequencies, temperature, and water vapor (purple bar). In (D), five scenarios are simulated: winter (blue bar); summer (red bar); winter with summertime temperature (green bar); winter with summertime photolysis frequencies and temperature (orange bar); and winter with summertime photolysis frequencies, temperature, and water vapor (purple bar). For (C) and (D), the impact of temperature on OH includes temperature-induced changes in reaction rate constants and isoprene concentrations.

The uncertainty in the simulated ϕ arising from uncertainties in key reaction rate constants associated with radical termination and cycling is estimated to be 12% (see the “The uncertainty of the model simulation” section).

Given that the OH radical is a key oxidant that determines O₃ sensitivity (12, 23, 24), we investigate the impact of temperature on OH concentrations with the box model by accounting for the changes in reaction rate constants and isoprene emissions induced by temperature change. As shown in Fig. 1 (C and D), the change in temperature has a larger effect on OH concentrations than the changes in photolysis frequencies and humidity, with the rise in temperature from winter to summer increasing OH. Note that the only difference between panels (C) and (D) of Fig. 1 is the order in which changes of temperature and photolysis frequency are applied, confirming that temperature change plays a key role regardless of the order. The combined effects of changes in temperature, humidity, and photolysis frequencies cannot fully explain the observed difference in OH concentrations between winter and summer, as indicated by the difference between the purple and red bars in Fig. 1 (C and D). This residual difference is attributed to additional influences from changes in concentrations of VOCs, NO_x, and oxidation products.

As shown in Fig. 2A, the box model-simulated ϕ shows a moderate negative correlation with temperatures in winter (blue triangles) and a notable negative correlation with temperatures in summer (red circles), consistently decreasing as temperatures increase from -10° to 37°C . As a comparison, we also calculate ϕ values by using observed concentrations of NO₂, OH, HO₂, and RO₂ in winter 2016 in Beijing (orange solid triangles) and in summer 2014 in Wangdu (green solid circles), a city that is 170 km away from Beijing, showing a similar temperature dependence to the results of the box model simulations.

The mechanism driving the temperature dependence of O₃ sensitivity

Although previous studies have shown that rising temperature can increase O₃ production (4, 14–18, 25), how global warming affects O₃ sensitivity regime is still not well understood. Here, we explore the underlying chemical mechanism causing the temperature dependence of O₃ sensitivity. A change in temperature can alter the reaction rate constants of many reactions involved in cycling and termination of RO_x radicals (table S3) (26). Nevertheless, it remains unclear how the net effect of these changes affects O₃ sensitivity. In the model simulation, we take the summer scenario as a base scenario and conduct sensitivity tests by changing the reaction rate constant of the investigated reaction over a large temperature range (-10° to 50°C) (see the “Evaluating the mechanism driving the temperature dependence of ϕ ” section). As shown in Fig. 2B and fig. S4, temperature affects O₃ sensitivity mainly through changing the reaction rate constants of radical termination, rather than changing the reaction rate constants of radical cycling, although radical cycling is considered the most important process for O₃ production (12, 23). Specifically, higher temperatures accelerate the thermal decomposition of acyl peroxy nitrates species [R(O)O₂NO₂ or peroxyacetyl nitrates (PANs)] [PANs $\rightarrow$ NO₂ + R(O)O₂], which increases concentrations of RO₂ and HO_x radicals via accelerated radical cycling. The increased RO_x then accelerates the removal of NO_x, resulting in reduced NO_x concentration (fig. S5). Overall, the increase of RO_x concentrations and the decrease of NO₂ concentrations jointly lead to a decrease in ϕ and a shift toward a NO_x-limited regime.

Furthermore, a higher temperature increases biogenic emissions of VOCs such as isoprene (fig. S6) and monoterpenes (25), promoting the production of secondary carbonyls (such as formaldehyde), which increases the primary production of RO_x radicals (fig. S7) and thus reduces the lifetime of NO_x, causing a further shift toward a NO_x-limited regime. By accounting for the temperature dependence of chemistry and biogenic VOC emissions, the box model simulation shows a nonlinear dependence of ϕ on temperature (black lines in Fig. 2, A and B). Overall, both chemical processes and biogenic VOC emissions lead to a negative ϕ -temperature relationship, with associated slopes of $-0.012^{\circ} \pm 0.004^{\circ}\text{C}^{-1}$ and $-0.015^{\circ} \pm 0.005^{\circ}\text{C}^{-1}$, respectively, at temperatures above 20°C .

As a comparison with the box model simulation results, we use the GEOS-Chem model to investigate the underlying chemical mechanism behind the impact of temperature on O₃ sensitivity in Beijing (see the “GEOS-Chem simulations” section). The model simulation can well reproduce the observed O₃, NO_x and VOC^R with average model deviations of <15% in Beijing (table S4). As shown in Fig. 2A and fig. S8, by accounting for the temperature dependence of chemistry and biogenic emissions (emissions of biogenic VOCs and soil NO_x) in the GEOS-Chem simulation, the simulated relationship between ϕ and temperature is generally consistent with that calculated by the observation-based box model. The impact of temperature on soil NO_x emissions plays a minor role in O₃ sensitivity change compared with the impact of temperature on biogenic VOCs emissions, according to our model simulation. The temperature dependence of soil NO_x emissions leads to an increase in ϕ of 0.03 from winter to summer, which is much smaller than the impact of the temperature dependence of biogenic VOC emissions (a reduction of 0.24 in ϕ).

According to the model simulations, the value of the slope between ϕ and temperature is rather small (about $-0.0033^{\circ}\text{C}^{-1}$) at temperature of $<20^{\circ}\text{C}$, which is identified as a temperature-insensitive regime (Fig. 2A). The temperature-insensitive regime is attributed to the thermal stability of PAN (fig. S18) and the substantial decrease in biogenic VOC emissions (fig. S6) at temperatures below 20°C . The absolute value of the slope becomes larger at higher temperatures ($>20^{\circ}\text{C}$), which is identified as a temperature-sensitive regime. Notably, the slope is again smaller at extremely high temperatures of $>40^{\circ}\text{C}$ (Fig. 2A), which arises because the thermal decomposition of PANs has less effect on chemistry and the biogenic emission of isoprene decreases due to biophysical high-temperature constraints at extremely high temperatures (27).

