



Supplement of

Summertime ozone sensitivity to temperature in China: observational evidence and mechanistic attribution in urban and rural areas in the Yangtze River Delta region

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Sect. S1 Model tuning description

All tuning runs used common JJA 2022 baseline conditions ($T = 30\text{ }^{\circ}\text{C}$, $q = 0.0184\text{ kg kg}^{-1}$, $\text{RH} = 70\%$, surface pressure = 1000 hPa, and PBL height = 590 m). Each configuration was integrated for 1 year with a 10 min chemical time step and a repeating 1 July 2022 solar cycle. Initial chemical fields were taken from the UKCA ST_urban configuration (Table S5). All other species were set to a negligible background value of $10^{-15}\text{ kg kg}^{-1}$. Anthropogenic emissions were prescribed from CEDS, biogenic emissions from MEGAN (Wu et al., 2020), and dry deposition from the UKCA implementation of the Wesely resistance scheme (Wesely, 1989).

The 0-D configuration does not resolve horizontal transport, vertical mixing, clouds, or wet removal. Direct use of the inventory fluxes therefore caused some species to accumulate and others to be removed too rapidly. Emission and deposition adjustments were treated as effective residual source or loss terms required to construct stable Shanghai and Lishui precursor environments. The objective was not to fit every simulated species, but to reproduce the observed values ($\pm 20\%$ or order of magnitude, described in the following tuning strategy, and observations see Table S2 for SH and S4 for LS) where suitable measurements were available, prevent unrealistic accumulation or depletion, and retain the expected chemical regime at each site. O_3 was not tuned directly.

Model configurations used the Ori settings, in which temperature is held constant, and C_5H_8 emissions vary only with the diurnal solar cycle.

To prevent an unrealistically high buildup of long-lived species, any species not involved in rapid photochemistry that showed substantial concentration growth over two months was fixed at a constant value at this stage. These fixed values (Table S4) were taken from the ST_urban configuration (Table S5).

Species emitted in the model:

NO , C_5H_8 , HCHO , CO , C_2H_6 , C_3H_8 , monoterpene (Monoterp)

Species deposited in the model:

O_3 , CO , HCHO , NO_2 , and NO_y species other than NO and NO_2 (include NO_3 , N_2O_5 , HO_2NO_2 , HNO_2 , PAN, PPAN, and MPAN)

The tuning framework grouped the model inputs into four functional types and applied them separately to Shanghai and Lishui.

Type 1 covers CO , C_2H_6 , and C_3H_8 , for which emissions and, where applicable, depositions were adjusted to keep CO within $\pm 20\%$ of observations and to prevent unrealistic alkane build-up or over-removal. Those species are considered less active species in building the O_3 precursor environment.

Type 2 covers NO emissions and NO_2 deposition, which were treated separately to establish the intended high- NO_x , VOC-limited Shanghai environment and low- NO_x , NO_x -limited Lishui environment while preventing NO accumulation.

Type 3 covers C_5H_8 and monoterpene emissions, which were adjusted to represent the different regional biogenic influences and to satisfy the available concentration constraints.

Type 4 covers HCHO emissions and O_x deposition other than NO_2 ; these inputs were retained at their original values and used to assess the final chemical environment rather than to force agreement with O_3 . O_3 was not tuned directly and remained a model result.

All final settings were fixed before the temperature experiments.

Term definition:

1. Stable conditions: avoid build-up or over-removal of species, measured by daily mean variation of species' concentration within 0.1%;
2. O_x species: $\text{O}_x = \text{O}_3 + \text{O}(^1\text{D}) + \text{O}(^3\text{P}) + \text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5 + \text{HNO}_4 + \text{HNO}_3 + \text{PANs}$;
3. NO_y species: include NO , NO_2 , NO_3 , N_2O_5 , HO_2NO_2 , HNO_2 , PAN, PPAN, and MPAN.

