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Accelerated O₃ formation triggered by summer heatwaves in megacity Seoul

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As compelling evidence of global warming, heatwaves are expected to elevate O₃ mixing ratios in highly polluted urban areas. In summer 2018, Seoul, an Asian megacity, experienced elevated O₃ levels in conjunction with a temperature surge (maximum of 38.9 °C). This study quantitatively estimates the O₃-climate penalty through measurements of nitrogen oxide species, volatile organic compounds (VOCs), and the boundary-layer height, as well as model simulations. The results highlight an acceleration of O₃ concentration increment with increased temperature and elevated ozone production efficiency in NO_x-saturated conditions. Furthermore, it emphasizes the importance of dynamic boundary-layer processes and increased VOC concentrations resulting from fugitive emissions during the heatwave.

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Environmental significance

With global warming, surface ozone levels are expected to increase with more frequent heatwaves, but the detailed process of interaction between ozone and heatwaves is still unclear. In summer 2018, we observed an ozone enhancement in conjunction with an extreme heatwave, quantified its temperature dependency, and elucidated its driving processes. We found that reinforced vertical mixing of air mass with the additional fugitive emission of volatile organic compounds in the reactive nitrogen oxide saturated megacity plays a key role in boosting ozone production efficiency increase, and it accelerates the daytime ozone enhancement. This implies that more frequent heatwaves due to climate change could induce faster and greater ozone increases in megacities than expected.

1. Introduction

Numerous spatiotemporal observations and modeling studies indicate an ongoing and projected continuous increase in global surface temperature.¹ Under the worst-case scenario of the Shared Socioeconomic Pathways (SSPs), the rise in climate change pollutants could cause a significant increase in global temperature. For example, climate simulation models project a rise in average temperature up to 7.0 °C in Northeast Asia by 2100.^{2–4} This temperature surge is anticipated to elevate O₃ mixing ratios, particularly in urban areas with high emissions of NO_x and volatile organic compounds (VOCs) under extreme meteorological conditions. Notably, O₃ concentrations spiked during the 2018 heatwaves in European and Asian cities.^{5–10} This drew attention to O₃ as both a short-lived climate pollutant

(SLCP) contributing to global warming^{11–13} and a key air pollutant deteriorating air quality.¹⁴

To recognize the positive feedback between surface O₃ and global warming, a comprehensive understanding of the interplay between chemical ozone production mechanisms and climate variables is imperative. In recent years, increases in surface O₃ due to climate change have been labeled the “O₃-climate penalty”, underscoring this gas’ adverse impacts on the climate system and the associated costs of climate change mitigation and damage repair measures.^{15,16} Recent studies have suggested methods for quantifying the O₃-climate penalty as an “O₃-climate penalty factor” (CPF_{O₃}) using statistical fitting^{17–19} or discretization methods combined with model simulations.^{20–22} Despite the various factors that influence O₃ increase across different regions, the CPF_{O₃} calculated from long-term measurement data is quite similar in most areas, particularly at background sites (0.1–3.2 ppbv °C⁻¹).^{16,21,23}

As global warming intensifies, megacities around the world are experiencing increased O₃ levels during heatwaves.²⁴ These extreme events are clear indicators of global warming and highlight the urgent need for research to explore the mechanisms and key factors contributing to elevated O₃ levels during heatwaves. In summer, the chemical reactivity linked to precursor emissions is significantly increased. Therefore, in this season, the chemical processes driving O₃ formation tend

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to outweigh the physical processes associated with its long-range transport, which can lead to a pronounced increase in CPF_{O_3} in urban areas.²⁵

Various studies have shown a correlation between O_3 formation and temperature in polluted regions during short-term heatwaves,^{26–28} suggesting that O_3 formation reinforced over time. Given the significant impact of O_3 on human health, its accelerated formation due to temperature rise can lead to dangerously high levels, posing serious risks to residents of megacities.

Seoul, a megacity in South Korea, experienced an extreme heatwave in summer 2018, which saw an unprecedented daily maximum temperature exceeding 38 °C accompanied by a significant increase in O_3 . Since 2000, Seoul has witnessed a continuous annual increase in the 99th percentile temperature of 0.09 °C per year and in the annual average O_3 concentration of 1.28 ppbv per year (Fig. 1). These variations of 99th percentile O_3 concentration and temperature value represent the changes in summer season, when the O_3 level is strongly determined by the photochemical reaction. The 2018 heatwave caused the rate of increase in the annual average temperature and O_3 to rise to 0.15 °C per year and 1.73 ppbv per year, respectively,²⁹ approximately 67% and 54% larger than before the heatwave. The exceptionally high temperatures recorded during the 2018 heatwave exemplify the effects of climate change^{30–32} and resulted in surface O_3 concentrations exceeding South Korean

air quality standards.³³ These observations suggest that, in the future, the rise in extreme temperatures due to global warming may cause critical O_3 -related challenges in megacities, similar to those observed during the 2018 heatwaves.

This study aimed to estimate the CPF_{O_3} during a short heatwave in a highly polluted urban area in Seoul and explore the crucial factors determining this parameter using observational data and model results obtained in the summer of 2018. The findings provide vital information for policies to abate O_3 pollution and for addressing emerging challenges in megacities during heatwaves, potentially intensified by future warming.

2. Materials and methods

2.1. Field measurements

All measurements were conducted between 13 July and 20 August 2018 in urban Seoul, South Korea. Trace gases and aerosol composition were measured at the Korea University campus (KU, 37.59° N, 127.03° E, 27 m a.g.l.). Additionally, 55 VOC species and vertical winds were measured in the districts of Jongro-gu (37.57° N, 127.01° E) and Jungnang-gu (37.59° N, 127.08° E, 22 m a.g.l.), located near KU (Fig. S1).

O_3 , NO , and NO_2 were measured using commercial instruments—respectively, a 49i, Thermo Scientific; a 42i, Thermo Scientific; and a T500U, Teledyne API. The detection limits of these instruments were 1, 0.4, and 0.04 ppbv, respectively.