DISCUSSION

The impact of global warming on O₃ sensitivity

Given the large effect of temperature change on O₃ sensitivity and rising temperature due to global warming (28, 29), the potential impact of global warming on O₃ sensitivity is investigated through the GEOS-Chem model simulation. Here, we focus on the difference in O₃ sensitivity between summer 2019 and a future scenario in summer 2100 characterized by the largest temperature increase [Shared Socioeconomic Pathway 5-8.5 (SSP5-8.5) scenario derived from Coupled Model Intercomparison Project Phase 6 (CMIP6) simulations] (30). Under the SSP5-8.5 scenario, summertime mean temperatures are projected to increase by 4° to 6°C from 2019 to 2100 across northern India, the North China Plain, and the southwestern United States. Notably, during the past 3 years (2023–2025), temperature

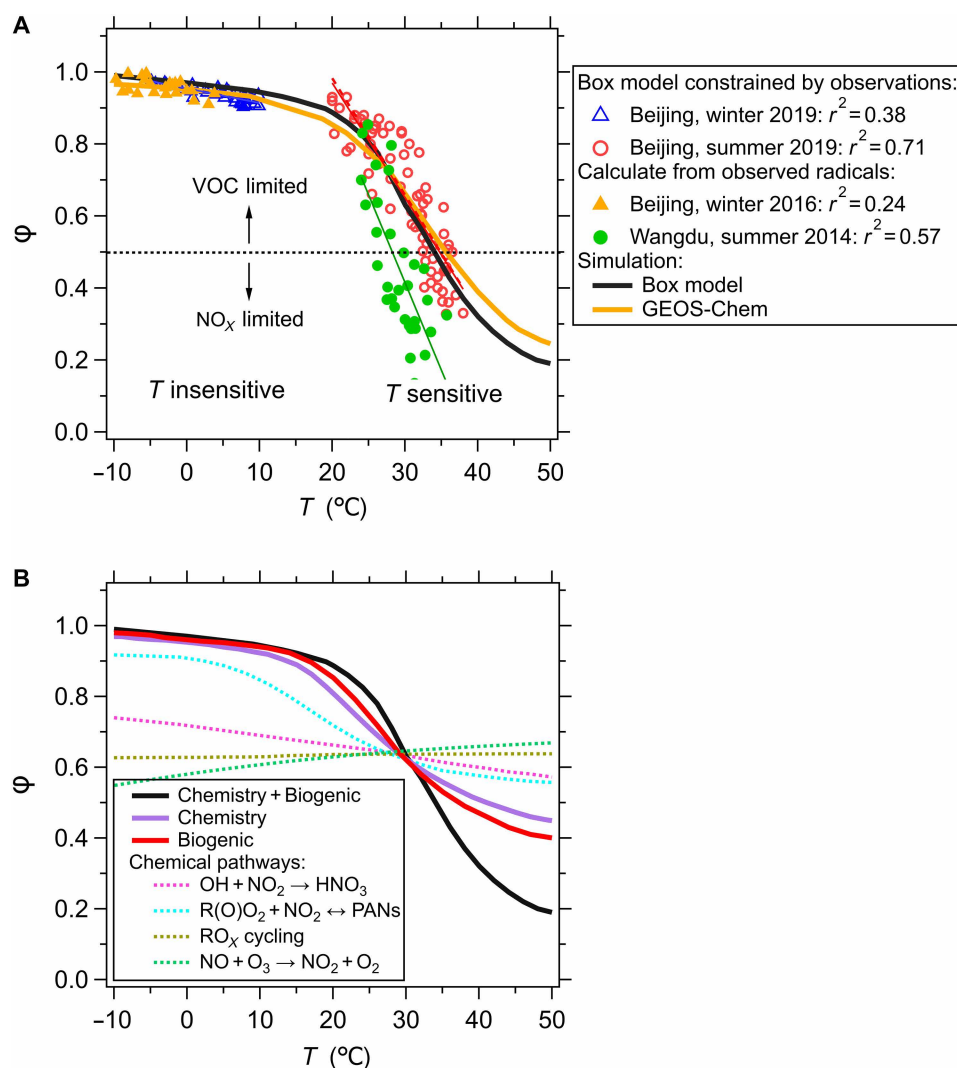


Fig. 2. The mechanism driving the impact of temperature on O₃ sensitivity. (A) Correlation between ϕ and temperature. ϕ values in winter (blue triangles) and summer (red circles) in Beijing are calculated by the box model with constraints of observations of O₃, O₃ precursors, and meteorological factors in Beijing. As a comparison, ϕ values in winter in Beijing (orange solid triangles) and in summer in Wangdu (green solid circles) calculated from observed NO₂, OH, HO₂, and RO₂ radicals are presented. Each data point represents a daily daytime average. Also presented is the temperature dependence of ϕ in Beijing simulated by the box model (black line) and the GEOS-Chem model (orange line). r^2 , coefficient of determination. (B) The temperature dependence of ϕ induced by chemistry and biogenic VOC emissions (black line), chemistry alone (purple line), and biogenic VOC emissions alone (red line), and individual chemical reactions (dashed lines), which is simulated by the box model.

anomalies of 4° to 6°C above the 2019 summertime mean have already occurred frequently in these regions on synoptic timescales, persisting for more than 10 days (31). Consequently, although SSP5-8.5 scenario may overestimate the long-term temperature increase by 2100, such extreme conditions are likely to occur under the exacerbated warming climate, particularly if future anthropogenic emission reductions are ineffective. Even if the monthly mean temperature in 2100 cannot reach up to such high values, the frequency and duration of extremely hot days are expected to increase substantially. In addition, selecting the SSP5-8.5 scenario for the analysis of O₃ sensitivity is directly related to O₃ pollution control strategy for extremely hot days, when O₃ pollution is generally most severe.

