Supporting Information for

Accelerated O_3 formation triggered by summer heatwaves in megacity Seoul

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Supplementary Text

Text S1. Turbulent Diffusion Coefficient (Kz)

The turbulent diffusion coefficient (K_z) was calculated as follows:

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

(Eq.S1)

where z < L (Pielke and Mahrer, 1975; Cao et al., 2016; Herrmann et al., 2019), $k_z(L)$ is turbulent diffusivity above the boundary layer (= 1.0 cm^2 s^{-1}), z is the height, L is the boundary-layer height, L_0 is the surface layer height (~ 0.1L), and $k_z(L_0)$ is the turbulent diffusivity at the top of the surface layer. The term $k_z(L_0)$ can be calculated using the equation $k_z(L_0) = \kappa u^* L_0$, where $u^* = \frac{\kappa W}{ln(L_0/Z_0)}$. The term κ is the von Kármán coefficient (=0.41), u^* is the friction velocity, W is the wind speed in the surface layer, and Z_0 is the surface roughness length (= 0.8 m in urban regions).

Supplementary Figures and Tables

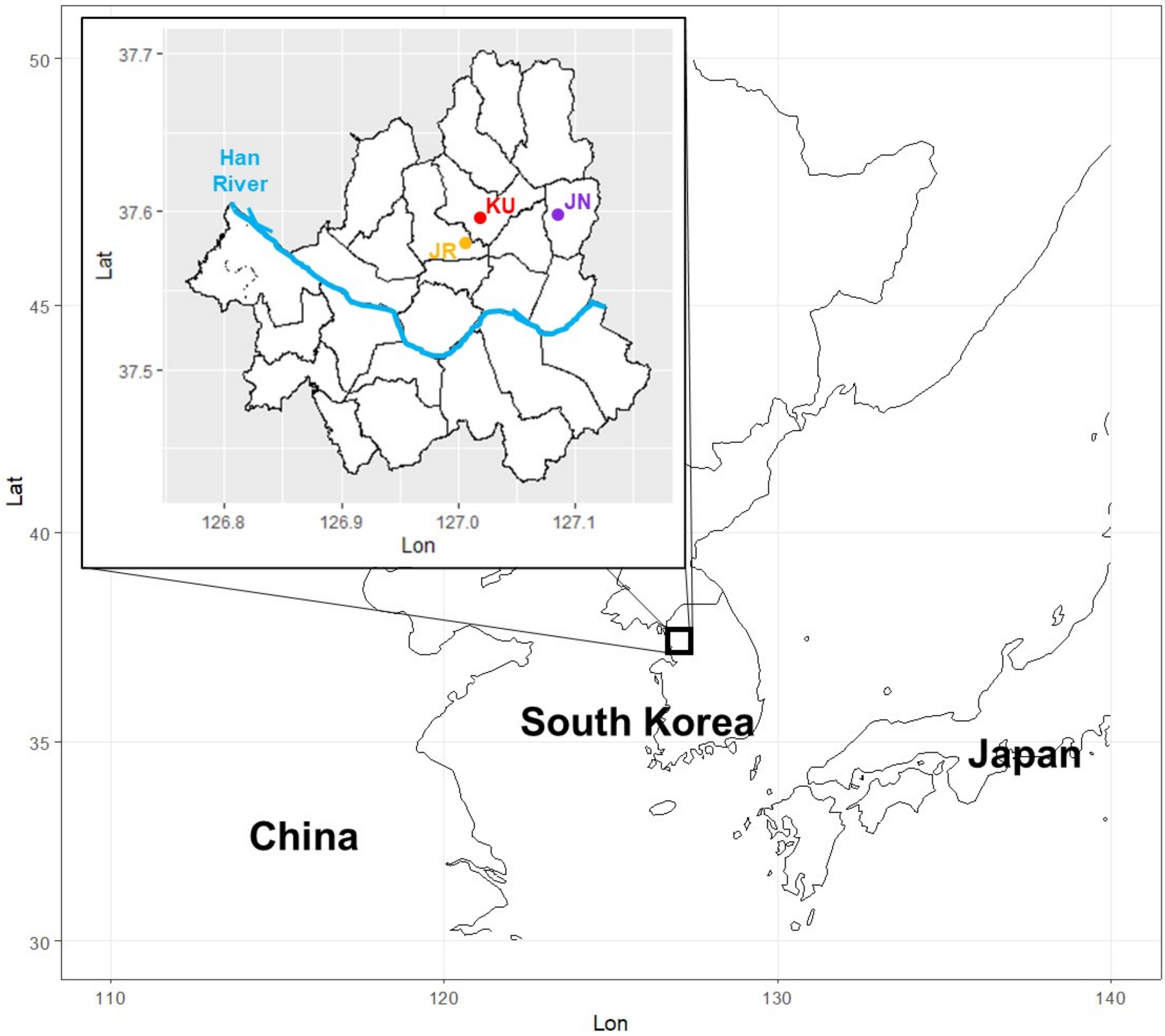

Figure S1 The measurement sites in South Korea.

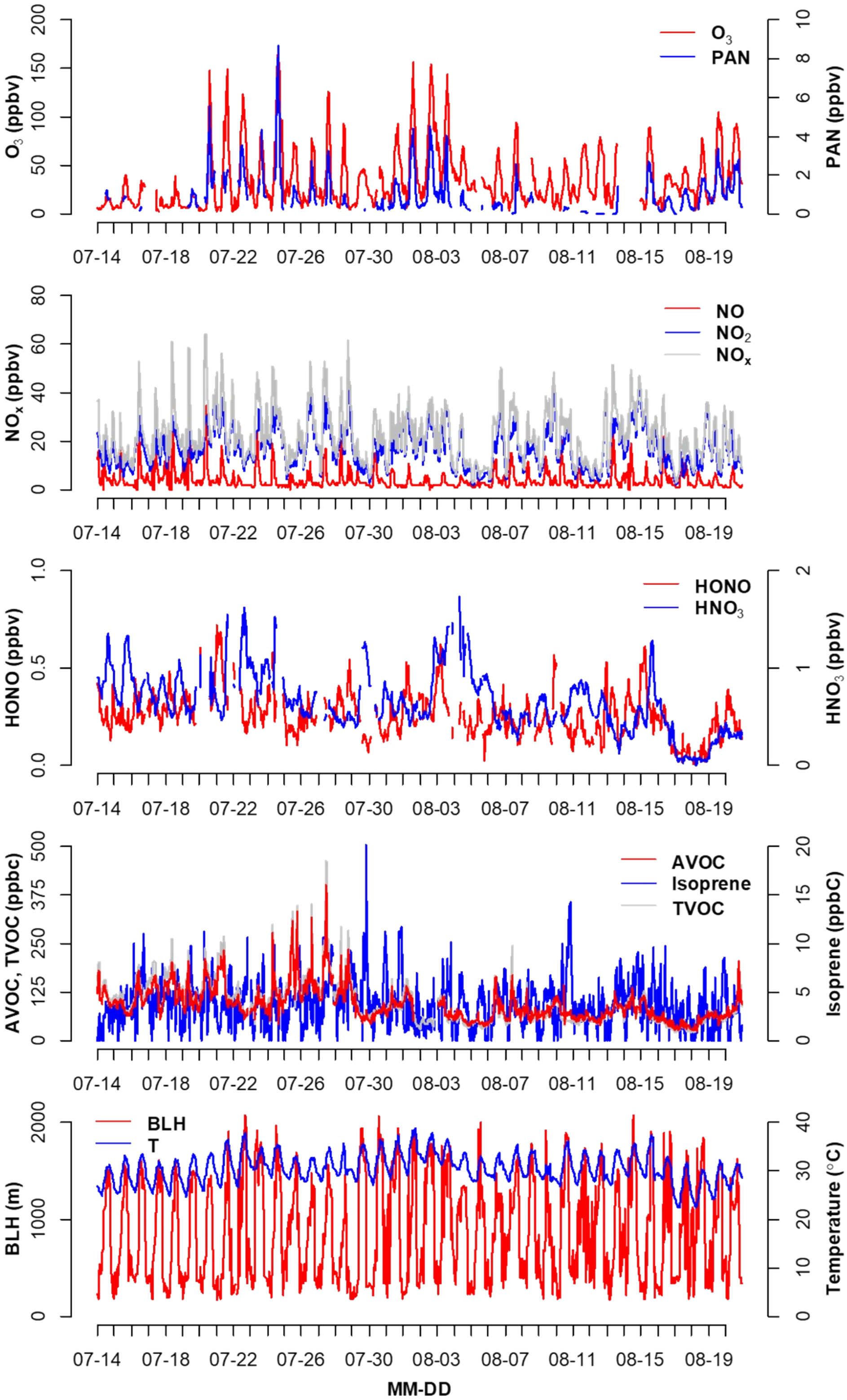

Figure S2 The variation of the measured variables (O_3, NO_x, PAN, HONO, HNO_3, VOCs, Boundary Layer Height (BLH), and Temperature) during summer (Jul–Aug) 2018.