The mixing ratios of 55 VOCs were measured in real-time using an automatic gas chromatography-flame ionization detector (GC-FID; Clarus 500, PerkinElmer) with a Thermal Desorption (TD; TurboMatrix 300, PerkinElmer) unit. Ambient air samples (600 mL) were collected using a small pump for 40 min at a flow rate of 15 mL min⁻¹. The pump was controlled by a mass flow controller. A Nafion dryer was used to remove water from each sample, and the VOCs in the moisture-depleted sample were concentrated at -30 °C in a cold trap using a thermal desorption unit. Then, the temperature of the trap was rapidly increased to >300 °C to induce desorption, and the desorbed sample was transferred to the high-resolution capillary column of the GC-FID through a transfer line with high-purity nitrogen carrier gas. Each desorbed sample was separated through two columns, one polar (plot column) and one non-polar (bp-1 column), before the VOCs were detected by the FID.

Peroxyacetyl nitrate (PAN, $\text{CH}_3\text{COO}(\text{O})\text{NO}_2$) was measured using gas chromatography-luminol chemiluminescence detection (GC-LCD).^{34,35} A 10 m capillary column (DB-1, Agilent, USA) was used and a photomultiplier tube (HC135-01, Hamamatsu, USA) was connected to the reaction cell where the luminol solution and PAN were mixed. The height of the PAN peak was quantified using a Molybdenum- NO_x instrument (T500U, Thermo Scientific). The PAN standard was formed by reacting with vaporized liquid acetone with standard NO_2 gas under UV light in a chamber. Data was ensemble into one-hour data every two minutes.

The HONO concentration was measured using a parallel-plate diffusion scrubber coupled with an ion chromatography (PPDS-IC) system. Ambient air was sampled slowly (0.8 L min⁻¹) through a 1 m long 1/4" PTFE tube and was solubilized in the collected solution (deionized water, HPLC grade, J. T. Baker) by

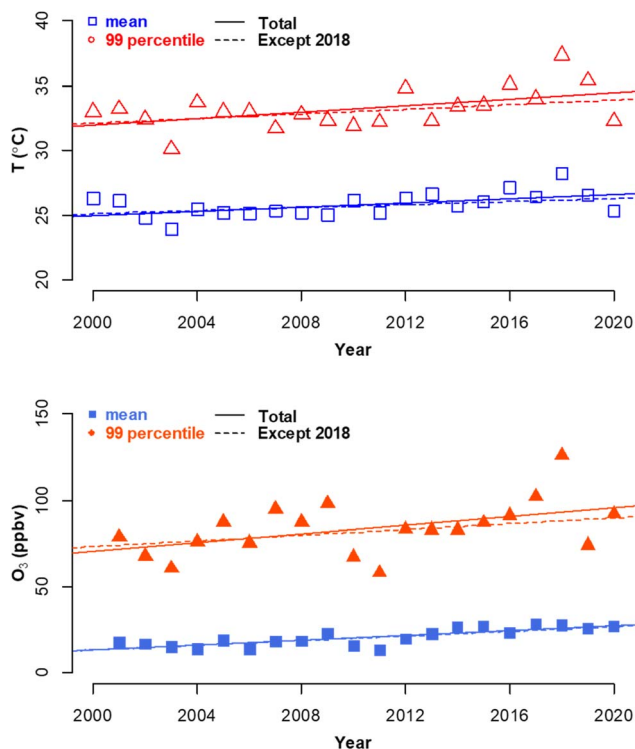


Fig. 1 Annual mean variation (blue square) and annual maximum variation (red triangle) of the atmospheric temperature (open symbol) and surface O_3 (solid symbol) during the hot-summer (Jul–Aug) at Jongro-gu in Seoul, South Korea (data are from the Korea Meteorological Administration and Korea Ministry of Environment website). The dashed linear regression line describes the annual variation until 2020, and solid linear regression line implies the change of annual variation when add the 2018 data.



penetrating a membrane filter (0.2 μm pore size, Osmoncis) in the PPDS. The collected solution was injected into the analysis column (AS14, Dionex IonPac™) with an eluent solution (3.5 mM Na_2CO_3 , NaHCO_3 mixed solution). The time resolution of the HONO and HNO_3 measurements was 15 min, and hourly average data were used for the analysis. The detection limit was 20 pptv. Details of the measurement and calibration methods are provided in previous paper.³⁶

A ceilometer (CL51, Vaisala) was used to obtain vertical profiles of backscattering coefficients at intervals of 10 m to 15.4 km using a laser (InGaAs diode laser) with a wavelength of 910 nm.³⁷ A wind lidar (Windcube-200, Leosphere) was used to measure the vertical profile of wind speed and direction using a Doppler beam swinging scanner with a 1532 nm wavelength laser.³⁸ A microwave radiometer (MWR) was used to observe the atmospheric attenuation and brightness temperature based on electromagnetic radiation emitted from the atmosphere using 14 channels (seven channels between 22 and 31 GHz for water vapor, seven channels between 51 and 58 GHz for temperature).³⁹ This instrument measures two types of temperature profiles: zenith scanning for the entire troposphere (0–10 km) and elevation scanning for the boundary layer (0–2 km). The atmospheric boundary-layer height was estimated with the Integrated System for Atmospheric Boundary Layer height Estimation (ISABLE) algorithm using the vertical profile of the backscatter coefficient obtained from a ceilometer and the vertical temperature profile obtained by a MWR.⁴⁰

2.2. Model simulations

This study employed an open-source box model (For 0-D Atmospheric Modelling, FOAM) to conduct a sensitivity test of O_3 precursors in response to temperature changes using measurement data. The FOAM, developed by Wolfe *et al.* (2016), is suitable for modeling changes in atmospheric pollutants under biogenic influence.⁴¹ By applying the Master Chemical Mechanism (MCMv3.3.1), the FOAM model effectively estimates the variation in O_3 levels in response to changes in temperature and concentrations of precursor gases such as NO_x and VOCs.

