



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

Chang Su¹, Massimo Bollasina¹, James Weber², and David Stevenson¹

¹School of GeoSciences, University of Edinburgh, Edinburgh, UK

²Department of Meteorology, University of Reading, Reading, UK

Correspondence: Chang Su (chang.su@ed.ac.uk)

Received: 11 February 2026 – Discussion started: 12 March 2026

Revised: 26 August 2026 – Accepted: 28 September 2026 – Published: 13 October 2026

Abstract. As climate change increases frequency and intensity of hot extremes, understanding how elevated temperatures influence surface ozone (O_3) across different chemical regimes is critical. We combine observations from summer 2022 in the Yangtze River Delta (YRD) with controlled United Kingdom Chemistry and Aerosols (UKCA) Box experiments for urban Shanghai and a lower- NO_x , biogenically influenced Lishui regional environment. Observed daily-maximum O_3 increases with temperature at both sites, with a stronger response in Shanghai. Two-dimensional T -RH distributions show that O_3 rises with temperature and decreases with relative humidity (RH), implying that part of the temperature response is mediated by drying. Factorial box-model experiments separate the roles of temperature-driven shifts in chemical partitioning, diurnal thermal structure, temperature-dependent isoprene emissions, and humidity. In Shanghai, the increase in O_3 between 30 and 40 °C is dominated by BVOC-driven chemistry, with temperature-amplified isoprene emissions explaining most of the observed response. In Lishui, O_3 sensitivity is governed primarily by radical- NO_x chemistry and thermal PAN- NO_x cycling, with a much smaller role for BVOCs. Fixed RH scenarios substantially reduce the apparent contribution of “thermal chemistry”, highlighting humidity-dependent O_x loss and HO_x - NO_x cycling as key modifiers of the climate penalty. Because the 0-D framework excludes transport and meteorological dynamics, the reported fractions isolate the local chemical and emission-driven component of the O_3 -temperature relationship. Within this scope, the results identify robust regime-specific mechanisms linking heat, humidity, precursor chemistry, and surface O_3 in the YRD and demonstrate the value of observation-constrained box models as a bridge to regional chemistry-climate simulations.

1 Introduction

Surface ozone (O_3) remains a prominent air-quality and public-health concern, and its variability reflects a tight coupling between meteorology (temperature, humidity, stability, radiation, etc.) and precursor emissions, with co-occurring heat and O_3 extremes documented (Bloomer et al., 2010; Wang et al., 2022a). As heat extremes, e.g., heatwaves (HWs), increase in frequency, duration, and intensity under continued warming (World Meteorological Organization, 2019), quantifying how O_3 responds to hot conditions is becoming increasingly critical for policymakers (Ebi et al.,

2021). In China, summertime O_3 has remained elevated despite recent controls on nitrogen oxides ($NO_x = NO + NO_2$), underscoring the need to diagnose the meteorological and chemical drivers of O_3 during hot periods (Wang et al., 2022b).

Ozone is a significant air pollutant that adversely affects human health, particularly respiratory functions. Exposure to elevated O_3 concentrations has been linked to increasing rates of respiratory diseases, including asthma and other pulmonary disorders (Cohen et al., 2017; Pope et al., 2023). The Global Burden of Disease Study (Forouzanfar et al., 2015) estimated that in 2015 alone, approximately 254 000 fatali-

ties were attributed to O₃ exposure worldwide, with about 55 300 to 80 300 of those deaths occurring in China (Cohen et al., 2017; Liu et al., 2018). The impacts extend beyond human health: high O₃ levels impair plant physiological processes, detrimentally affect crop yields, and hinder biomass accumulation, thereby threatening food security and ecosystem stability (Meehl et al., 2018; Meng et al., 2023). Moreover, O₃ is also a significant greenhouse gas that further enhances surface warming (Szopa et al., 2021), with positive feedbacks on O₃ levels (Meng et al., 2023).

The underlying relationship between high temperatures and the resultant increase in surface O₃ concentration can be modulated by four primary mechanisms: (i) emissions of O₃ precursors (NO_x and VOCs), (ii) rates of chemical reaction, (iii) transport and entrainment from the free troposphere, and (iv) deposition of O₃ and its precursors. The meteorological conditions associated with high-temperature events are the key mediators in each pathway and provide the causal links between temperature and the surface O₃ response.

- i. *Emissions.* The production and destruction of O₃ are highly dependent on its precursors, particularly NO_x and volatile organic compounds (VOCs) (Liu et al., 2021b; Solberg et al., 2008). Biogenic VOC (BVOC) emissions, especially isoprene (C₅H₈), increase exponentially with leaf temperature and light intensity, amplifying O₃ formation under warm, sunny conditions (Chen et al., 2022; Ma et al., 2022a). In addition to BVOC emissions, temperature-dependent evaporative anthropogenic VOC (AVOC) sources, such as petrochemical processing, solvents, and vehicles, will also increase with temperature and have a significant impact in urban environments (Wu et al., 2024; Yamada, 2013).
- ii. *Chemistry.* High temperatures impact net photochemical processing in the NO_x-hydrogen oxides (HO_x = OH + HO₂)-VOC system by changing rate coefficients, while enhanced actinic flux under persistent clear-sky conditions during heat extremes always increases photolysis rates; the shift in the radical budget generally results in a net production of O₃, although the reaction rates of several important processes are negatively correlated with increasing temperature (Archibald et al., 2020b; Gu et al., 2020). Thermal decomposition of peroxyacyl nitrate (PAN) type reservoirs (e.g., CH₃C(O)OONO₂ (PAN) → CH₃C(O)OO• (PA) + NO₂) at high temperatures further shifts reactive nitrogen toward NO_x, enriching O₃ precursor in local environments (Steiner et al., 2010; Wu et al., 2008). In addition, low humidity at high-temperature conditions reduces the impact of the reaction O(¹D) + H₂O → 2OH, thus favouring net O₃ production (Li et al., 2021).
- iii. *Transport.* High-temperature extremes like HWs frequently coincide with synoptic stagnation, weak circu-

lation and ventilation, and a deeper planetary boundary layer (PBL) (Archibald et al., 2020b; Duc et al., 2022; Utembe et al., 2018; Wu et al., 2019). Stagnation and weak ventilation consistently concentrate O₃ and its precursors, reducing dilution and export, thereby strengthening near-surface accumulation during hot periods (Zhang et al., 2018). On the other hand, a deeper boundary layer at high temperatures generally enhances the ventilation of surface O₃, thereby making it harder for ground-level O₃ to build up (Pfister et al., 2014). The impact of a deeper boundary layer ventilation at high temperatures is partly offset by O₃ entrained from the residual layer aloft (Bloomer et al., 2010).