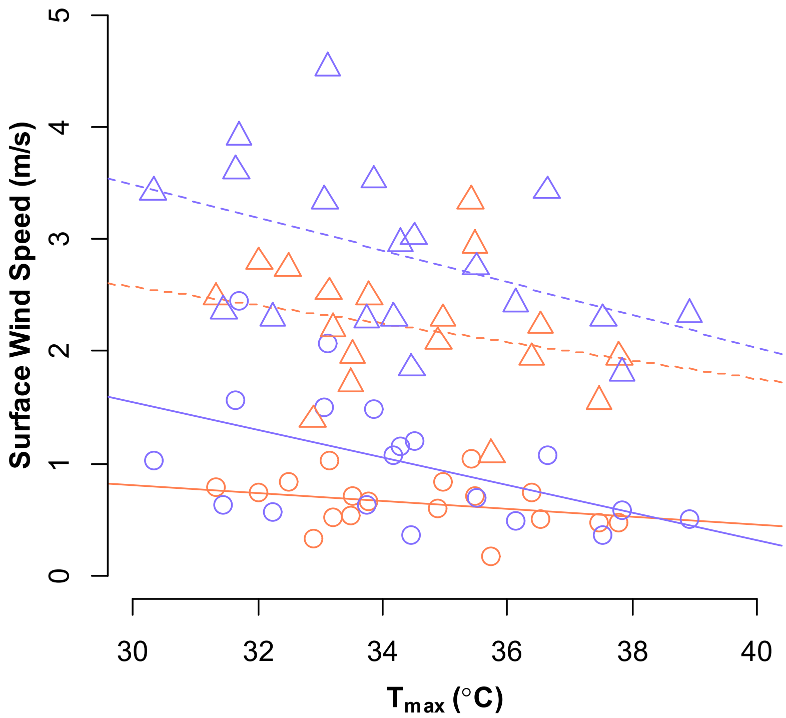

Figure S3 The correlation between the daily maximum temperature and the daily average wind speed (circles) and daily maximum wind speed (triangles). The dashed lines indicate the monthly mean values based on the statistical minimum and maximum values (mean ± 1.5 Inter Quartile Range).