To facilitate the calculations, the OH reactivity of all VOCs (Table S1) was assessed and the top 10 VOCs were selected (Table S2), which accounted for 70% of the total OH reactivity. In the model simulations, the average diurnal O_3 variation profile was calculated using the measurement data, and the modeled value was optimized using a daily maximum O_3 concentration as the criterion. Since *m,p*-xylene could not be distinguished, it was treated as *m*-xylene in the simulation. Following the model optimization process, the bias of the results was under 1.1 ppbv, with the uncertainty attributed to *m,p*-xylene being estimated at approximately 0.4 ppbv.

For testing the changes in temperature, NO_x , and VOCs to the daily maximum O_3 concentration, we controlled each parameter following under conditions.

M_T : other parameters in the model were fixed and only the temperature was changed. Two SSPs were used (SSP1 and SSP5), conditions in which the temperature increased every hour following the SSP results (SSP1: +2.6 °C and SSP5: +7.0 °C) of

previous studies.^{2,3} The M_A – M_S scenario was simulated based on these temperature change condition.

M_A : increasing the VOCs (excluding isoprene) from anthropogenic sources (“AVOCs”). Incremental ratio of AVOCs is set to 1.3% $^\circ\text{C}^{-1}$,⁴² considering the emission characteristics in this region that vehicle sources are dominant.⁴³

M_B : isoprene (C_5H_8) was selected as a representative VOC from biogenic sources (“BVOC”). Its increase ratio was calculated using the temperature response factor (Table S6), which is discussed elsewhere.^{44,45}

M_N : the temperature dependency of NO_x is not well understood; therefore, NO_x was considered to have originated from anthropogenic vehicle emissions, and the increase ratio was set to 1.3% $^\circ\text{C}^{-1}$ (*i.e.*, the same as that used for AVOCs).^{27,46}

M_S : all variables (AVOCs, isoprene, and NO_x) were changed.

Additionally, the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem) v3.9.1 was used to simulate the variation in O_3 and VOC concentrations during both heatwave and non-heatwave periods. The WRF-Chem (version 3.9.1) model^{47,48} was used to simulate O_3 and other atmospheric pollutants, including $\text{PM}_{2.5}$, SO_2 , and NO_2 , during both heatwave and non-heatwave periods. The model domain encompassed Northeast Asia (105–145° E, 25–50° N) and was configured with a grid spacing of 27 km and 28 vertical layers extending from the surface to 50 hPa. Meteorological initial and boundary conditions were sourced from the National Center for Environmental Prediction Final (NCEP/FNL) Operational Global Analysis data,⁴⁹ which have a horizontal resolution of 1° \times 1°. The Regional Atmospheric Chemistry Mechanism (RACM)⁵⁰ was used for the gas-phase chemical scheme and the Modal Aerosol Dynamics Model for Europe/Volatility Basis Set (MADE/VBS)⁵¹ for the aerosol scheme. Biogenic emissions were derived from the Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2.04,⁴⁵ while anthropogenic emissions were obtained from the KORUSv5 emission inventory, which was developed by a joint research group from Konkuk University and the National Institute of Environmental Research for the 2016 KOREA-United States Air Quality (KORUS-AQ) field campaign.⁵² The physical and chemical model options used in this study are summarized in Table S3.

2.3. O_3 -climate penalty and CPF_{O_3}

Multiannual observation studies have found that O_3 levels increase with rising temperature. While the sensitivity of O_3 to temperature change is consistent in long-term observations, variability has been reported in short-term measurements.^{26,53,54} The relationship between O_3 and temperature change is often expressed using linear regression or quadratic equations to capture changing dynamics. Based on the quadratic regression curve relating O_3 and temperature ($[\text{O}_3]_{\text{max}} = b_0 + b_1[T]_{\text{max}} + b_2[T]_{\text{max}}^2$), the CPF_{O_3} can be defined by the slope of the quadratic curve ($2b_2$), and the O_3 -temperature dependency ($\frac{d[\text{O}_3]_{\text{max}}}{d[T]_{\text{max}}}$) can be calculated using the following equation (eqn (1)):

$$\frac{d[\text{O}_3]_{\text{max}}}{d[T]_{\text{max}}} = 2b_2[T]_{\text{max}} + b_1 \quad (1)$$



However, accurately estimating the O₃ variation caused by increasing temperature is challenging due to multiple influencing factors, including physicochemical changes and anthropogenic–biogenic emissions related to temperature increase. The response of O₃ to temperature can be assessed through (i) direct methods that examine the relationship between the observed O₃ concentration and temperature, and (ii) indirect methods that analyze how temperature impacts various O₃-influencing factors.^{55–57} Definitions of the O₃-climate penalty vary across studies, with some using the slope of O₃ concentration *versus* temperature¹⁶ and others deriving it from the results of chemical transport models related to increases in anthropogenic emissions.¹⁵ Rasmussen *et al.* (2013) proposed the following equation (eqn (2)) to express the indirect relationship between O₃ concentration and temperature:

$$\begin{aligned} \frac{d[\text{O}_3]}{dT} &= \frac{d[\text{O}_3]}{d(\text{Phy})} \times \frac{d(\text{Phy})}{dT} + \frac{d[\text{O}_3]}{d(\text{Chem})} \times \frac{d(\text{Chem})}{dT} + \frac{d[\text{O}_3]}{d(\text{Emi})} \\ &\quad \times \frac{d(\text{Emi})}{dT} + \dots \\ &= \left. \frac{d[\text{O}_3]}{dT} \right|_{\text{Phy}} + \left. \frac{d[\text{O}_3]}{dT} \right|_{\text{Chem}} + \left. \frac{d[\text{O}_3]}{dT} \right|_{\text{Emi}} + \dots \end{aligned} \quad (2)$$

where $d(\text{Phy})$ represents the change in physical processes (*e.g.*, stagnation or transport of air masses), $d(\text{Chem})$ refers to the changes in chemical parameters affected by temperature (*e.g.*, reaction rate constants), and $d(\text{Emi})$ indicates the variation in precursor emissions with rising temperature.²⁰ Other factors influencing the O₃–temperature relationship, such as relative humidity, have a negligible impact in urban areas.^{20,58} The terms $\left. \frac{d[\text{O}_3]}{dT} \right|_{\text{Phy}}$, $\left. \frac{d[\text{O}_3]}{dT} \right|_{\text{Chem}}$, and $\left. \frac{d[\text{O}_3]}{dT} \right|_{\text{Emi}}$ were estimated by considering the change in atmospheric chemical conditions and synoptic meteorology, allowing the sensitivity of O₃ to temperature changes during heatwaves in a megacity to be determined.