Figure 3 (A to F) shows the impacts of relevant influential factors on O₃ sensitivity change from 2019 to 2100 in summer in Beijing (see the “Evaluating the dependence of ϕ on different influential factors”

section). The temperature in Beijing is expected to increase from 28.5° to 35°C (30), which exactly falls into a temperature-sensitive regime. As a result, the temperature increase will cause a prominent decrease of ϕ by 0.21 (from 0.69 to 0.48), leading to a rapid shift toward the NO_x-limited regime. Anthropogenic NO_x emission abatement will lead to a decrease in ϕ by 0.47, whereas anthropogenic VOC emission abatement will lead to an increase in ϕ by 0.13. The enhancement in actinic flux and the increase in specific humidity play minor roles in ϕ compared with temperature change. Figure 3G shows the temporal evolution of ϕ from 2019 to 2100 with and without the impact of rising temperature considered. If the impact of rising temperature is not considered (blue line), then changes in anthropogenic emissions alone will shift O₃ sensitivity from a VOC-limited regime to a NO_x-limited regime in 2070. Additionally, considering the impact of rising temperature (brown line), this shift will occur earlier (in

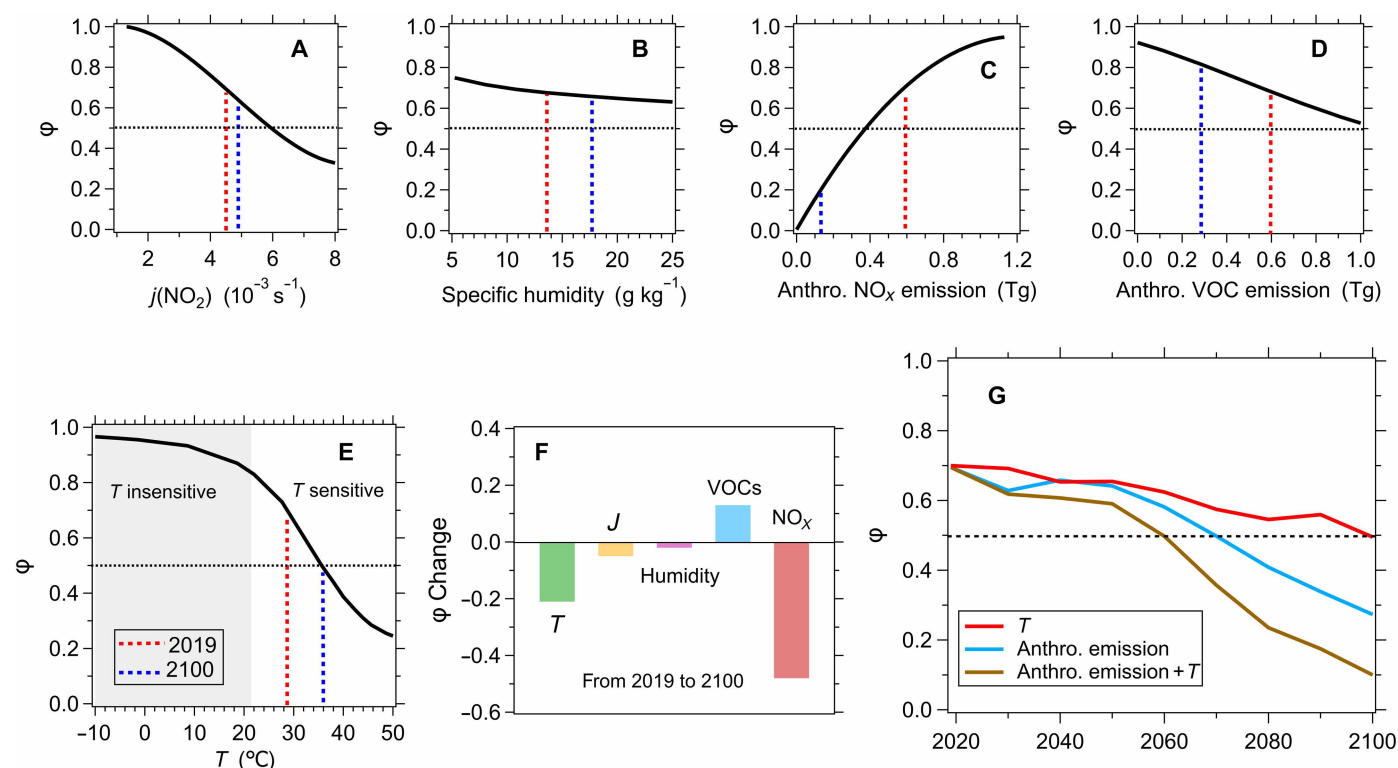


Fig. 3. Drivers of O_3 sensitivity change from 2019 to 2100 in July in Beijing. (A to E) GEOS-Chem model simulations showing the dependence of the monthly daytime average ϕ on key influential factors, including temperature (T), photolysis frequencies [e.g., $j(\text{NO}_2)$], specific humidity, and anthropogenic emissions of NO_x and VOCs. Red and blue dashed lines mark the corresponding values in 2019 and 2100, respectively. For each dependence, all conditions other than the investigated factor are fixed to the averages in 2019. The grey line represents the threshold value of 0.5. (F) The contributions of individual influential factors to the ϕ change from 2019 to 2100. (G) Temporal evolution of ϕ from 2019 to 2100 induced by temperature change (red line), changes in anthropogenic emissions (blue line), and changes in anthropogenic emissions and temperature (brown line). The temperature effect includes changes in reaction rate constants, biogenic emissions, and anthropogenic evaporative emissions. For all simulations, the influential factors were changed across the entire model domain (the North China Plain).

2060), suggesting that rising temperature accelerates the shift of O_3 sensitivity into a NO_x -limited regime.