- iv. *Deposition.* The deposition velocity (V_d) of O₃ and its precursors is often parameterised as $V_d = (R_a + R_b + R_c)^{-1}$, which represents O₃ deposition as a function of an aerodynamic resistance (R_a), a quasi-laminar boundary layer resistance (R_b), and overall canopy resistance (R_c ; stomatal + cuticular + soil) (Stella et al., 2011; Zhang et al., 2003). Here, R_a represents turbulent transport above the canopy (mainly affected by wind speed and stability), R_b describes a quasi-laminar boundary layer resistance for vegetation that depends on the diffusion coefficient of species, and R_c is the surface resistance, combining stomatal, cuticular and soil resistances (Clifton et al., 2020b; Wesely, 1989). During high-temperature extremes, synoptic stagnation and weak near-surface winds reduce turbulent transport near the surface, increasing R_a and R_b resistances and thereby lowering deposition velocity (Wesely, 1989; Zhang et al., 2003). Under hot and dry conditions, high vapour pressure deficit (VPD) and depleted soil moisture reduce stomatal conductance, so the stomatal part of R_c increases, lowering V_d for stomata-controlled species (O₃, NO₂) (Kavassalis and Murphy, 2017; Wilson et al., 2022). Concurrently, hot/dry leaves have minimal surface water films, which raises cuticular resistance and further increases R_c (Clifton et al., 2020b). In contrast, dry soils tend to exhibit lower soil resistance than moist soils, so soil/litter uptake of O₃ strengthens as surfaces dry – partly offsetting the stomatal signal. (Clifton et al., 2020a; Stella et al., 2011).

Complicating this picture are spatial variations in precursor-sensitivity regimes. In NO_x-limited (VOC-rich) environments – typically found in rural and regions downwind of ozone precursor emissions – O₃ production increases nearly linearly with NO_x concentrations and shows limited sensitivity to further VOC additions (Steiner et al., 2006; Utembe et al., 2018). Conversely, in highly urbanised areas with high NO_x/VOC ratios (VOC-limited regime), additional NO_x (mainly emitted in the form of NO) can suppress O₃ by titrating ozone back to NO₂ (O₃ + NO → NO₂ + O₂), and O₃ formation becomes more strongly driven by available VOCs (Simon et al., 2015). The existence of two regimes implies

that identical temperature-driven chemical and meteorological forcings can yield contrasting O_3 responses if background pollutant levels differ, such as in urban versus rural settings, highlighting the need to assess urban-rural differences explicitly.

Most observation-based studies indicated a positive correlation between temperature and tropospheric O_3 levels as a result of the combined effects of O_3 's temperature responses, while some reported a non-monotonic relationship between temperature and climate penalty factor (O_3 -temperature slope, $\Delta O_3/\Delta T$) when ambient temperature exceeds thresholds (Kalisa et al., 2018; Nguyen et al., 2022; Ning et al., 2022; Pusede et al., 2015; Shen et al., 2016; Steiner et al., 2010). Unravelling this complexity requires a careful distinction of how temperature interacts with various atmospheric factors, including solar radiation, humidity, planetary boundary layer height (PBLH), wind speed, precipitation, and both anthropogenic and biogenic emissions (Bloomer et al., 2010; Nguyen et al., 2022; Sun et al., 2017; Wang et al., 2022a; Wu et al., 2008).

Despite the growing body of work on O_3 -temperature coupling, significant gaps remain. Observation-constrained box models treat each site as a well-mixed air parcel, apply detailed chemical mechanisms to diagnose local photochemical production and loss rates, provide adjustable environmental parameters, and help separate local chemical controls from transport influences, and are therefore a useful complement to 3-D chemical transport models in studies of extremes (McDuffie et al., 2016). However, few studies have combined observations with process-level box-model budget analyses to quantify the relative contributions of chemical kinetics and precursor changes under extreme-heat conditions. Besides, urban-rural contrasts in O_3 temperature sensitivity have not been systematically explored using consistent methodological frameworks. This is particularly true for rapidly urbanising regions of East Asia, where emission patterns and warming trends interact to shape local O_3 dynamics.

In this study, we investigate the mechanisms of surface O_3 's chemical response to high temperatures in two contrasting environments within the Yangtze River Delta (YRD) in China: urban Shanghai and rural (forest-influenced) Lishui. Focusing on summer 2022, we combine surface observations with controlled UKCA Box experiments over a temperature range of 25–40 °C. The box-model experiments isolate temperature-dependent gas-phase chemistry, humidity effects, diurnal thermal structure, and temperature-dependent isoprene emissions, allowing the O_3 response to be attributed to local chemical and emission-related processes under prescribed environmental conditions. By quantifying O_3 production, chemical loss, and deposition of ozone and precursors, we then identify how the two chemical regimes respond differently to warming.

The attribution presented in this study focused on processes that can be isolated within the UKCA Box model. Within this framework, we isolate the local chemical and

precursor-emission responses to temperature with prescribed environmental conditions. Consequently, three-dimensional physical influences such as transport, entrainment, boundary-layer development, stagnation, clouds, and precipitation are not separately resolved. Our attribution therefore addresses the chemical component of the O_3 -temperature relationship.

2 Data and Methods

2.1 Study Locations and Observations

The locations of the monitoring sites, the YRD urban boundaries, and the NO_2 gradient are shown in Fig. 1.

The observational analysis uses surface air-quality measurements from Shanghai and Lishui as two contrasting environments within the YRD. Shanghai represents a densely urbanised megacity environment with strong anthropogenic precursor influence, while Lishui provides a lower- NO_x environment with stronger influence from surrounding vegetated areas. These two cases are used to examine how O_3 -temperature sensitivity differs across contrasting precursor and land-surface settings.

To place the selected monitoring sites within the broader YRD context, AQMS locations were compared with the 2018 Global Urban Boundary (GUB) dataset (Li et al., 2020). The GUB dataset delineates physical urban extents at 30 m resolution using Global Artificial Impervious Area (GAIA) data. The 2018 boundaries were used to identify whether individual AQMS sites were located within or outside mapped urban areas.