Sect. S1.1 Shanghai tuning strategy

Table S1. Species tuned and the scaling factors in Shanghai

Emitted Species	Adjustment	Deposited Species	Adjustment
CO	0.045	CO	4
NO	0.50	NO ₂	5
C ₂ H ₆	0.50		
C ₃ H ₈	0.40		
C ₅ H ₈	2.00		
Monoterp	4.00		

Table S1 summarises the final emission and deposition scaling factors applied in the Shanghai configuration. The following four types explain the purpose of these adjustments, the constraints applied to each group of species, and how the final Shanghai precursor environment was established. Emissions and depositions unchanged are not included in this table.

Type 1 (CO emission and deposition, C₂H₆ emission, C₃H₈ emission):

Strategy description:

Increase emissions/reduce deposition to represent unresolved inputs;

Reduce emissions/increase deposition to represent unresolved losses.

Target:

CO within $\pm 20\%$ of observations;

C₂H₆ and C₃H₈ remain at stable conditions where observations are unavailable;

Type 1 species summary: Less active species in building the O₃ precursor environment;

Type 2 (NO emissions and NO₂ deposition):

Strategy description:

Increase NO₂ deposition as an effective NO_x loss representing unresolved ventilation and dilution;

Reduce NO emissions to avoid NO accumulation.

Target: NO₂ within $\pm 20\%$ of the observed value, with NO at stable condition.

NO accumulation: The inventory-derived NO source exceeded the chemical oxidation capacity and removal capacity of the box environment. Increasing NO₂ deposition did not directly remove the accumulated NO. The effective NO source was therefore reduced to establish a stable, representative high-NO_x precursor environment.

Type 3 (C₅H₈ emissions and Monoterp emissions)

Strategy description:

Increase C₅H₈ and Monoterp emissions to represent unresolved regional biogenic influence from forests south and southwest of Shanghai (Liu and Miao, 2026; Xu et al., 2021).

Target: C₅H₈ and Monoterp within the observed order of magnitude

Temperature sensitivity of additional C₅H₈ emissions: C₅H₈ emission originally tuned to reach the observed level. However, the added part, which represents transport from nearby forest, should be considered less temperature-sensitive due to dilution and chemical loss during transport. To avoid overproducing the temperature response from BVOC at high temperatures, the additional emission was reduced by 50% to account conservatively. This retained C₅H₈ within the observed order of magnitude without exaggerating its high-temperature response.

Type 4 (O_x deposition other than NO₂, and HCHO emissions)

Strategy description:

Retain the original O₃, NO₃, N₂O₅, HO₂NO₂, HNO₂, PAN, PPAN, and MPAN deposition and HCHO emission values

These inputs remain at their original values.

O₃ deposition was not adjusted to fit observed O₃; the purpose of tuning in Shanghai is to build an observation-like precursor environment instead of forcing O₃ fitting.

For species with available observations (O₃, PAN and HCHO), we would rather monitor them to evaluate how we build the environment rather than tune them.

HCHO was used as an integrated indicator of the carbonyl and VOC-oxidation environment. Agreement within ±20 % of observations shows that the model reproduces the overall reactive VOC environment well and supports the adopted effective AVOC representation.

The final settings from all four types were then applied together to produce the Shanghai baseline environment used in the temperature experiments. Table S2 compares the resulting baseline concentrations with the observations used either as tuning constraints or as independent checks of the final chemical environment.

Table S2. Mass mixing ratio of constrained species in Shanghai at baseline Ori conditions and their observational constraints. Model values are daily mean unless specified.

Species	Baseline condition (kg/kg)	Observation (kg/kg)	Time and location	Source
<i>Type 1</i>				
CO	5.42E-07	4.88E-7 (581 ug/m ³)	Summer 2022, Shanghai	CNEMC
<i>Type 2</i>				
NO ₂	2.02E-08	1.74E-8 (20.6 ug/m ³)	Summer 2022, Shanghai	CNEMC
<i>Type 3</i>				

C ₅ H ₈	2.86E-10	7.1E-10 (0.3ppbv)	Jul 2018, Shanghai	Gu et al. (2022)
Monoterp	3.74E-10	5.20E-10 (0.11 ppbv)	Summer 2014, Beijing	Cheng et al. (2018)
<i>Type 4 (evaluation only)</i>				
O ₃	7.12E-08	7.40E-8 (87.5 ug/m ³)	Summer 2022, Shanghai	CNEMC
PAN	7.34E-09	3.76E-9 (0.9 ppbv)	Summer 2017, Shanghai	Zhang et al. (2021)
HCHO	3.03E-09	3.43E-9 (3.31 ppbv)	Jun-Aug 2018, Shanghai	Guo et al. (2021)