We further investigate the impact of future global warming on O_3 sensitivity over the global scale by using the GEOS-Chem model (see the “Evaluating the impact of global warming on O_3 sensitivity across the world” section). In the current scenario (2019), many cities in the North China Plain, northern India, and northwest of Europe are in a VOC-limited regime (fig. S10), which is consistent with previous studies (8, 32, 33). We simulate the worldwide change in summertime ϕ ($\Delta\phi$) from 2019 to 2100 resulting from the meteorological changes (including temperature, humidity, solar radiation, winds, and boundary layer height) (as shown in Fig. 4A) and from both meteorological and anthropogenic emission changes (as depicted in fig. S15) under the SSP5-8.5 scenario. As shown in Fig. 4A, global warming will lead to a decrease in ϕ in many regions worldwide. In the hot-spot regions of O_3 pollution such as the North China Plain (34) and northern India (35), ϕ will decrease by up to 0.3 (corresponding to 60%), indicating a prominent transition toward a NO_x -limited regime. In addition, in Western Europe, southern Africa, southeast of Australia, and some coastal regions in America, ϕ also shows substantial decreases. As shown in Fig. 4 (B to D), O_3 sensitivity in many cities over China, South Asia, and Europe will shift from a VOC-limited regime to a NO_x -limited regime by 2100 due to climate change.

Our GEOS-Chem simulations suggest that, from 2019 to 2100, the overall contribution of temperature changes to $\Delta\phi$ is substantially larger than that of nontemperature meteorological changes (fig. S11). In this case, the rising temperature amplifies the benefit of NO_x abatement in O_3 mitigation under the warming climate, confirming that persistent NO_x abatement will be favorable for long-term O_3 pollution mitigation. Given that O_3 is an important short-lived greenhouse gas (36), persistent NO_x abatement for O_3 pollution mitigation not only benefits for air quality improvement but also helps to alleviate global warming. The future variability in temperature will become an important source of uncertainty for accurate prediction of O_3 sensitivity, which should be fully considered for the development of long-term O_3 control strategies.

Moreover, climate change can influence O_3 sensitivity regimes through meteorological changes beyond temperature, including changes in weather patterns, humidity, cloud cover, and the frequency and intensity of extremes. For example, more persistent summer heat waves can prolong photochemical episodes and may extend the duration of NO_x -limited regimes through enhanced RO_x radical production and increased biogenic VOC emissions. Warmer and wetter winters may also favor a shift toward NO_x -limited regimes. Increased cloud cover can reduce photolysis frequencies, which may lead to a shift toward VOC-limited regimes. In addition, the covarying

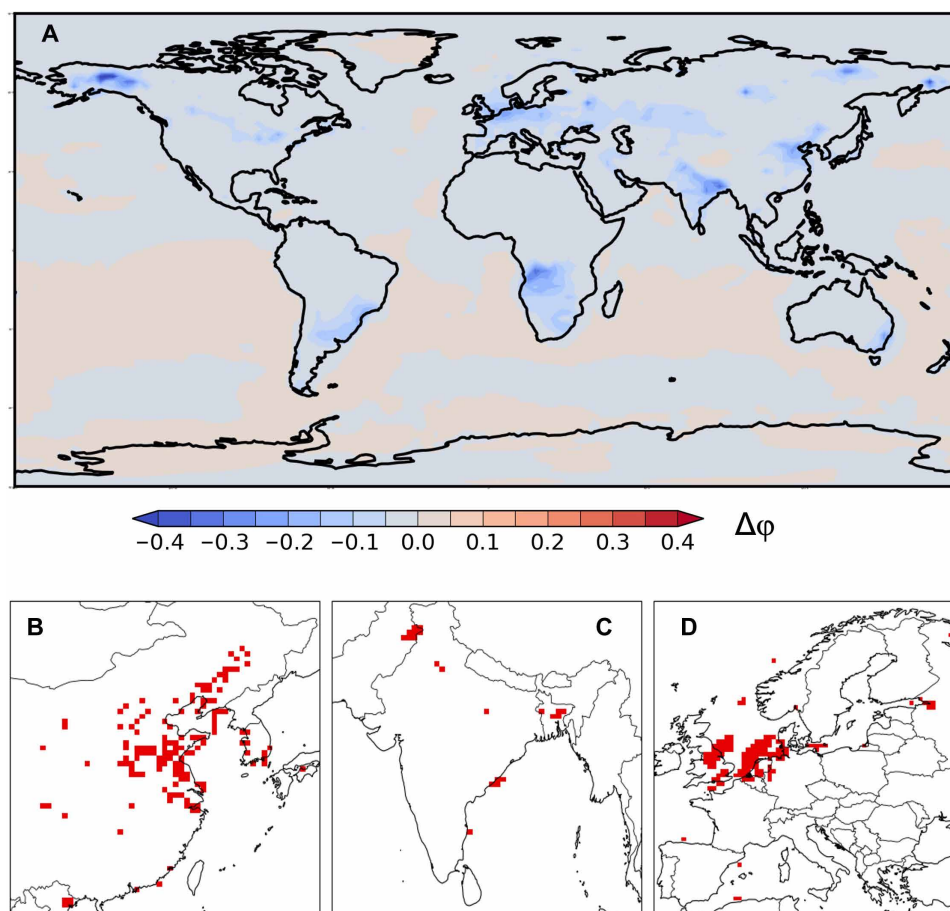


Fig. 4. The impact of global warming on O₃ sensitivity change from 2019 to 2100 across the world. GEOS-Chem simulated monthly daytime (8:00 to 18:00) average ϕ in July is used for analysis. (A) Global distribution of the change in ϕ ($\Delta\phi$) from 2019 to 2100 due to the projected meteorological changes. (B to D) Red squares indicate the areas where O₃ sensitivity shifts from a VOC-limited regime to a NO_x-limited regime by 2100 in East Asia (B), South Asia (C), and Europe (D). Note that (A) is calculated using a $2^\circ \times 2.5^\circ$ horizontal resolution but (B) to (D) are at $0.5^\circ \times 0.625^\circ$. Each red square in (B) to (D) represents a grid in the GEOS-Chem simulation with a resolution of $0.5^\circ \times 0.625^\circ$.

meteorological factors may locally modulate the magnitude and timing of regime changes and should be considered when interpreting effectiveness of future O₃ mitigation strategies.