The YRD-wide comparison included 250 valid AQMS sites in JJA 2022. Validation defined by hourly data in June–August (JJA) 2022 with a threshold of 75 %. The selected Shanghai sites are located within GUB urban settlement polygons and occupy the high- NO_2 part of the YRD AQMS distribution, with a mean NO_2 concentration of $20.58 \mu\text{g m}^{-3}$, corresponding to approximately the 87th percentile among valid YRD sites.

The selected Lishui sites occupy a lower- NO_2 part of the YRD AQMS distribution, with a mean NO_2 concentration of $11.46 \mu\text{g m}^{-3}$, corresponding to approximately the 18th percentile among valid YRD sites. Two of the three selected Lishui sites fall within GUB urban settlement polygons, indicating populated urban/suburban receptor locations within a broader lower- NO_x and more biogenically influenced regional setting.

As far as population density and land-use type are concerned, Shanghai is a megacity with a population density of 3900 km^{-2} (Shanghai Municipal Statistics Bureau, 2024), and construction land covered 42.4 % of its total area (Gong et al., 2022). Lishui is an area where 81.7 % of the land is covered with forest (Tang et al., 2022). The population density of Lishui is 140 km^{-2} , and the urban district accounts for about 8.6 % of its total area (Lishui Municipal Statistics Bureau, 2025).

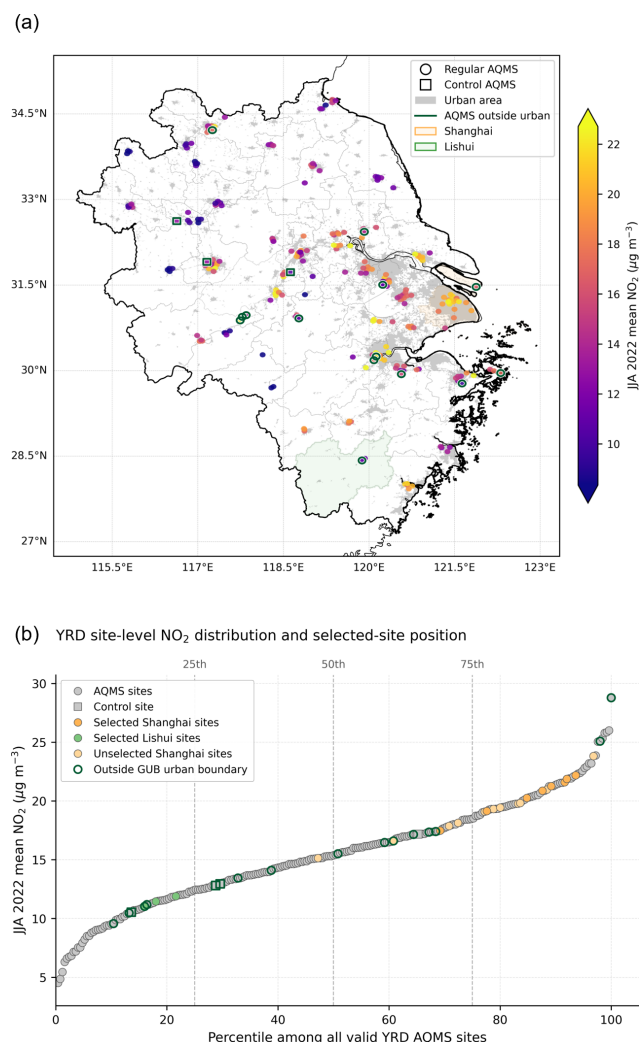


Figure 1. (a) Spatial distribution of Air Quality Monitoring Sites (AQMS) across the YRD in summer 2022, coloured by JJA 2022 mean NO₂. Grey shading indicates the 2018 Global Urban Boundaries (GUB) urban settlement extent. Circular markers denote regular AQMS, square markers denote control sites, and green outlines indicate sites located outside the GUB urban settlement boundary. Shanghai and Lishui are highlighted by coloured city polygons. (b) Ranked distribution of JJA 2022 mean NO₂ across all valid YRD AQMS, expressed as site percentile. Selected Shanghai and Lishui sites (listed in Table 1) are highlighted in orange and green, respectively; unselected Shanghai sites are shown in pale orange, and sites outside the GUB urban boundary are outlined in dark green. Administrative boundaries from the GADM database (<http://www.gadm.org>, last access: 11 March 2026).

We collected ground-level hourly O₃ observation data from the China National Environmental Monitoring Center (CNEMC). The AQMS are in the busiest areas of Shanghai (30.67–31.88° N, 120.85–122.2° E) and in the populated centre area of Lishui (27.44–28.78° N, 118.70–120.41° E).

The analysis focuses on JJA 2022, when the YRD experienced severe and persistent high-temperature conditions. This period provides a well-observed recent heatwave case with routine surface O₃ measurements from the national monitoring network. Earlier major heatwave summers in the region, such as 2003 and 2013, predate the availability of constant O₃ observations (see <https://quotsoft.net/air/>, last access: 14 July 2025). The 2022 data are therefore used to examine O₃–temperature sensitivity under a heat extreme setting.

We assessed O₃ and meteorological data for June–August 2022 (JJA 2022). Eight AQMS and two Meteorological Monitoring Sites (MMS) in Shanghai, and three AQMS and one MMS in Lishui met this criterion (spatial distribution see Fig. 1). For each retained site, we extracted hourly surface O₃ and then formed two aggregated series: an urban mean (average across the 8 Shanghai sites at each hour) and a rural mean (average across the 3 Lishui sites at each hour). Meteorological observations originate from the China Meteorological Monitoring System (CMMS) stations; we accessed the archived data via the NOAA National Climatic Data Center (NCDC).

The meteorological and air-quality monitoring sites retained for the analysis are summarised in Table 1 below.

The AQMSs in Lishui (1267A–1269A; Table 1) are located in a populated environment that is best characterised as urban or suburban. The Lishui emission inputs used in the box model (explained later in Sect. 2.2), however, represent regional mean conditions with relatively low NO_x and stronger biogenic influence. The resulting chemical regime therefore characterises the regional photochemical environment influencing Lishui, rather than the immediate atmosphere at the monitoring sites.