3. Results and discussions

3.1. Estimation of the O₃-climate penalty factor

During the measurement period, there were 29 days of heatwaves according to the South Korean criteria, which defines a heatwave as a daily maximum temperature exceeding 33 °C. During this time, an extremely high temperature of 38.9 °C was recorded under blocking conditions over the Korean Peninsula (Fig. S2).^{30–32} On eight days during this high-temperature period, high-O₃ episodes occurred which exceeded the national ambient air quality standard (hourly average O₃ concentration of >100 ppbv). Throughout the heatwave period, the average O₃ concentration was 36.6 ppbv, with a daily maximum of up to 169.4 ppbv. Additionally, the average and daily maximum O₃ levels were higher than in the non-heatwave period by approximately 9 and 54 ppbv, respectively. Ozone levels consistently increased with rising temperatures throughout the measurement period, with the most significant increase observed during the heatwave period, as is clear from the daily maximum values (Fig. 2).

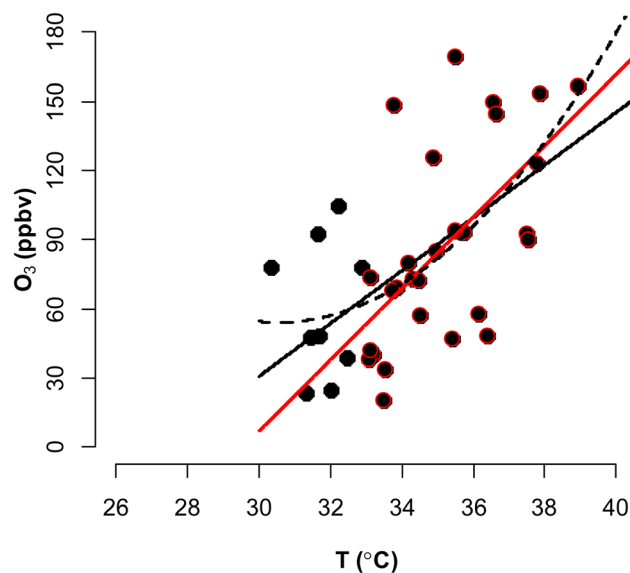


Fig. 2 The relationship between daily maximum O₃ and temperature (black solid circle). The “heatwave periods” (daily maximum temperature > 33 °C) are colored in red. Solid lines and dashed curve represent the linear (entire period (black solid line): $p < 0.05$, heatwave period (red solid line): $p < 0.05$) and quadratic regression (entire period (black dashed line): $p < 0.05$), respectively.

The O₃-climate penalty factor (CPF_{O₃}) was calculated based on the linear relationship (CPF_{O₃-L}) between the daily maximum O₃ concentration and the daily maximum temperature. The value was 11.5 ppbv °C⁻¹ for the entire measurement period and 15.5 ppbv °C⁻¹ during the heatwave (Table 1). The inclusion of extreme heatwave cases resulted in a higher CPF_{O₃-L} for the entire measurement period compared to previous studies (~3 ppbv °C⁻¹).^{16,17,19,23} Further the maximum daily 8 h average (MDA8) O₃ based CPF_{O₃-L} also shows high value (8.1 ppbv °C⁻¹) during the whole periods, and it indicates that increase in O₃ concentration during the heatwave period may be appeared with the increase of temperature.

The acceleration of the O₃ increase at higher temperatures also can be attributed to the quadratic relationship between O₃ concentration and temperature. By applying a quadratic regression curve to the relationship between the daily maximum O₃ level and the daily maximum temperature, the coefficient of the quadratic function was calculated to represent the slope at each temperature point (eqn (1)). The derivative of CPF_{O₃-Q} provides the CPF_{O₃-L} as a function of temperature. Based on the measurement data, the following values were obtained: $b_0 = 1371.1$; $b_1 = -86.2$; $b_2 = 1.4$. Thus, the O₃-temperature dependency of the quadratic curve can be expressed by the following equation (eqn (3)):

$$\left. \frac{d[\text{O}_3]}{dT} \right|_{\text{QR}} = 2.8 \times T_{\text{max}} - 86.2 \quad (3)$$

The calculated coefficient of CPF_{O₃-Q} (2.8) exceeded the upper boundary of the CPF_{O₃-Q} range observed in previous studies (0.1–1.3).^{26,27}



Table 1 The climate penalty factor of O₃ (CPF_{O₃}) estimated from linear regression ([O₃] = b₀ + b₁[T]) and quadratic regression ([O₃] = b₀ + b₁[T] + b₂[T]²) using the daily maximum O₃ and daily maximum temperature

Period	b ₀	b ₁	b ₂	CPF _{O₃}
Heatwave (linear)	-458.0	15.5		15.5
Total (linear)	-313.2	11.5		11.5
Total (quadratic)	1371.1	-86.2	1.4	2.8T - 86.2

The CPF_{O₃,Q}, obtained through quadratic regression, varied widely from 1 to 23 ppbv °C⁻¹ above the observed inflection temperatures of over 30 °C (Tables S4 and S5). Interestingly, in previous studies in Seoul, temperatures exceeding 30 °C were identified as a prerequisite for elevated O₃ concentrations exceeding national air quality standards.^{59,60} The CPF_{O₃,L} for the entire measurement period and the heatwave period aligned with the CPF_{O₃,Q} at temperatures of 35 and 36 °C, respectively. At the highest daily maximum temperature of 38.9 °C, the CPF_{O₃} was 22.8 ppbv °C⁻¹. These results highlight an accelerated O₃ increase during a heatwave in a megacity, which is appropriately represented by different values of O₃-temperature dependency at each temperature. This raises the following question: Why does the CPF_{O₃} be different with temperature?