MATERIALS AND METHODS

Measurement data

Comprehensive measurements were conducted at urban sites in 2019 in Beijing (39.99°N, 116.31°E, PKUERS site) and Shanghai (31.17°N, 121.43°E), the two largest cities in China. In addition, we also conducted comprehensive measurements in summer 2014 in Wangdu, another city in the North China Plain. Beijing, Shanghai, and Wangdu suffer from severe O₃ pollution and high oxidation capacity (12, 37), serving as a useful reference for other Chinese cities that are still experiencing rapidly increasing O₃ concentrations. Beijing and Wangdu are located within the North China Plain, a region that exhibits the highest O₃ concentrations in China. Our GEOS-Chem simulations suggest that summertime daytime mean ϕ is 0.63 in Beijing and 0.51 in Wangdu, values that are close to the average across 24 cities in the North China Plain (0.60). Owing to their representativeness, these two cities have been the focus of numerous

previous studies, including extensive field campaign measurements (12, 37–40).

O₃, nitric oxide (NO), nitrogen dioxide (NO₂), VOCs, formaldehyde (HCHO), carbon monoxide (CO), sulfur dioxide (SO₂), fine particulate matter (PM_{2.5}), aerosol optical properties, and aerosol surface-area concentration (S_a); photolysis frequencies of O₃, NO₂, NO₃, HONO, and HCHO; and meteorological factors including temperature, relative humidity, wind speed, wind direction, and air pressure were measured during the study period. The measurement techniques are summarized in table S1, which have been well described in previous studies (12). Measurement data of O₃, NO₂, CO, and PM_{2.5} concentrations at other sites covering the whole cities were acquired from the public website of the China Ministry of Ecology and Environment (<https://quotsoft.net/air/>). OH, HO₂, and RO₂ radicals were measured by a laser-induced fluorescence technique in summer 2014 in Wangdu (37) and in winter 2016 in Beijing (41). Table S2 summarizes the measured species and measurement period of field campaigns used in this study.

Given that OH reactivity of VOCs (VOC^R) is more related to O₃ production compared to VOCs concentrations, we used VOC^R to quantify VOCs. VOC^R is defined as

$$\text{VOC}^{\text{R}} = \sum_i^n k_{\text{VOC}_i} [\text{VOC}_i] \quad (2)$$

where k_{VOC_i} represents the reaction rate constants of OH radicals with VOC species i and $[\text{VOC}_i]$ represents the concentration of VOC species i . Here, VOC^{R} includes both observed $\text{C}_2\text{-C}_{10}$ NMHCs and modeled oxidation intermediates.

Observation-based photochemical box model

Model description

An observation-based photochemical box model is used to investigate the O_3 sensitivity to precursors in typical Chinese cities (Beijing, Shanghai, Guangzhou, and Wangdu) in summer and winter. The box model applies the state-of-the-art chemical mechanism (MCM v3.3.1), which contains 5832 species and 17224 reactions (42, 43), and can accurately simulate the radical source, cycling, and termination to understand the O_3 formation. In this study, the model was initialized with 46 parent $\text{C}_2\text{-C}_{10}$ NMHCs, and 11030 reactions are active in the simulation. Model calculations are constrained to measured meteorological factors (i.e., photolysis frequencies, temperature, relative humidity, and air pressure), inorganic species (CO , SO_2 , and NO_x), $\text{C}_2\text{-C}_{10}$ NMHCs with 46 species, and aerosol surface-area concentrations (S_a). Aerosol surface-area concentrations were used to quantify heterogeneous uptake of HO_2 radicals and reactive nitrogen species onto aerosols based on the method of Wang *et al.* (12). HO_2 uptake coefficient used in the model is 0.08, which is derived from radical measurements and relevant budget analysis in the North China Plain (44). This approach takes the advantage of allowing detailed treatment of VOC oxidation chemistry, which is expected to be more accurate than lumped VOC mechanism such as Carbon Bond Mechanism (CBM), Statewide Air Pollution Research Center (SAPRC), and Regional Acid Deposition Model (RADM). The near-explicit model of radical sources, propagation, and amplification allow a robust analysis of the factors that govern the sensitivity of O_3 production to its precursors. This approach has been successfully applied to study the nonlinear $\text{NO}_x\text{-VOC-}\text{O}_3$ relationship (20, 45–48).

The model considers physical processes, including dilution, dry deposition, and transport. A first-order dilution parameter was used to represent all nonchemical loss of species through mixing to prevent the accumulation of unconstrained species within the model. The dilution rate was determined according to the diurnal variations in long-lived species (such as chloroform and methane) and boundary-layer height, according to the method reported by Edwards *et al.* (20). According to the model sensitivity test, a 50% change in dilution rate leads to variations of less than 15% in OH, HO_2 , RO_2 , and ϕ and less than 25% in key oxidation products such as HCHO, methyl vinyl ketone and methacrolein (MVK and MACR), and PAN. In addition to this dilution loss, the dry deposition rate for O_3 was set as 0.42 cm s^{-1} in the daytime and 0.14 cm s^{-1} in the nighttime, as the deposition rate is known to decrease after sunset (47, 49, 50). Furthermore, the convection of O_3 between near surface air and the residual layer aloft was considered in the box model, according to the method reported by Womack *et al.* (47). The model runs were performed in a time-dependent mode with a 1-hour resolution and 4-day spin-up. Model sensitivity test suggests that a 4-day spin-up produces the same modeled OH, HO_2 , and ϕ values as a 10-day spin-up, demonstrating that a 4-day spin-up is sufficient for the box model simulations. The box model used in this study is based on the Framework for 0-D Atmospheric Modeling (F0AM) (51). It integrates chemical rate

equations with MATLAB's ode15s solver, which is designed specifically for stiff systems. We simulated the scenarios in February and July in 2019, representing winter and summer respectively. In winter, periods with extremely high NO_x concentrations [>50 parts per billion (ppb)] were excluded from the analysis to avoid the influence of excessive NO_x titration.