In this study, a heatwave is defined as a period of at least 3 consecutive days during which the daily maximum temperature exceeds the 90th percentile of the reference period (2000–2019), as used by Zhao et al. (2019). The 90th percentile threshold has been widely used in studies examining heatwave patterns, health impacts, and interactions with air quality (Engdaw et al., 2022; Fischer and Schär, 2010; Sun et al., 2020). To remove day-to-day variation, a 15 d smoothing window centred on the investigated day was applied to threshold calculation (based on the reference period) (García-Martínez and Bollasina, 2021). The years 2020 and 2021 were excluded from the reference period calculation to eliminate any effects resulting from the COVID-19 lockdowns in China.

For the ozone–temperature analysis, we use daily maximum surface O₃ (O_{3max}) and daily maximum air temperature (T_{max}) because climate-penalty assessments are conventionally based on daily peak metrics (e.g. daily max 1 h O₃ versus daily T_{max}), which target the photochemical period, reduce confounding nocturnal NO-titration and inter-site timing offsets (Nolte et al., 2021; Otero et al., 2021). We stratify by environment type (urban Shanghai vs. rural Lishui) and by

Table 1. Information on the MMS (XJH, BS, and LS) and AQMS in SH and LS.

Site code	Full name	Coordinates (° N, ° E)	Area	Environment	Variables	Temporal resolution	Period used
XJH	Xujiahui	31.12, 121.26	Shanghai	Urban	Temperature & Dew-point temperature	1 h	Jun–Aug 2022
BS	Baoshan	31.24, 121.27	Shanghai	Urban	Temperature & Dew-point temperature	3 h	Jun–Aug 2022
LS	Lishui	28.27, 119.55	Lishui	Rural	Temperature & Dew-point temperature	3 h	Jun–Aug 2022
1142A	Shiwuchang	31.20, 121.48	Shanghai	Urban	O ₃	1 h	Jun–Aug 2022
1143A	Hongkou	31.30, 121.47	Shanghai	Urban	O ₃	1 h	Jun–Aug 2022
1144A	Xuhui Shangshida	31.17, 121.41	Shanghai	Urban	O ₃	1 h	Jun–Aug 2022
1145A	Yangpu Sipiao	31.27, 121.54	Shanghai	Urban	O ₃	1 h	Jun–Aug 2022
1147A	Jing'an Station	31.23, 121.43	Shanghai	Urban	O ₃	1 h	Jun–Aug 2022
1148A	Pudong Chuansha	31.19, 121.70	Shanghai	Urban	O ₃	1 h	Jun–Aug 2022
1149A	Pudong Xinqu Station	31.23, 121.53	Shanghai	Urban	O ₃	1 h	Jun–Aug 2022
1150A	Pudong Zhangjiang	31.21, 121.58	Shanghai	Urban	O ₃	1 h	Jun–Aug 2022
1267A	Jiancezhan Dalou	28.45, 119.91	Lishui	Urban/Suburban	O ₃	1 h	Jun–Aug 2022
1268A	Dandu Primary School	28.46, 119.93	Lishui	Urban/Suburban	O ₃	1 h	Jun–Aug 2022
1269A	Yuzhuang Qian	28.42, 119.88	Lishui	Urban/Suburban	O ₃	1 h	Jun–Aug 2022

period (all JJA days vs. heatwave days), thus yielding four subsets of ozone-temperature analysis: urban-all, urban-HW, rural-all, and rural-HW.

The XJH site (Shanghai; 31.12° N, 121.26° E) reports hourly air temperature and dew-point temperature. The BS site (Shanghai; 31.24° N, 121.27° E) and the LS site (Lishui; 28.27° N, 119.55° E) provide three-hourly records of air temperature and dew-point temperature. Daily maximum air temperature values at sites XJH and BS were averaged to obtain the representative Shanghai temperature conditions. To evaluate the joint influence of surface air temperature and humidity on ground-level O₃, we aligned the temporal resolution by applying a 3 h mean to the hourly O₃ series, ensuring that O₃, temperature, and humidity share the same 3-hourly meteorological sampling times.

2.2 Model configurations and inputs

2.2.1 UKCA Box model configuration

We use the United Kingdom Chemistry and Aerosols (UKCA) Box Model (equivalent to the Unified Model (UM) version 13.0), which executes the identical UKCA chemistry-aerosol code used in the Met Office UM over a single grid cell (1.25° × 1.9°; zero-D), run independently of the UM. The UKCA Box Model, like other box models, treats each site as a well-mixed air parcel, provides adjustable environmental parameters, and helps separate the contributions of local chemical controls (McDuffie et al., 2016). The box model, by design, does not include advection, convection,

and diffusion, enabling fast simulations with direct code-level traceability to UM-UKCA/UK Earth System Model (UKESM) (UKCA, 2025).

Compared to the full 3-D UM-UKCA (e.g. UKESM-AMIP), the box model isolates local chemical-microphysical responses to prescribed forcings (temperature, humidity, photolysis) without transport processes, and completes controlled perturbation experiments orders of magnitude faster, while retaining the StratTrop chemical mechanism used in UKESM1 (Archibald et al., 2020a; UKCA, 2025).

The aim of the UKCA Box model simulation in this study is to build two contrasting chemical environments: an urban case dominated by anthropogenic transport/industrial emissions (Shanghai-like chemical environment) and a rural case dominated by biogenic VOC emissions (Lishui-like chemical environment). The highly controllable climate forcing enables attribution of the O₃ temperature response to (1) chemical-kinetic temperature dependence, (2) the dependence of the chemistry on humidity, (3) temperature dependence of BVOC (isoprene) emissions, and (4) diurnal temperature structure. A 3-D UKESM-AMIP simulation was performed to compare the box against a fully resolved chemistry-meteorology system, providing grid-cell-mean O₃ production and loss diagnostics under the same chemistry scheme and indicating the budget contributions absent from the box configuration, particularly transport/export. To ensure comparability and avoid ambiguity arising from administrative-area differences between Shanghai and Lishui, O₃ budget calculations were carried out by configur-

ing the box to match the UM grid size ($1.25^\circ \times 1.9^\circ$). The emission and deposition inputs used to define these baseline environments are described below with Fig. 2 and Supplement.