The increase in O₃ resulting from a temperature increase can be elucidated through the discrete mechanisms governing O₃ enhancement. The CPF_{O₃} is attributed to variations in chemical reactions leading to O₃ production, emissions linked to biological activities or evaporation, and physical processes such as advection, diffusion, and vertical mixing, as represented by $\frac{d[O_3]}{dT}|_{Chem}$, $\frac{d[O_3]}{dT}|_{Emi}$, and $\frac{d[O_3]}{dT}|_{Phy}$, respectively.²⁰

The chemical term $\left(\frac{d[O_3]}{dT}\right)|_{Chem}$ and emission term $\left(\frac{d[O_3]}{dT}\right)|_{Emi}$ were initially computed together. Using the FOAM model, the change in O₃ levels in response to temperature and emission variations was simulated based on the several cases (M_T-M_S) described in Section 2.2. Using the measurement data and FOAM, the CPF_{O₃} attributable to chemistry and emissions was approximately 1.7-1.8 ppbv °C⁻¹ (Fig. 3 and Table S7). When considering the uncertainties of temperature dependent emission factors from various VOCs emission sources that can be increased up to 6.7% °C⁻¹, it makes the variation in simulated $\frac{d[O_3]}{dT}|_{Chem} + \frac{d[O_3]}{dT}|_{Emi}$ value as 0.2 ppbv °C⁻¹ (Table S7).⁶¹ This upper bound of $\frac{d[O_3]}{dT}|_{Chem} + \frac{d[O_3]}{dT}|_{Emi}$ (~2 ppbv °C⁻¹) is near to the previous studies on the CPF_{O₃,L} (~3 ppbv °C⁻¹);²¹ however, it is lower than the CPF_{O₃,L} for the whole measurement period.

The physical term $\left(\frac{d[O_3]}{dT}\right)|_{Phy}$ of eqn (2) primarily pertains to dynamic processes such as reinforced or decelerated long-range O₃ transport caused by the temperature increase, and consequently influenced surface O₃ levels. The transport of O₃

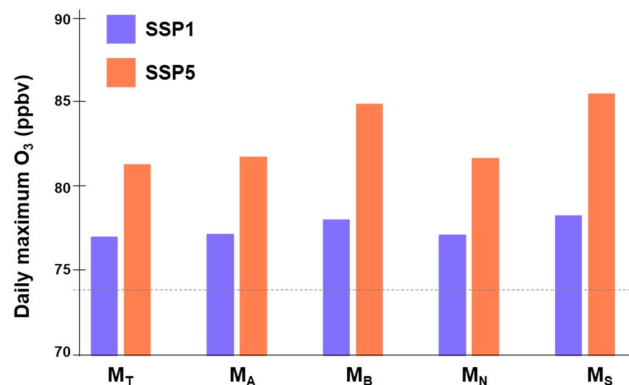


Fig. 3 Calculated daily maximum O₃ concentration during July to August. The gray dashed line indicates the modeled daily maximum O₃ concentration at the observed temperature (ΔT = 0). Detail conditions of each 'M' scenario are described in Table S7.

and stagnant weather conditions facilitate the formation and accumulation of O₃.^{62,63}

In this study, during the prolonged heatwave, blocking conditions played a crucial role in occurrence of heatwave over the Korean Peninsula. In Seoul, blocking conditions are commonly associated with synoptic atmospheric circulation, resulting in persistent anticyclonic or stagnant conditions.³⁰ This scenario was observed during the KOREA-US Air Quality (KORUS-AQ) campaign accompanied by a significant elevation of O₃.⁶⁴ Similar to this previous study, in the present study, surface O₃ concentrations were significantly elevated under stagnant atmospheric conditions during heatwave periods in urban areas.

The boundary layer typically expands greatly under a persistent high-pressure system due to radiative heating. The daily evolution of this layer is thought to promote the photochemical production of O₃ through vertical turbulent mixing with the low NO_x concentration in the upper atmosphere above urban areas and also affects the surface O₃.⁶⁵⁻⁶⁷ During the measurement period, the boundary layer height (BLH) expanded by 1500 m during the daytime, reaching its maximum between 14:00 and 17:00 local standard time (LST) before collapsing to nearly 500 m at nighttime, with its minimum occurring between 00:00 and 05:00 LST. Similarly, the maximum O₃ was observed when BLH was maximum and the minimum was observed when BLH was minimum. While BLH generally increased with temperature, the ratio of the daily range of BLH to that of temperature (ΔBLH/ΔT) remained relatively consistent during both the heatwave and non-heatwave periods (Fig. S5). In comparison, the ratio of the daily range of O₃ to that of BLH (ΔO₃/ΔBLH) was greater during heatwave periods than non-heatwave periods. As a result, the rate of change of O₃ with increasing temperature $\left(= \frac{d[O_3]}{dT}\right)|_{Phy}$ was calculated to be 21.8% higher during the heatwave (10.6 ppbv °C⁻¹) than the non-heatwave period (8.7 ppbv °C⁻¹) (Table 2). Notably, both values of $\frac{d[O_3]}{dT}|_{Phy}$ were significantly larger than those estimated for emissions and chemical processes (<2 ppbv °C⁻¹). For the heatwave period, the



Table 2 Temperature dependency of boundary layer height (BLH) and the change of O₃ by a variation in BLH. All values were determined by the linear regression slope

	$\frac{dO_3}{dBLH} (= a) (\times 10^{-2} \text{ ppbv m}^{-1})$	$\frac{dBLH}{dT} (= b) (\times 10^2 \text{ m } ^\circ\text{C}^{-1})$	$\frac{dO_3}{dT} (= a \times b) (\text{ppbv } ^\circ\text{C}^{-1})$
Non-heatwave	4.5	1.9	8.7
Heatwave	5.2	2.1	10.6

discretization based on various measurement data resulted in a $CPF_{O_3} \left(= \frac{d[O_3]}{dT} \Big|_{\text{Phy}} + \frac{d[O_3]}{dT} \Big|_{\text{Chem}} + \frac{d[O_3]}{dT} \Big|_{\text{Emi}} \right)$ of 12.3–12.4 ppbv °C⁻¹, which is similar to the $CPF_{O_3,L}$ in heatwave periods of 15.5 ppbv °C⁻¹. During the heatwave, $\frac{d[O_3]}{dT} \Big|_{\text{Phy}}$ was about five times higher than $\left(\frac{d[O_3]}{dT} \Big|_{\text{Chem}} + \frac{d[O_3]}{dT} \Big|_{\text{Emi}} \right)$, indicating that physical processes were the primary drivers of the accelerated O₃ enhancement during the heatwave.