As shown in fig. S1, the agreement between the simulated and observed oxidation products is excellent, with average model deviations of +12% in summer and –6% in winter for MVK and MACR and +18% in summer and +7% in winter for PAN. MVK and MACR are key oxidation products of isoprene, an important biogenic VOC. PAN is a crucial acyl peroxy nitrates species [$\text{R}(\text{O})\text{O}_2\text{NO}_2$, collectively referred to as PANs], and their relevant reactions play a key role in the temperature dependence of O_3 sensitivity. The good performance of the model in simulating PAN suggests that the model can well capture the chemistry of the formation and decomposition of acyl peroxy nitrates. In addition, the box model can well simulate formaldehyde and acetaldehyde in Beijing, with discrepancies between observation and model simulation of less than 20%, which is consistent with a previous study (12). To consider primary emissions, we set the emission rates of formaldehyde and acetaldehyde in the model based on local emission inventories, specifically the Multi-resolution Emission Inventory for China (MEIC) (www.meicmodel.org/).

Construction of the O_3 isopleth

The O_3 isopleth as a function of NO_x and VOCs was used here to assess the sensitivity of O_3 to NO_x and VOCs. The observed average diurnal variations of trace gaseous and meteorological factors in winter and summer were used to constrain the box model as the base scenario. To construct the O_3 isopleth, we performed sensitivity simulations for each season by varying NO_x concentrations and VOC^{R} from 0 to 200% (relative to the base scenario) with an interval of 10%. Note that model conditions other than VOCs and NO_x , including photolysis frequencies, temperature, and humidity, kept the same as the base scenario. These sensitivity simulations provide sufficient data to illustrate the response of O_3 to VOCs and NO_x that could be used for diagnosing O_3 sensitivity regimes.

Evaluating the mechanism driving the temperature dependence of ϕ

We used the box model to evaluate the mechanism driving the temperature dependence of O_3 sensitivity. To evaluate the impact of temperature through altering reaction rate constants, in the model simulation, all conditions were fixed to summer 2019 in Beijing, and sensitivity tests were conducted by changing the reaction rate constant of the investigated reaction over a large temperature range (-10° to 50°C). To evaluate the impact of temperature through altering biogenic VOC emissions, in the model simulation, all conditions were fixed to summer 2019 in Beijing, and sensitivity tests were conducted by changing concentrations of isoprene and monoterpenes (α -pinene, β -pinene, and limonene) according to the observed temperature dependence of these biogenic VOCs (fig. S6). Notably, the OH reactivity of isoprene is higher than the OH reactivity of monoterpenes by a factor of 5 in Beijing and Shanghai, resulting in a dominant role of isoprene in determining the temperature dependence of ϕ .

Future reductions in NO_x emissions are expected to increase O_3 concentrations in urban areas where the VOC-limited regime dominates, partly due to weakened NO titration of O_3 . The box model simulations indicate that a 20% reduction in NO_x leads to an increase of ~ 10 ppb in O_3 in Beijing. We further examined the impact of a 20% and 50% NO_x reduction on the temperature dependence of

O₃ sensitivity in Beijing. As shown in fig. S12, a 20% reduction in NO_x results in only a small change in the temperature dependence of ϕ , whereas a 50% reduction in NO_x has a larger effect.

The uncertainty of the model simulation

Uncertainty in the model simulations arises in part from uncertainties in key reaction rate constants relevant to O₃ sensitivity, including those governing radical termination and cycling. Using the uncertainty factors listed in table S5, we conducted n model runs, where n equals the number of reactions considered. In each run, the rate constant of one reaction was perturbed by its uncertainty factor while all others were held constant. The overall model uncertainty was then quantified by propagating the errors from all perturbed reactions. Based on this approach, the uncertainty in the simulated ϕ is estimated to be 12%.

We have compared the key inorganic reaction rate constants in MCM v3.3.1 with the latest International Union of Pure and Applied Chemistry (IUPAC) recommendations (last accessed April 2026). The differences are mostly within 5%. For OH + NO → HONO, the difference is around 20%, resulting in only a slight change in ϕ , around 1.5%. The $k(\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3)$ derived from MCM v3.3.1 is the same as that of the IUPAC evaluation. In addition, the MCM v3.3.1–derived $k(\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3)$ increases by 18% from 274 K (winter) to 301 K (summer), whereas the IUPAC-recommended value shows a comparable increase of 17% over the same temperature range. This indicates that the temperature dependence of $k(\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3)$ in MCM v3.3.1 is consistent with that in the latest IUPAC evaluation.

Similarly, model uncertainty also arises from uncertainties in measured trace gas concentrations and meteorological inputs, including photolysis frequencies (J), temperature, relative humidity, and air pressure. Using the uncertainty factors listed in table S1, we performed n model simulations (n equals the number of parameters considered). In each simulation, the value of the selected parameter was adjusted according to its uncertainty. The overall model uncertainty was then quantified through error propagation of uncertainties from all considered parameters. The resulting uncertainty in the simulated ϕ is ~24%.

Temperature changes can affect $j(\text{O}^1\text{D})$ by altering the quantum yield and absorption cross section of this photolysis process. Our calculations indicate that a temperature change from summer to winter results in a ~3% decrease in $j(\text{O}^1\text{D})$. In addition, the same temperature change leads to increases of 2 to 4% in the rate constants for reactions of O¹D with H₂O, O₂, and N₂. When these effects are considered together, the resulting change in ϕ due to the summer-to-winter temperature difference is less than 2%.