In the box model simulations in this study, photolysis varies diurnally with the solar-zenith angle at the target latitude/longitude. Prescribed meteorological inputs were held at the baseline values (70 % RH when at 30°C , Pressure = 1000 hPa, and PBLH = 590 m), which are consistent with YRD summer-average values. The temperature and humidity perturbation settings are described in Table 3 (see Sect. 2.3).

We repeat a representative summer-day radiation cycle until the system attains a steady state (defined as a state in which the variation in the output daily mean values of key chemical species is within $\pm 0.1\%$ of the previous day). To avoid analysing relatively unimportant partitioning between O_3 and closely related odd-oxygen species, we focus our analysis on the wider odd-oxygen family (O_x) (using UKCA definition as $\text{O}_x = \text{O}_3 + \text{O}(^1\text{D}) + \text{O}(^3\text{P}) + \text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5 + \text{HNO}_4 + \text{HNO}_3 + \text{PANs}$) (Bates and Jacob, 2020; Hu et al., 2017). The model time resolution is 10 min. Initial trace-gas fields follow the standard ST_urban UKCA box initial-condition set, except the initial concentrations of key O_3 precursors, the concentrations of which are consistent with observations where available (See NO_2 , CO, and C_5H_8 in Table 2; see other observations in Table S1 in the Supplement). Localised adjustments to emissions, deposition, and selected baseline species are described below and in Tables S1 and S3.

To show how the inventory fields were translated into the two box-model environments, Fig. 2 presents the spatial selection of CEDS emissions together with the final anthropogenic and biogenic emission inputs used for Shanghai and Lishui.

Anthropogenic emissions were prescribed from the Community Emissions Data System (CEDS; version 2024_11_25) for JJA 2022. The dashed UKCA/UM grid-cell outlines in Fig. 2 are shown only to indicate the spatial relationship between the box-model emission selection and the UKESM-AMIP grid cells; they were not used to calculate or average the CEDS emission inputs. The anthropogenic VOC input included the emitted tracers available in the StratTrop box configuration, C_2H_6 , C_3H_8 , and HCHO, and therefore represents an effective subset rather than the complete urban AVOC mixture. Biogenic emissions of C_5H_8 and monoterpenes (Monoterp) were based on the MEGAN v2.1 inventory for China reported by Wu et al. (2020). Dry deposition was applied using the UKCA implementation of the Wesely (1989) resistance scheme for O_3 , CO, HCHO, NO_2 , and the deposited NO_y species (include NO, NO_2 , NO_3 , N_2O_5 , HO_2NO_2 , HNO_2 , PAN, PPN, and MPAN) represented in the mechanism. Table 2 summarises the principal observational constraints used to establish the two baseline environments.

The inventory-derived emissions and standard deposition terms were used as the starting inputs, but they could not be applied directly in the closed 0-D system. The absence of horizontal transport, resolved vertical mixing, ventilation, physical export, clouds, and wet removal caused some species to accumulate and others to be removed too rapidly during the repeated clear-sky integrations. Emission and deposition adjustments were therefore treated as effective residual source or loss terms representing these unresolved processes. The objective was to reproduce the available reference concentrations within $\pm 20\%$ or the observed order of magnitude, prevent unrealistic build-up or over-removal, and retain the intended precursor regime at each site. O_3 was not tuned directly, and its deposition was not adjusted to force agreement with observed O_3 .

The remaining constraints were applied according to the chemical role of each species. CO was constrained to within $\pm 20\%$ of the available observations. Where suitable observations were unavailable, C_2H_6 and C_3H_8 emissions were adjusted only to prevent persistent accumulation or excessive removal. HCHO was used as an integrated indicator of the carbonyl and VOC-oxidation environment instead of being tuned; agreement within $\pm 20\%$ of observations shows that the model reproduces the overall reactive VOC environment well and supports the adopted effective AVOC representation. O_3 , PAN, and other observed species that were not direct constraints were used to evaluate the resulting chemical environment.

For Shanghai, the adjustment was designed to establish a stable high- NO_x , VOC-limited environment. NO_2 deposition was increased to represent unresolved NO_x removal by ventilation and dilution, while the NO emission source was reduced only because inventory-derived NO accumulated in the closed box. Together, these changes maintained NO under stable conditions (defined as daily mean variation of species' concentration within 0.1 %) and reproduced the observed NO_2 level within $\pm 20\%$. C_5H_8 and monoterpene emissions were increased to represent the regional biogenic influence of forests south and southwest of Shanghai (Liu and Miao, 2026; Xu et al., 2021). Because the additional C_5H_8 source represents transported regional influence rather than purely local emission, its temperature-dependent component was reduced by 50 % to account conservatively for dilution and chemical loss during transport. The resulting C_5H_8 and monoterpene concentrations remained within the observed order of magnitude.

For Lishui, the adjustment was designed to establish a clean, low- NO_x , NO_x -limited regional environment with strong biogenic influence. The available Lishui air-quality monitoring sites are located in populated urban or suburban areas and were therefore not used as direct NO_2 targets for the regional box environment. Instead, forest-canopy and mountain-background observations provided order-of-magnitude references for NO_2 (see Table 2). The original NO_2 deposition was retained, and the NO source was re-

Table 2. Observational NO₂, CO, and C₅H₈ constraints for key species used to define the Shanghai- and Lishui-like baseline chemical environments.

Species	Observational urban constraints (Shanghai)	Source, period, and location	Observational rural constraints (Lishui)	Source, period, and location
NO ₂	20.6 µg m ⁻³	CNEMC, summer 2022, Shanghai	0.9–2.7 ppb	Min et al. (2014), summer 2009, Forest canopy & Yin et al. (2022), 2006–2016, Wuyishan
CO	581 µg m ⁻³	CNEMC, summer 2022, Shanghai	438 µg m ⁻³	CNEMC, summer 2022, Lishui
C ₅ H ₈	0.3 ppbv	Gu et al. (2022), Jul 2018, Shanghai	1 to 3 ppbv	Geng et al. (2011), Sep 2009, Lishui

duced only when NO accumulated. C₅H₈ emissions were reduced to represent export and dilution from the vegetation-rich source region, producing a daytime C₅H₈ concentration within ±20 % of the available Lishui observation. Monoterpene emissions were retained at their inventory value because suitable observations were unavailable.