3.2. Vertical mixing as a physical driver of accelerated surface O₃ enhancement

In NO_x-saturated regions, model calculations demonstrate that surface O₃ is titrated by NO_x in the early morning and accumulates in the afternoon.⁶⁸ Recent studies conducted in tall towers have demonstrated that free convection and vertical mixing facilitate efficient O₃ formation, leading to elevated O₃ and PAN concentrations at higher altitudes.^{69,70} This is consistent with our results that, in discretization methods, physical processes exert the most significant influence on CPF_{O_3} .

The degree of atmospheric vertical mixing within the boundary layer can be expressed by the turbulent diffusion coefficient (k_z),⁷¹ which is calculated using the following equations for $z < L$ (eqn (4)):⁷²

$$k_z(z) = k_z(L) + \left(\frac{L-z}{L-L_0} \right)^2 \times \left[k_z(L_0) - k_z(L) + (z-L_0) \left(\frac{k_z(L_0)}{L_0} + 2 \frac{k_z(L_0) - k_z(L)}{L-L_0} \right) \right] \quad (4)$$

where $k_z(L)$ is the turbulent diffusivity above the boundary layer ($=1.0 \text{ cm}^2 \text{ s}^{-1}$), z is the height, L is the height of the boundary layer, L_0 is the height of the surface layer ($\sim 0.1L$), and $k_z(L_0)$ is the turbulent diffusivity at the top of the surface layer (Text S1). Here, k_z is presented with the measured BLH for the heatwave and non-heatwave periods (Fig. 4). k_z exhibited higher values during the heatwave, coinciding with the earlier development and greater expansion of the boundary layer compared to the non-heatwave period. These trends in k_z and BLH were mirrored in the diurnal variations of O₃ for the two cases shown in Fig. S6.

Similar to the variation of k_z , the diurnal variation of O₃ simulated using the WRF-Chem model also showed large differences between the heatwave and non-heatwave periods (Fig. 5). The diurnal evolution of O₃ was strongly correlated with changes in BLH, with O₃ levels remaining low (below 10 ppbv) under a stable boundary layer until early morning and then rapidly increasing with the rise in BLH. The two cases exhibited sharply contrast in change of O₃, that the morning upward and afternoon downward gradient in O₃ concentration was more pronounced during the heatwave. These highlight the influence of physical terms in the CPF_{O_3} equation, which were estimated from the measurements of reactive gases including O₃, nitrogen oxide species, and VOCs, and BLH based on discretization methods.

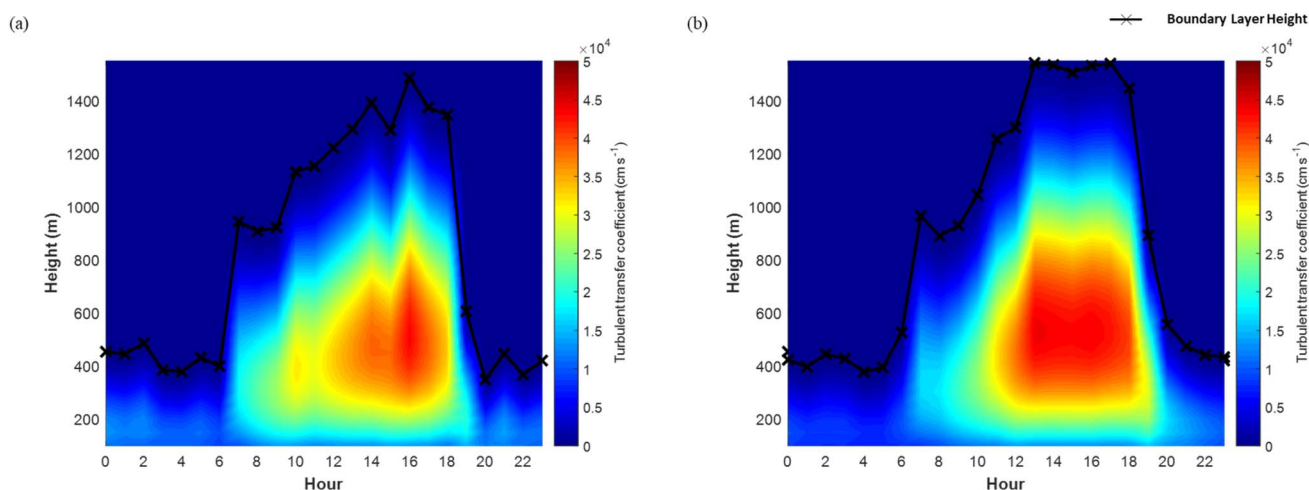


Fig. 4 Turbulent transfer coefficient (k_z) based on the wind speed at the top of surface layer during (a) non-heatwave period and (b) heatwave period.