GEOS-Chem simulations

Model description

To explore the impact of future changes in temperature on O₃ sensitivity regime, we conducted simulations by applying the three-dimensional chemical transport model GEOS-Chem (version 13.3.3; <https://geoschem.github.io/>). The model fully simulates NO_x + O_x + CO + VOCs + HO_x + Br + Cl + I + aerosols chemistry in the troposphere and stratosphere, and its good performance in simulating surface O₃ in summer has been well evaluated in previous studies (52, 53). In this study, we conducted the simulations over the globe. Global anthropogenic emissions used are from the Community Emission Data System inventory. In China, anthropogenic emission data are obtained from MEIC (www.meicmodel.org). Biogenic emissions are processed by the Model of Emissions of Gases and Aerosols from Nature (MEGAN) model version 2.1 according to the work of

Guenther *et al.* (54). We used the assimilated meteorological data of Modern-Era Retrospective Analysis for Research and Applications, Version 2 (MERRA-2) to drive the model. The model simulations were conducted at a horizontal resolution of 2.5° longitude × 2.0° latitude with 47 layers for the global scale and at a horizontal resolution of 0.625° longitude × 0.5° latitude with 47 layers for regional scales including China, India, and Europe. For the key reactions governing O₃ sensitivity—such as PANs ↔ RO₂ + NO₂, OH + NO₂ → HNO₃, HO₂ + HO₂ → H₂O₂, HO₂ + NO → OH, isoprene oxidation by OH, and NO titration of O₃—GEOS-Chem uses the same kinetics of reactions as MCM v3.3.1. To test whether the GEOS-Chem mechanism reproduces the temperature dependence of ϕ from MCM, we conducted parallel box model simulations using both mechanism under otherwise consistent conditions. As shown in fig. S13, the resulting temperature dependence of ϕ simulated with MCM v3.3.1 closely matches that obtained with the GEOS-Chem mechanism. This comparison supports the use of GEOS-Chem for capturing the dominant chemical controls on the temperature sensitivity of ϕ in this study.

We validated the model performance by comparing simulation results with observations in Beijing. As shown in table S4, the model simulation can well reproduce the observed O₃, VOC^R, and NO_x, with average model deviations being smaller than ±15%. In addition, the model-simulated temperature dependence of isoprene is consistent with observed results (fig. S6). Our results show that the model overestimates surface O₃ concentrations by 8 ppb in Beijing and by 5 ppb in the Beijing-Tianjin-Hebei region, comparable to the 6- to 8-ppb overestimation reported by Lu *et al.* (55). In Beijing, an overestimation in O₃ of 8 ppb results in a 4.5% underestimation of ϕ (i.e., ϕ decreases from 0.65 to 0.62).

Evaluating the dependence of ϕ on different influential factors

Using the GEOS-Chem model, we investigated the driving forces governing O₃ sensitivity by testing the responses of ϕ to the changes in relevant influential factors in July over Beijing. The investigated influential factors include temperature, photolysis frequencies, specific humidity, anthropogenic VOCs emissions, and anthropogenic NO_x emissions. The simulation domain covers the North China Plain (fig. S14). For the simulation of each response, all conditions other than the investigated influential factor were fixed at July 2019. Over the simulation domain, each investigated influential factor was changed to span extremely low and extremely high values in real environments. As a result, the dependence of ϕ on each influential factor in Beijing was acquired as shown in Fig. 3. For the simulation of temperature dependence (orange line in Figs. 2A and 3E and fig. S8), the GEOS-Chem model accounts for the temperature dependence of chemistry and biogenic emissions including biogenic VOCs and soil NO_x. In addition, we additionally test the impact of temperature dependence of evaporative anthropogenic VOC emissions including solvent use and transportation according to the parameterization method proposed by Wu *et al.* (56), which suggests a minor effect on ϕ compared to temperature dependence of chemistry and biogenic emissions (fig. S8). For all scenarios, the global background concentrations of O₃, NO_x, VOCs, and aerosols in July 2019 were used to drive the model simulations. Because O₃ sensitivity is primarily governed by local photochemical reactions, using a fixed global background across scenarios is considered appropriate.

The diurnal variations of temperature, humidity, and photolysis frequencies are accounted for in the simulations. For the base scenario, hourly values of temperature and specific humidity from MERRA-2,

along with hourly values of photolysis frequencies from the FAST-JX radiative transfer model, were used as model inputs for July 2019. To evaluate the impact of each influential factor on ϕ , temperature was varied over the range -30° to $+30^{\circ}\text{C}$ with 2°C increments, specific humidity was scaled by factors ranging from 0.8 to 2.0 with 0.2 increments, and photolysis frequencies of all photolysis reactions were varied by modifying the solar zenith angle in FAST-JX to represent higher or lower latitudes relative to the base domain. This approach ensures that diurnal variations remain consistent with the base scenario, despite changes in absolute values.

Notably, in Fig. 3 (A to E), temperature, photolysis frequencies and specific humidity correspond to the conditions in Beijing, whereas anthropogenic VOCs emissions and anthropogenic NO_x emissions correspond to the conditions over the Beijing-Tianjin-Hebei region as the photochemistry in Beijing is largely influenced by emissions from Tianjin and Hebei. The data of these influential factors in future scenarios were acquired from model simulations of WCRP CMIP6 (<https://esgf-data.dkrz.de/search/cmip6-dkrz/>). The SSP5-8.5 scenario was used to test the potential influence of the largest increase of temperature.

According to CMIP6, near-surface photolysis frequencies in Beijing are projected to increase by $\sim 9\%$ from 2019 to 2100. This increase accounts for the effects of declining cloud cover and aerosol loading and leads to a reduction in ϕ of 0.05 (Fig. 3A). Specifically, cloud cover in Beijing is projected to decrease by 11.2%, contributing to a decrease in ϕ of 0.03.

Evaluating the impact of global warming on O_3 sensitivity across the world

We used the GEOS-Chem model to simulate the change in O_3 sensitivity from 2019 to 2100 across the world. For the base scenario, the simulations were run under conditions in July 2019. Based on the conditions in July 2019, we simulated the future scenario for July 2100 by using (1) meteorology in July 2100, (2) temperature alone in July 2100, (3) meteorology other than temperature in July 2100, (4) anthropogenic emissions in July 2100, (5) both meteorology and anthropogenic emissions in July 2100. As a result, the change in ϕ ($\Delta\phi$) from 2019 to 2100 can be calculated. $\Delta\phi$ is shown in Fig. 4A for scenario 1, in fig. S11 for scenarios 2 to 4, and in fig. S15 for scenario 5. Table S7 summarizes the model input fields for GEOS-Chem simulations in 2019 and 2100.