The final Shanghai and Lishui emission and deposition settings were fixed before the temperature, humidity, diurnal-cycle, and isoprene-temperature sensitivity experiments. Consequently, the simulated O₃ responses arise from controlled perturbations applied to the same baseline chemical environment rather than from retuning at each temperature. The final scaling factors, observational references, and achieved baseline concentrations are reported in Tables S1–S4. The 2022 observations and inventories define the baseline environments, while the subsequent experiments impose temperatures from 25 to 40 °C under controlled conditions and do not attempt to reproduce the full meteorological evolution of summer 2022.

2.2.2 UKESM-AMIP configuration

A full 3-D UKCA model simulation reproducing the 2022 summer was conducted and compared with the Box model simulations. This simulation was performed using the UKESM-AMIP setup with the UM version 13.3. The model was run with a horizontal resolution of 1.25° by 1.9° (as shown on Fig. 2) with 85 vertical levels up to 85 km (Walters et al., 2019), and the GLOMAP-mode aerosol scheme, which simulates sulfate, sea salt, BC, organic matter, and dust but does not simulate nitrate aerosol (Mulcahy et al., 2020). The chemistry scheme used was Strat-Trop (Archibald et al., 2020a), identical to the box model. Anthropogenic and biomass burning emissions were from the SSP3-7.0 scenario from the CEDS (shown in Fig. 2), as described by Hoesly et al. (2018). Oceanic emissions were from the POET 1990 data set (Olivier et al., 2003), and all biogenic emissions except isoprene and monoterpenes were based on 2001–2010 climatologies from the Model of Emissions of Gases and Aerosols from Nature under the Monitoring Atmospheric

Composition and Climate project (MEGAN-MACC) version 2.1 (Guenther et al., 2012). Isoprene and monoterpene emissions were generated interactively using the iBVOC parameterisation and were shown in Fig. 2c (Pacifico et al., 2011).

Temperature and horizontal wind fields were nudged (Telford et al., 2013) in the model run to the ECMWF ERA5 reanalyses for 2022 from ECMWF (Dee et al., 2011) to constrain the atmospheric conditions as close to the observations as possible. Nudging only occurred above ∼ 1200 m in altitude to avoid surface effects, and thus, the majority of the planetary boundary layer was not nudged.

A 6-month run from 1 March 2022, to 31 August 2022, was conducted with the nudged UKESM-AMIP model. In the UKESM-AMIP input environment settings, monthly sea surface temperature (SST) and sea ice concentration (SIC) under the SSP2-4.5 scenario were used. The first three months are considered the model spin-up. The output of the nudged UKESM-AMIP simulation was provided as monthly mean values, while the grid cells for Shanghai and Lishui were chosen as in Fig. 2.

2.3 Sensitivity experiments

To separate the effects of temperature, humidity, diurnal temperature variation, and temperature-dependent isoprene emissions, we defined 16 sensitivity configurations, summarised in Table 3.

Each of the 16 configurations was repeated at seven target temperatures from 25 to 40 °C at 2.5 °C increments, while all other settings were held according to the experiment definition. These follow the naming convention <location>_<RH>_<process>:

- *Location*. SH = Shanghai, urban background; LS = Lishui, rural background.
- *RH setting*. VRH = relative humidity varying with temperature, fixed absolute humidity (= RH 70 % at 30 °C); FRH = relative humidity fixed at 70 %, variable absolute humidity (see Table S2).