Sect. S1.2 Lishui tuning strategy

Table S3. Species tuned and the scaling factors in Lishui

Emitted Species	Adjustment	Deposited Species	Adjustment
CO	0.05	CO	2
NO	0.50		
C ₅ H ₈	0.50		

Table S3 summarises the final emission and deposition scaling factors applied in the Lishui configuration. The same four-type framework was used, but the adjustments were selected to establish the intended low-NO_x, NO_x-limited, vegetation-influenced environment and to reflect the observational constraints available for Lishui.

Type 1 (CO emission and deposition, C₂H₆ emission, C₃H₈ emission):

Strategy description:

Increase emissions/reduce deposition to represent unresolved inputs;

Reduce emissions/increase deposition to represent unresolved losses;

Target:

CO within $\pm 20\%$ of observations;

C₂H₆ and C₃H₈ remain stable conditions where observations are unavailable;

Type 1 species summary: Less active species in building the O₃ precursor environment;

Type 2 (NO emissions and NO₂ deposition):

Strategy description:

Retain the original NO₂ deposition;

Reduce NO emissions to avoid NO accumulation;

Target:

NO₂ within the observed order of magnitude for forest and mountain background sites, with NO at stable conditions.

NO accumulation: The inventory-derived NO source exceeded the chemical oxidation capacity of the box environment. The effective NO source was therefore reduced to establish a stable, representative low-NO_x, NO_x-limited precursor environment.

NO₂ level: Available Lishui monitors are urban or suburban and do not represent the intended rural regional environment. Forest-canopy and mountain-background observations were therefore used as order-of-magnitude references. Given this representativeness uncertainty, the original NO₂ deposition was retained.

Type 3 (C₅H₈ emissions and Monoterp emissions)

Strategy description:

Reduce C₅H₈ emissions to represent unresolved export and dilution from the vegetation-rich source region

Retain Monoterp emissions due to lack of observations

Target: C₅H₈ within $\pm 20\%$ of the observed value; Monoterp remains stable conditions

Type 4 (O_x deposition other than NO₂ deposition, HCHO emissions)

Strategy description:

Retain the original O₃, NO₃, N₂O₅, HO₂NO₂, HNO₂, PAN, PPAN, and MPAN deposition and HCHO emission values

These inputs remain at their original values

O₃ deposition was not adjusted to fit observed O₃; tuning instead established a clean, rural-like precursor environment

Other observed species were used as independent diagnostics rather than tuning targets.

The final settings from all four types were then applied together to produce the Lishui baseline environment used in the temperature experiments. Table S4 compares the resulting baseline concentrations with the available observations used either as tuning constraints or as independent checks of the final chemical environment.

Table S4. Mass mixing ratio of constrained species in Lishi at baseline Ori conditions and their observational constraints. Model values are daily mean unless specified.

Species	Baseline condition (kg/kg)	Observation (kg/kg)	Time and location	Source
<i>Type 1</i>				
CO	4.22E-07	3.68E-7(438 ug/m ³)	Summer 2022, Lishui	CNEMC
<i>Type 2</i>				
NO ₂	1.14E-09	1.43E-09 to 4.29E-09 (0.9-2.7 ppb)	Forest canopy (summer 2009) and Wuyishan (annual mean, 2006-2016)	(Min et al., 2014; Yin et al., 2022)
<i>Type 3</i>				
C ₅ H ₈	6.51E-09 (daytime)	7.30E-09 (8.3 µg m ⁻³ ; daytime)	Sep 2009, Lishui	Geng et al. (2011)
<i>Type 4</i> (evaluation only)				
O ₃	3.40E-08	4.67E-8 (55.2 ug/m ³)	Summer 2022, Lishui	CNEMC
PAN	3.22E-09	1.57E-9 (0.375 ppbv)	summer 2020, Nanjing	Xu et al. (2024)