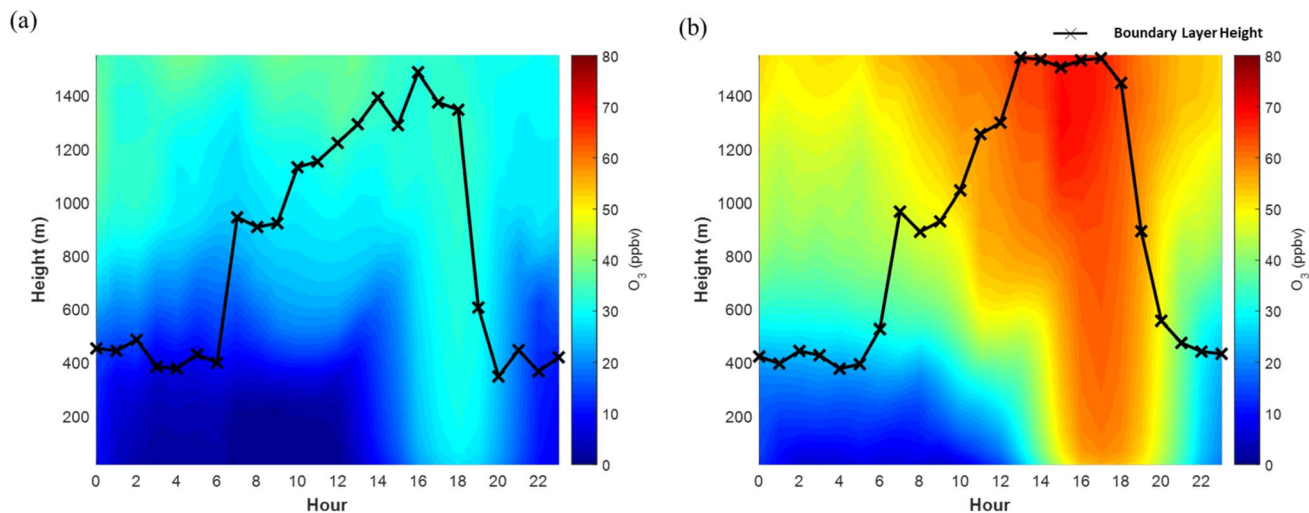


Fig. 5 Diurnal-vertical variations in O_3 concentrations during the (a) non-heatwave and (b) heatwave periods in Seoul simulated by WRF-Chem v3.9.1.

3.3. Ozone production efficiency

In a megacity such as Seoul, NO_2 levels typically reach their minimum in the afternoon, coinciding with the O_3 peak.⁶⁴ However, it was not observed in this study. Instead, NO_2 concentration remained high in the afternoon, especially when

the boundary layer was most expanded (Fig. 6(a) and (b)), indicating a rapid chemical cycling of nitrogen oxides. Based on the O_3 production ($=P(O_3)$) and loss of NO_x ($=L(NO_x)$) chemistry, the ozone production efficiency (OPE) was obtained using

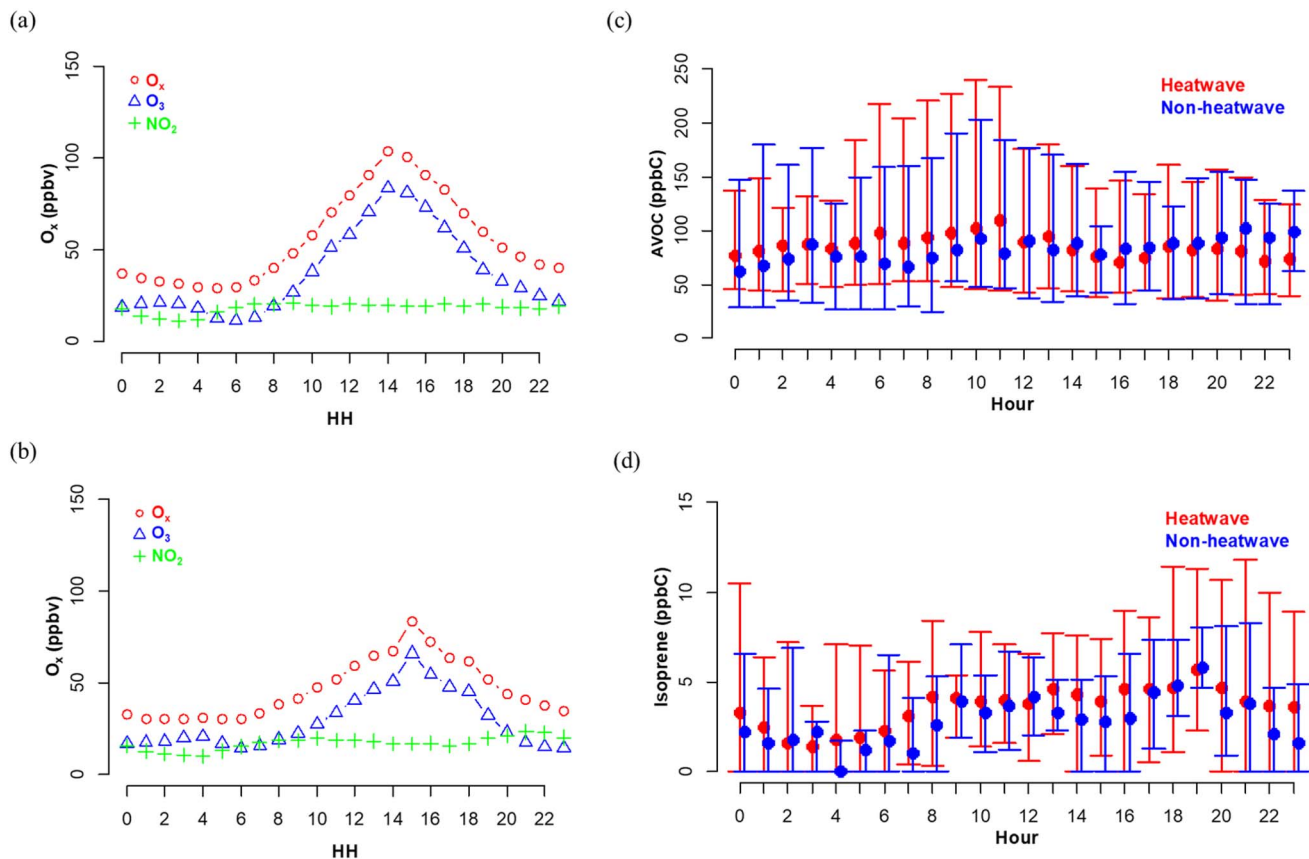


Fig. 6 (Left panels) Diurnal variation of O_x , O_3 , and NO_2 during the (a) heatwave period and (b) non-heatwave period, respectively. (Right panels) Diurnal variation of (c) AVOCs and (d) isoprene during the heatwave and non-heatwave period, respectively. Each symbol and solid bar imply averaged values and their standard deviations.



the level of O_x ($=O_3 + NO_2$) and NO_z , where $[NO_2] + [NO_z] \ll [O_3]$ ^{73,74} (eqn (5)–(7)).