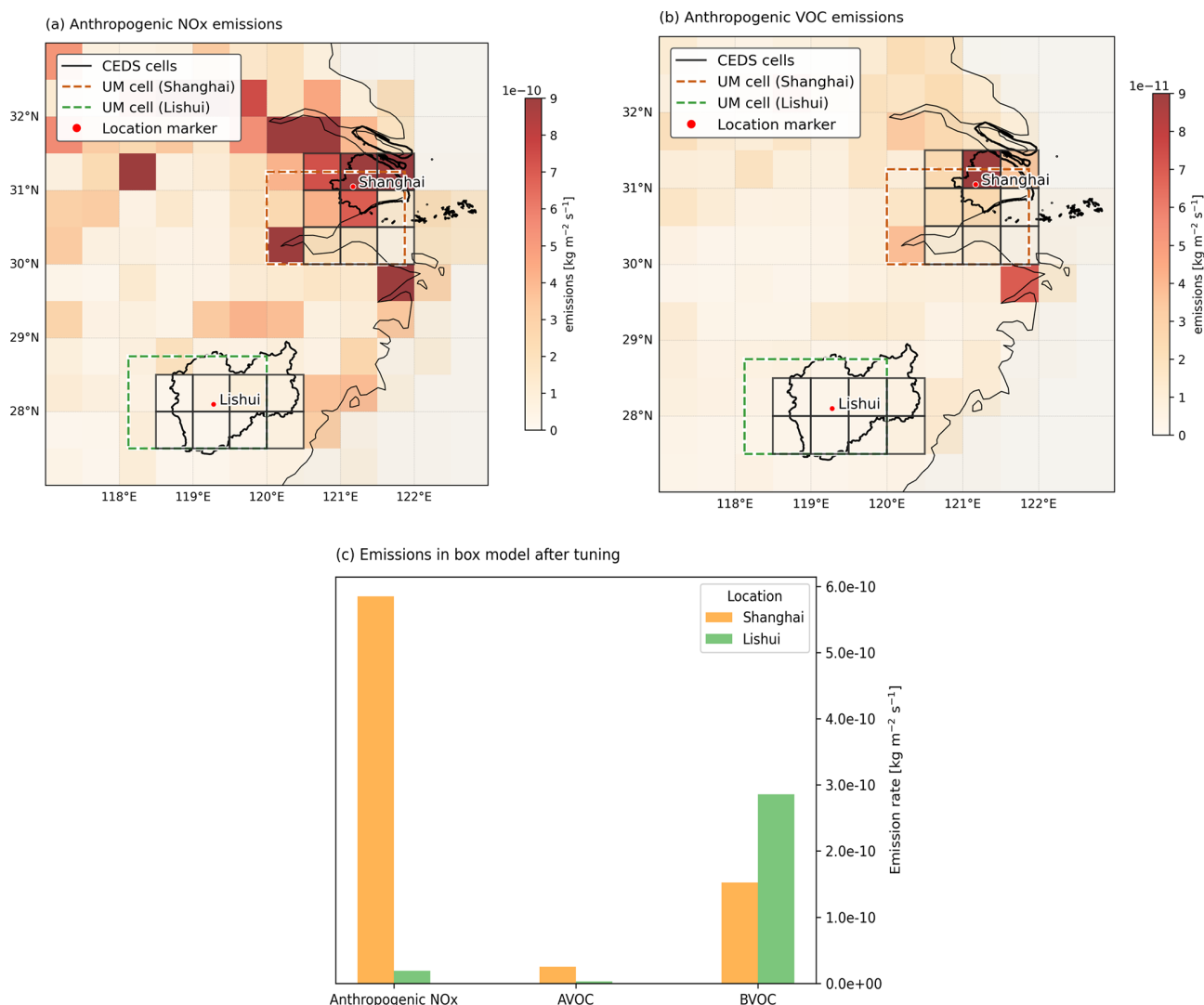


Figure 2. Anthropogenic and biogenic emission fields and box-model emission inputs. **(a)** CEDS anthropogenic NO_x emissions over the study region for JJA 2022 (kg NO m⁻² s⁻¹). **(b)** CEDS anthropogenic VOC species included in the box-model emission input, calculated as the sum of C₂H₆, C₃H₈, and HCHO emissions (kg VOC m⁻² s⁻¹). **(a, b)** Spatial selection used to define the Shanghai and Lishui model emissions: municipal outlines (black); Grey cells indicate the CEDS grid cells selected to calculate the Shanghai and Lishui anthropogenic emission inputs. The dashed orange (Shanghai) and green (Lishui) outlines show the corresponding grid cells used in the UKESM-AMIP and are included only to show their spatial relationship to the selected CEDS cells. **(c)** Final box-model emission inputs for anthropogenic NO_x, sum of AVOC species included in the box-model input, and BVOCs (units: kg m⁻² s⁻¹). Coastlines from Natural Earth (naturalearth-data.com). Administrative boundaries from the GADM database (<http://www.gadm.org>, last access: 11 March 2026).

- *Process*. D = diurnal cycle in air temperature enabled; ft = temperature-dependent isoprene emission factor ft enabled; Dft = both enabled; Ori = both disabled

The temperature-dependent isoprene-emission response and the two humidity configurations used in the sensitivity experiments are illustrated in Fig. 3.

Two binary switches modify the model processes: D and ft. D (diurnal temperature enabled) applies a realistic diurnal cycle to the target-temperature (daily maximum) day; when D is off, air temperature is held constant at the target value,

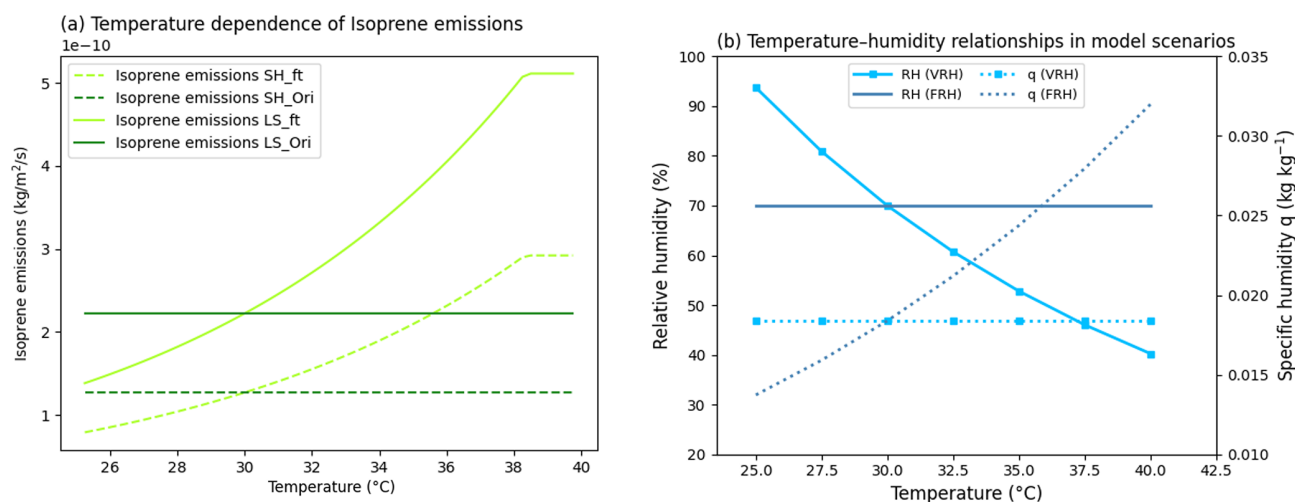
an extreme condition in which daily minimum values equal daily maximum values. The temperature-dependent isoprene emission factor ft enables the temperature response of isoprene.

The temperature response of isoprene followed the equations below:

$$\text{isoprene emissions} = \text{local summer average emissions} \cdot \text{ft} \quad (1)$$

Table 3. Sensitivity experiments of the UKCA Box Model (VRH = fixed absolute humidity (= RH 70 % at 30 °C); FRH = variable absolute humidity (= RH 70 %)).

Index	Experiment	RH	Diurnal cycle (D)	<i>T</i> -dependent isoprene emission (ft)	Environmental background
Shanghai – Variable RH (VRH)					Urban
1	SH_VRH_Ori	Change with <i>T</i>	No	No	Urban
2	SH_VRH_D	Change with <i>T</i>	Yes	No	Urban
3	SH_VRH_ft	Change with <i>T</i>	No	Yes	Urban
4	SH_VRH_Dft	Change with <i>T</i>	Yes	Yes	Urban
Lishui – Variable RH (VRH)					Rural
5	LS_VRH_Ori	Change with <i>T</i>	No	No	Rural
6	LS_VRH_D	Change with <i>T</i>	Yes	No	Rural
7	LS_VRH_ft	Change with <i>T</i>	No	Yes	Rural
8	LS_VRH_Dft	Change with <i>T</i>	Yes	Yes	Rural
Shanghai – Fixed RH (RH = 70 %)					Urban
9	SH_FRH_Ori	Fixed at 70 %	No	No	Urban
10	SH_FRH_D	Fixed at 70 %	Yes	No	Urban
11	SH_FRH_ft	Fixed at 70 %	No	Yes	Urban
12	SH_FRH_Dft	Fixed at 70 %	Yes	Yes	Urban
Lishui – Fixed RH (RH = 70 %)					Rural
13	LS_FRH_Ori	Fixed at 70 %	No	No	Rural
14	LS_FRH_D	Fixed at 70 %	Yes	No	Rural
15	LS_FRH_ft	Fixed at 70 %	No	Yes	Rural
16	LS_FRH_Dft	Fixed at 70 %	Yes	Yes	Rural