Table S5. Long-lived fixed species

Fixed Species	Fixed Mass mixing Ratio (kg/kg)
CH ₄	9.7168E-07
MeBr	7.0400e-11
H ₂	1.0000e-8
CS ₂	1.0000e-15
COS	1.0000e-15

Table S6. UKCA ST_{urban} tracer initial configuration and conditions in Shanghai and Lishui

Species	Shanghai	Lishui
O(3P)	3.00E-16	3.00E-16
O3*	7.44E-08	4.67E-08
N	0.00E+00	0.00E+00
NO	6.90E-09	6.90E-09
NO3	1.87E-12	1.87E-12
NO2*	1.68E-08	1.43E-08
N2O5	1.21E-11	1.21E-11
HO2NO2	1.61E-11	1.61E-11
HONO2	9.16E-09	9.16E-09
H2O2	1.96E-09	1.96E-09
CH4	9.72E-07	9.72E-07
CO*	5.37E-07	3.68E-07
HCHO*	3.43E-09	3.43E-09
MeOO	3.32E-12	3.32E-12
MeOOH	3.29E-10	3.29E-10
H	1.29E-26	1.29E-26
H2O	1.84E-02	1.84E-02
OH	9.69E-14	9.69E-14
HO2	1.24E-11	1.24E-11
Cl	4.43E-19	4.43E-19
Cl2O2	7.40E-22	7.40E-22
ClO	9.56E-17	9.56E-17
OCIO	1.45E-19	1.45E-19

Br	1.20E-15	1.20E-15
BrO	7.36E-11	7.36E-11
BrCl	2.91E-19	2.91E-19
BrONO2	2.50E-14	2.50E-14
N2O	4.86E-07	4.86E-07
HCl	3.98E-09	3.98E-09
HOCl	4.74E-14	4.74E-14
HBr	1.95E-12	1.95E-12
HOBr	1.27E-13	1.27E-13
ClONO2	1.34E-15	1.34E-15
CFCI3	1.82E-09	1.82E-09
CF2Cl2	4.19E-09	4.19E-09
MeBr	7.04E-11	7.04E-11
HONO	2.96E-11	2.96E-11
C2H6	2.17E-08	2.17E-08
EtOO	2.93E-13	2.93E-13
EtOOH	2.40E-11	2.40E-11
MeCHO	2.75E-10	2.75E-10
MeCO3	1.11E-12	1.11E-12
PAN	1.75E-09	1.75E-09
C3H8	6.03E-09	6.03E-09
n-PrOO	5.02E-14	5.02E-14
i-PrOO	1.32E-13	1.32E-13
n-PrOOH	5.02E-12	5.02E-12
i-PrOOH	9.78E-12	9.78E-12
EtCHO	2.51E-11	2.51E-11
EtCO3	2.12E-14	2.12E-14
Me2CO	8.82E-09	8.82E-09
MeCOCH2OO	8.60E-14	8.60E-14
MeCOCH2OOH	1.09E-11	1.09E-11
PPAN	2.64E-11	2.64E-11
MeONO2	7.89E-11	7.89E-11
C5H8*	7.00E-10	7.00E-10
ISO2	6.32E-12	6.32E-12
ISOOH	1.39E-10	1.39E-10
ISON	1.84E-09	1.84E-09
MACR	3.04E-09	3.04E-09
MACRO2	1.70E-12	1.70E-12
MACROOH	8.24E-11	8.24E-11
MPAN	1.63E-09	1.63E-09
HACET	2.59E-09	2.59E-09
MGLY	2.61E-10	2.61E-10
NALD	2.28E-10	2.28E-10
HCOOH	2.41E-10	2.41E-10
MeCO3H	1.91E-10	1.91E-10
MeCO2H	1.37E-10	1.37E-10
H2	1.00E-08	1.00E-08
MeOH	1.94E-08	1.94E-08

DMS*	4.80E-11	4.80E-11
SO2*	3.91E-09	3.91E-09
Monoterp*	5.20E-10	5.20E-10

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