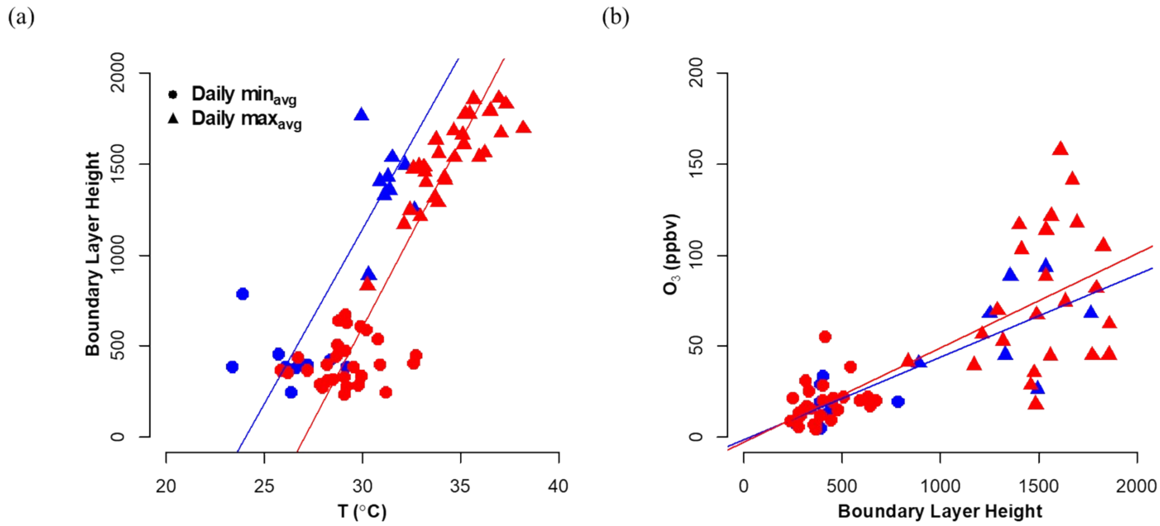

Figure S4 (a) The temperature dependency of the boundary-layer height and (b) the variation of O_3 concentration with mixing-layer height. Red symbols indicate the heatwave period and blue symbols the non-heatwave period.

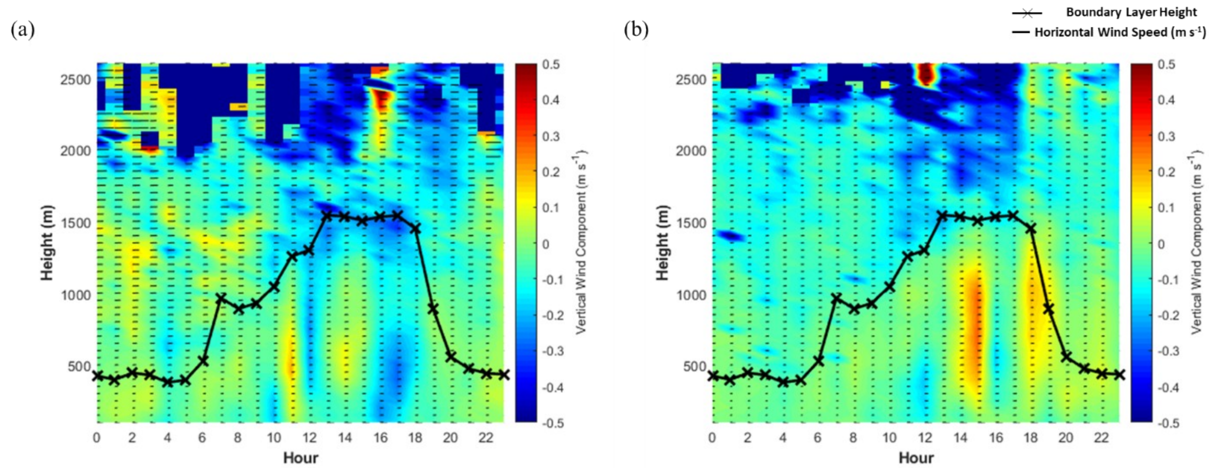

Figure S5 The diurnal variation of the vertical wind component and boundary-layer height during (a) the non-heatwave period and (b) the heatwave period. The colors indicate the vertical wind component (*w*) and the black line represents the horizontal wind velocity. The maximum horizontal wind speed expressed in this figure is clipped at 10 ms^{-1}, that is, numbers larger than this value are assigned a value of 10 ms^{-1}.

Table S1 The average mixing ratio and OH reactivity (OHR) of 55 volatile organic compounds (VOCs).

	Mixing ratio (ppbv)	**k_{OH} (× 10^{12})**	**OHR (s^{-1})**	**Reference**
Alkanes				
Ethane	7.048	0.25	0.043	a
Propane	6.599	1.09	0.177	a
i-Butane	1.796	2.34	0.104	a
n-Butane	3.071	2.36	0.179	a
Cyclopentane	0.296	4.97	0.036	a
i-Pentane	1.897	3.90	0.182	a
n-Pentane	1.013	3.80	0.095	a
2,2-Dimethylbutane	0.220	2.23	0.012	a
2,3-Dimethylbutane	0.191	5.78	0.027	a
2-Methylpentane	0.465	5.20	0.060	a
3-Methylpentane	0.289	5.20	0.037	a
n-Hexane	0.992	5.20	0.127	a
Methylcyclopentane	0.458	7.04	0.080	b
2,4-Dimethylpentane	0.073	4.77	0.009	a
Cyclohexane	0.261	6.97	0.045	a
2-Methylhexane	0.178	–	–	
2,3-Dimethylpentane	0.277	–	–	
3-Methylhexane	0.225	–	–	
2,2,4-Trimethylpentane	0.187	3.34	0.015	a
n-Heptane	0.221	6.76	0.037	a
Methylcyclohexane	0.169	9.64	0.040	a
2,3,4-Trimethylpentane	0.088	6.60	0.014	a
2-Methylheptane	0.076	–	–	
3-Methylheptane	0.091	–	–	
n-Octane	0.151	8.11	0.030	a
n-Nonane	0.164	9.70	0.039	a