$$P(O_3) = k_{HO_2+NO}[HO_2][NO] + \sum_i k_{RO_2,i+NO}[RO_{2,i}][NO] \approx [O_x] \quad (5)$$

$$L(NO_x) = k_{OH+NO_2}[OH][NO_2] + \sum_i k_{RO_2,i+NO}[RO_{2,i}][NO] + \sum_i k_{RCO_3,i+NO_2}[RCO_{3,i}][NO_2] - \sum_i k_{RCO_3NO_2,i}[RCO_3NO_{2,i}] \approx [NO_z] \quad (6)$$

$$OPE = \frac{P(O_3)}{L(NO_x)} \approx \frac{[O_x]}{[NO_z]} \quad (7)$$

Using measurements of the nitrogen oxide species HONO, PAN, and HNO_3 , the OPE, represented by the ratio of O_x ($O_3 + NO_2$) to NO_z ($=PAN + HONO + HNO_3$), was compared between the heatwave and non-heatwave periods. The OPE during the heatwave was 18.9, while it was 16.4 during the non-heatwave period (Fig. 7), with both values being higher than the range of 3–8 reported in previous studies that heatwave had not been occurred.^{73,74} Hence, the OPE likely played a pivotal role in enhancing O_3 levels in the summer heatwave periods.^{24,67}

The formation of O_3 was found to be sensitive to the concentrations of VOCs under NO_x -saturated conditions. During the heatwave, anthropogenic VOCs (AVOC) and isoprene mixing ratios were larger than in the non-heatwave period, correlated with an increase in daytime temperature (Fig. 6(c) and (d)). Particularly, in the morning, AVOC concentrations were consistently elevated during the heatwave period compared to the non-heatwave period ($2.7\% \text{ } ^\circ\text{C}^{-1}$), surpassing the typical temperature dependency of VOCs observed in previous studies ($1.3\% \text{ } ^\circ\text{C}^{-1}$).⁴² This observation aligns with

VOC patterns previously observed in Seoul, highlighting the fugitive emissions of AVOCs at elevated temperatures.⁴³

During the heatwave, the mean isoprene concentration increased by approximately four times ($10.3\% \text{ } ^\circ\text{C}^{-1}$), more than the increase in AVOCs. However, isoprene emissions are constrained at temperatures above the threshold of plant growth.⁷⁵ On the other hand, AVOCs from fugitive emissions are likely to continue to increase with temperature. But these increase in VOCs only can contribute to the 4–5 ppbv $^\circ\text{C}^{-1}$ of CPF_{O_3} , and it is hard to fully explain the increase of CPF_{O_3} during the heatwave period through only the increase in VOC concentration. Consequently, the heightened OPE, together with a change of boundary-layer related processes and increased VOC levels, was found to be a crucial physical factor in the significantly elevated O_3 concentrations during the heatwave. The results show that prolonged heatwaves likely promote deep vertical mixing, thereby increasing O_3 production by enhanced OPE due to increased fugitive emissions of VOCs. These findings underscore the importance of focusing on AVOCs to mitigate the accelerated O_3 increase in urban areas during heatwaves.

4. Conclusions

This study revealed a significant O_3 -climate penalty in urban Seoul during short-term heatwave periods in summer 2018, surpassing the values reported in previous long-term observations, with the rate of change of the penalty (penalty factor) increasing with temperature. Measurements and model simulations underscored the significance of dynamic boundary-layer processes as a key pathway for O_3 enhancement. However, the effect of the intricate interplay between dynamic processes and chemical reactions on change of O_3 -climate penalty factor remains incompletely understood.

These findings suggest that the increasing frequency of heatwaves due to global warming could lead to rapid O_3 increases in megacities, characterized by high levels of NO_x and VOCs due to vehicle emissions. Efficient O_3 production during heatwaves, facilitated by vertical mixing and fueled by increased fugitive emissions of VOCs, emphasizes the need to reduce AVOCs in megacity and its surrounding areas to mitigate the accelerating increase in O_3 observed during heatwaves. These dynamic processes combined with the change of chemical change can lead to the non-linear increase of O_3 climate penalty not only in the megacity, but further expanded to the metropolitan region especially during the warm season, which was reported as a critical problem in global ozone pollution.⁷⁶ Therefore, this study establishes a framework for analyzing O_3 enhancement mechanisms and estimating CPF_{O_3} during future heatwaves, providing insights for effective pollutant reduction policies under climate change.

Author contributions

JG and ML conceptualize and design this research. JG, MP, SK, and HR contributed to the data collection. JG, CK, JK, and HL conducted the modelling and contributed to the analysis. All authors contributed to the interpretation of the results and manuscript writing.

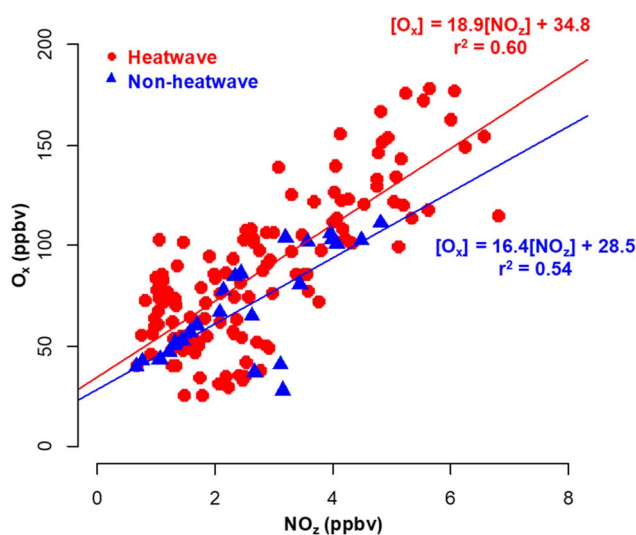


Fig. 7 The ozone production efficiency (OPE) as the ratio of O_x to NO_z during the midday (10–17 LST) for heatwave (red) and non-heatwave (blue) periods.



Conflicts of interest

The authors declare no competing interests.

Data availability

Data for this article, including the observation data, are available at the repository (<https://zenodo.org/records/11045153>).⁷⁷

Supplementary information (SI) is available. See DOI: <https://doi.org/10.1039/d5em00629e>.

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