Meteorological factors (including temperature, humidity, solar radiation, air pressure, wind fields, and boundary layer height) in 2100 were derived from CMIP6 (<https://esgf-data.dkrz.de/search/cmip6-dkrz/>). The SSP5-8.5 scenario was used in this study to test the potential influence of the largest increase of temperature. The outputs of 12 CMIP6 models (ACCESS-CM2, BCC-CSM2-MR, CanESM5, CESM2-WACCM, CMCC-ESM2, EC-Earth3-Veg-LR, FGOALS-f3-L, FGOALS-g3, GFDL-ESM4, NorESM2-MM, CESM2, and MIROC6) are averaged to quantify the changes in these meteorological factors from 2019 to 2100.

Running the GEOS-Chem model requires hourly meteorological data, whereas the CMIP6 provides only daily averages for the year 2100. The 2100 meteorological field was constructed by applying CMIP-derived 2100–2019 perturbations to the corresponding 2019 MERRA fields. Specifically, we calculated the daily mean difference between the CMIP simulations for 2100 and 2019 for a set of these variables (temperature, specific humidity, shortwave radiation, air pressure, and wind) and added the resulting perturbation to the corresponding hourly MERRA 2019 data, thereby generating a 2100 meteorological dataset based on the MERRA 2019 baseline (see text

S3 for details). To quantify the impact of humidity, both specific humidity and relative humidity were used in the model simulation.

We regridded the CMIP6 meteorological data to match the MERRA-2 grid used in the GEOS-Chem model. Horizontally, bilinear interpolation was applied to align CMIP6 data with the MERRA-2 resolution grid. Vertically, CMIP6 data were regridded onto the 72 vertical layers of MERRA-2 based on the corresponding air pressure distributions. These 72 layers span the entire atmosphere, from the surface to the stratosphere.

The average of multiple models may not capture “weather,” particularly synoptic systems. We compare GEOS-Chem–simulated ϕ values for July 2100 under the average meteorology from multiple CMIP6 models and under the meteorology from a single model (CESM2) (fig. S16). The two scenarios correspond to scenario 5 and scenario 6 listed in table S7, which yield similar spatial distribution of ϕ and its change (fig. S16). This suggests that the key conclusions regarding the temperature dependence of ϕ remain valid.

The updated anthropogenic emissions in 2100 are taken from Gidden *et al.* (57), one of the most commonly used inventories for CMIP6. It is an emission inventory developed on the basis of SSP pathways with harmonized scenario trajectories and then downscaled/gridded for CMIP6 use. Because reliable uncertainty estimate is only possible for historical data, Gidden *et al.* (57) did not provide a quantitative estimate for future scenario emissions. However, they adopted a harmonization approach, where integrated assessment models (IAM) trajectories are systematically adjusted to match a common CMIP6 historical baseline in 2015, thereby reducing uncertainties in emission estimate. The anthropogenic emission inventories used for both 2019 and 2100 include anthropogenic emissions of CH_4 and isoprene. Biogenic VOC emissions, including isoprene, monoterpenes, and sesquiterpenes, were calculated online using the MEGAN model, which accounts for the effects of meteorological variability and change. To quantify biomass burning emissions, the Quick Fire Emissions Dataset (QFED2) emission inventory for 2019 is used for the simulation in both 2019 and 2100 as a corresponding inventory for 2100 is not available.

In GEOS-Chem setup, the boundary layer height is taken from the meteorological datasets (MERRA-2), which is used to calculate the eddy-diffusivity profile. The GEOS-Chem adopted a nonlocal scheme formulated by Holtslag and Boville (58). The nonlocal scheme calculates the eddy-diffusivity profile based on the boundary layer height and a turbulent velocity scale, and it also accounts for nonlocal vertical transport of heat and moisture.

In our GEOS-Chem simulations, land use is held fixed at 2019 conditions for both the 2019 and 2100 scenarios. Therefore, direct impacts of land-use change on biogenic VOC emissions are not considered. On the other hand, the 2100 meteorological fields used to drive GEOS-Chem are taken from CMIP6 climate model output, in which land-use forcing is included as part of the climate scenario. Thus, impact of land-use change on the meteorology is implicitly considered. To provide context, we summarize CMIP6 land-use changes between 2019 and 2100 in fig. S17. This indicates that the largest changes occur primarily in high-latitude and tropical regions, whereas changes are comparatively smaller over several major O_3 -polluted regions. The small changes in land use are expected to have a limited impact on biogenic VOC emissions and O_3 sensitivity in these regions. For example, CMIP6 suggests that forest cover increases by $\sim 2\%$ in China and decreases by $\sim 3\%$ in the United States. A MEGAN-based sensitivity test indicates that these changes would

translate to a change of less than ~5% in biogenic VOC emissions, implying a relatively small impact on ϕ .

Figure S10 shows the spatial distribution of ϕ simulated by GEOS-Chem model in 2019 and 2100. As shown in fig. S10, under the current scenario (2019), many cities in the North China Plain, northern India, and northwest of Europe are in a VOC-limited regime ($\phi > 0.5$). Most cities in North America have entered a NO_x -limited regime ($\phi < 0.5$). The forests and oceans are mostly in a NO_x -limited regime ($\phi < 0.5$). These results are generally consistent with previous studies (8, 10, 32, 33, 59, 60).

Figure S11 shows the individual contributions of changes in temperature, nontemperature meteorological factors, and anthropogenic emissions to $\Delta\phi$. The results indicate that the contribution of nontemperature meteorological changes to the change in ϕ from 2019 to 2100 is much smaller than that of temperature change. For example, over the North China Plain, temperature changes lead to a decrease in ϕ of ~0.20, whereas nontemperature meteorological changes result in a decrease of only about 0.04. The contribution of anthropogenic emission changes to $\Delta\phi$ varies across regions, leading to a decrease in ϕ in East Asia but an increase in most regions of Africa and Australia.

Supplementary Materials

This PDF file includes:

Text S1 to S3

Figs. S1 to S18

Tables S1 to S7

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Wenjie Wang, Hang Su, David D. Parrish, Ruijing Ni, Xin Li, Fengxia Bao, Hongli Wang, Cheng Huang, Jonathan Williams, Hong Liao, Keding Lu, Yuanhang Zhang, and Yafang Cheng

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