n-Decane	0.299	11.00	0.081	a
n-Undecane	0.228	12.30	0.069	a
Alkenes				
Ethylene	3.411	8.52	0.716	a
Propylene	1.333	26.30	0.864	a
trans-2-Butene	0.274	64.00	0.432	a
1-Butene	0.456	31.40	0.352	a
cis-2-Butene	0.756	56.40	1.050	a
trans-2-Pentene	0.332	67.00	0.548	a
1-Pentene	0.263	31.40	0.203	a
cis-2-Pentene	0.256	65.00	0.410	a
Isoprene	0.734	100.00	1.810	a
1-Hexene	0.325	37.00	0.297	a
Alkyne				
Acetylene	1.567	0.82	0.031	a
Aromatic hydrocarbons				
Benzene	0.352	1.22	0.011	a
Toluene	6.006	5.63	0.833	a
Ethylbenzene	1.623	7.00	0.280	a
m,p-Xylene (average)	2.481	18.70	1.143	a
Styrene	0.130	58.00	0.185	a
o-Xylene	1.285	13.60	0.431	a
Isopropylbenzene	0.072	6.30	0.011	a
n-Propylbenzene	0.048	5.80	0.007	a
m-Ethyltoluene	0.159	18.60	0.073	a
p-Ethyltoluene	0.101	11.80	0.029	a
1,3,5-Trimethylbenzene	0.076	56.70	0.106	a
o-Ethyltoluene	0.094	11.90	0.027	a
1,2,4-Trimethylbenzene	0.291	32.50	0.233	a
1,2,3-Trimethylbenzene	0.205	32.70	0.165	a
m-Diethylbenzene	0.060	–	–	

p-Diethylbenzene	0.048	–	–

Table S2 The Top 10 VOCs in terms of OHR and the proportion of the total OHR for all VOCs.

Rank	Species	OHR (s^{-1})	Proportion (%)
1	Isoprene	1.8	15.4
2	m,p-Xylene	1.1	9.7
3	cis-2-Butene	1.1	8.9
4	Propylene	0.9	7.3
5	Toluene	0.8	7.1
6	Ethylene	0.7	6.1
7	trans-2-Pentene	0.5	4.6
8	trans-2-Butene	0.4	3.7
9	o-Xylene	0.4	3.7
10	cis-2-Pentene	0.4	3.5

Table S3 A summary of the physical and chemical options used in the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem) simulations.

Physics & Chemistry option	**Adopted scheme**
Microphysics	Lin et al. (1983) scheme
Longwave Radiation	Rapid Radiative Transfer Model (RRTM)
Shortwave Radiation	Goddard
Surface Layer	Monin-Obukhov similarity
Land Surface	Noah Land Surface Model
Planetary Boundary Layer	Yonsei University scheme (YSU)
Cumulus Parameterizations	Grell 3D
Photolysis	Madronich photolysis (TUV)
Gas Phase Chemistry	NOAA/ESRL Regional Atmospheric Chemistry (RACM)
Aerosols	Modal Approach Dynamics model for Europe/Volatility Basis Set (MADE/VBS)
Anthropogenic Emissions	Korea-United States Air Quality (KORUS) v5
Biogenic Emissions	Model of Emissions of Gases and Aerosols from Nature (MEGAN) v.2.04

Table S4 The daily maximum temperature and daily Climate Penalty Factor (CPF_{O3}) during the heatwave period calculated via the quadratic regression curve.

YYYY-MM-DD	T_{max}	CPF_{O3}
2018-07-15	33.2	6.8
2018-07-16	33.5	7.6
2018-07-19	33.5	7.5
2018-07-20	33.8	8.4
2018-07-21	36.5	16.1
2018-07-22	37.8	19.6
2018-07-23	35.0	11.7
2018-07-24	35.5	13.1
2018-07-25	33.1	6.6
2018-07-27	34.9	11.5
2018-07-28	35.7	13.9
2018-07-29	35.4	12.9
2018-07-30	36.4	15.7
2018-07-31	37.5	18.7
2018-08-01	38.9	22.8
2018-08-02	37.8	19.8
2018-08-03	36.6	16.4
2018-08-04	33.9	8.6
2018-08-05	33.1	6.4
2018-08-06	33.7	8.3
2018-08-07	35.5	13.2
2018-08-08	34.5	10.4
2018-08-10	36.1	15.0
2018-08-11	34.3	9.8
2018-08-12	34.2	9.5
2018-08-13	34.5	10.3

2018-08-14	35.6	13.6
2018-08-15	37.5	18.9
2018-08-16	33.1	6.5
2018-08-22	35.2	12.4
AVG	**35.2**	**12.4**

Table S5 The daily maximum temperature and daily Climate Penalty Factor (CPF_{O3}) during the non-heatwave period calculated via the quadratic regression curve.

YYYY-MM-DD	$\mathbf{T_{max}}$	$\mathbf{CPF_{O3}}$
2018-07-14	31.3	1.5
2018-07-17	32.0	3.5
2018-07-18	32.5	4.7
2018-07-26	32.9	5.9
2018-08-09	31.5	1.9
2018-08-17	31.7	2.5
2018-08-18	30.3	-1.3
2018-08-19	32.2	4.0
2018-08-20	31.7	2.4
2018-08-21	30.5	-0.7
AVG	**31.7**	**2.4**

Table S6 The change of the isoprene emission rate using the temperature response factor (γ_T) and the equation $\gamma_T = E_{opt} \times exp(C_{T1} \times x)/(C_{T2} - C_{T1} \times \left(1 - exp(C_{T2} \times x)\right)$, which is controlled by temperature only. In this study, temperature based on August. A detailed explanation of the temperature response factor equation can be found in [1] and [2].

	T_p	**γ_T**	**$d\gamma_T$ (%)**
T_0	300.9	0.91	-
SSP1 (T_0 + 2.6)	303.5	1.26	38.5
SSP5 (T_0 + 7.0)	3070.9	2.15	137.5

Table S7 The photochemical results of the Framework for 0-D Atmospheric Modelling (F0AM) model for the daily maximum O_3 concentration in July and August 2018 under two scenarios (SSP1 and SSP4) with variations of other variables. The term dO_3 is the daily maximum O_3 enhancement from the M_{obs} condition, and dO_3/dT is dO_3 divided by ΔT in each SSP scenario.

	Changed Variable	**$O_{3\ daily\ max}$ (ppbv)**	**dO_3 (ppbv)**	**$\frac{dO_3}{dT}$ (ppbv °C^{-1})**
M_{obs}	-	73.5	-	-
		SSP1 (ΔT = + 2.6 ℃)		
M_T	ΔT	77.0	3.5	1.4
M_A	ΔT + ΔAVOC	77.2	3.7	1.4 (1.6)*
M_B	ΔT + ΔIsoprene	78.0	4.5	1.7
M_N	ΔT + ΔNO_x	77.1	3.6	1.4
M_S	All	78.3	4.8	1.8 (2.0)*
		SSP5 (ΔT = + 7.0 ℃)		
M_T	ΔT	81.3	7.8	1.1
M_A	ΔT + ΔAVOC	81.8	8.3	1.2 (1.4)*
M_B	ΔT + ΔIsoprene	84.9	11.4	1.6
M_N	ΔT + ΔNO_x	81.7	8.2	1.2
M_S	All	85.5	12.0	1.7(1.9)*

*Values from the upper bound of VOC temperature-dependency (6.7%°C^{-1})[3]

Reference

1. L. K. Emmons, S. Walters, P. G. Hess, J.-F. Lamarque, G. G. Pfister, D. Fillmore, C. Granier, A. Guenther, D. Kinnison and T. Laepple, Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4), 2010.
2. A. Guenther, T. Karl, P. Harley, C. Wiedinmyer, P. Palmer and C. Geron, Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), 2006.
3. M. Qin, Y. She, M. Wang, H. Wang, Y. Chang, Z. Tan, J. An, J. Huang, Z. Yuan and J. Lu, Increased urban ozone in heatwaves due to temperature-induced emissions of anthropogenic volatile organic compounds, *Nature Geoscience*, 2025, **18**, 50-56.