**Figure 3.** Model settings for the isoprene temperature dependence and the humidity scenarios. **(a)** Isoprene emission response to temperature used in the sensitivity configurations. Solid lines (LS) and dashed lines (SH) show cases with the temperature-dependent factor ft enabled (_ft) versus the baseline with ft disabled (_Ori, isoprene emissions constant with baseline conditions). The ft response increases with *T* and saturates at 38.3 °C; emission rates are shown in kg m⁻² d⁻¹ (left axis). **(b)** Two humidity scenarios respond to temperatures in humidity settings. The VRH case (lines with markers) applies temperature-dependent RH and constant *q*, while the FRH case (lines) holds constant RH and temperature-dependent *q*. Axes show RH (%) on the left and *q* (kg kg⁻¹) on the right.

The f_t is the isoprene temperature dependence factor (Pacífico et al., 2011):

$$f_t = e^{0.1 \cdot (T-30)} \quad \text{when } e^{0.1 \cdot (T-30)} < 2.3 \quad (T \text{ in } ^\circ\text{C})$$

$$f_t = 2.3 \quad \text{when } e^{0.1 \cdot (T-30)} \geq 2.3 \quad (T \text{ in } ^\circ\text{C})$$

Where T is temperature in centigrade.

In these experiments, isoprene emissions increase with temperature until they reach their plateau at 38.3 °C (as shown in Fig. 3); when f_t is off, isoprene emissions are temperature-independent.

The reference conditions were set at 30 °C and 70 % RH (mass mixing ratio of water (q) = 0.0184 kg kg^{−1}), representing the average environmental conditions in the 2022 JJA summer in the YRD based on observed values. Unless stated otherwise, pressure and boundary-layer height are held at the baseline values (Pressure = 1000 hPa, PBLH = 590 m), which are the averaged YRD summer conditions based on observations and ECMWF ERA5 reanalyses in 2022. Photolysis varies diurnally with the solar zenith angle at the site's latitude/longitude, so it shows a sinusoidal variation peaking at midday and being zero at night. The clouds were ignored, and all simulations are under clear-sky conditions. The location settings determine initial species levels.

The aim of UKCA Box sensitivity experiments is to quantify the local chemical and emission-related response to prescribed temperature and humidity conditions. The results should be interpreted as contributions within this controlled chemical framework, rather than as a full decomposition of all meteorological controls on the observed O₃-temperature relationship.

3 Results

3.1 Observed O₃ response to temperature and humidity variations

The observed relationships between daily maximum O₃ and daily maximum temperature in Shanghai and Lishui are shown in Fig. 4.

Across both data subsets (JJA and HW days), and at both locations (Shanghai and Lishui), O_{3max} increases with T_{max} , resulting in positive correlations. Averaged over eight Shanghai sites, the summertime O₃ fractional change per unit temperature change is 7.27 µg m^{−3} °C^{−1} with a 95 % confidence interval (CI) [5.13, 9.41] and $p < 0.01$. The corresponding mean sensitivity across three Lishui sites is 3.36 µg m^{−3} °C^{−1} (95 % CI [2.30, 4.41], $p < 0.01$).

This urban-rural contrast is consistent with differences in the chemical regime. As reported by Gu et al. (2020), Shanghai exhibits a strong VOC-limited regime in O₃ formation, where temperature increases enhance BVOC emissions while NO_x remains abundant, leading to a relatively strong ozone-temperature relationship. By contrast, the rural areas in YRD generally show higher VOC abundance, and

the effect of temperature is less pronounced than in VOC-limited areas because BVOC changes here have a negligible impact (Jin and Holloway, 2015). Those differences in chemical regimes are also supported by model simulation results in this study (Sect. 3.2; Fig. 6). Thus, the doubled O₃ sensitivity to temperature in Shanghai compared to Lishui is consistent with stronger NO_x availability and generally higher pollution levels in Shanghai, and may relate to the capacity for PAN thermal decomposition in the YRD (detailed PAN analysis see Fig. 10) (Steiner et al., 2010).

Regressions during HWs indicate a different behaviour at the two locations. In Lishui, the heatwave-period O_{3max}– T_{max} sensitivity is 4.05 µg m^{−3} °C^{−1} (95 % CI [0.203, 7.899], $p < 0.05$), indicating a significant positive association between O_{3max} and T_{max} during HW periods. By contrast, in Shanghai, the Ordinary Least Squares (OLS) slope estimated from heatwave days is 3.49 µg m^{−3} °C^{−1} with 95 % CI [−1.464, 8.441] ($p = 0.16$, $n = 41$), so a statistically significant linear association is not supported. The range of 95 % CI includes zero, indicating substantial uncertainty in the direction and magnitude of ozone's temperature response during the 2022 summer heatwaves in Shanghai. Including more historical heatwave data may help diagnose whether this loss of significance is due to insufficient data or suggest that additional heatwave co-factors (e.g., stagnation, humidity, precursor variability, or chemical regime shifts) could modulate the O₃– T linkage in Shanghai.

To examine the joint influence of temperature and humidity, Fig. 5 shows the observed daytime O₃ distribution across T –RH space in Shanghai and Lishui.

In both regions, RH decreases systematically with warming. In Shanghai, the typical RH spread within a given temperature bin is about 20 % (e.g. 45 %–65 % at 35 °C), with larger variability at lower T and progressively narrower ranges at higher T (Fig. 5c). Lishui shows a similar tendency, with most samples concentrated between 32–37 °C and 35 %–55 % RH (Fig. 5d). Across the observed T –RH space, O₃ increases with temperature and decreases with RH, indicating a preference for warm, dry conditions.

Linear regression of RH on T yields slopes of −2.429 % °C^{−1} for Shanghai and −3.191 % °C^{−1} for Lishui ($p < 0.01$ in both cases). The weaker slope in Shanghai, together with its narrower T range, is consistent with the moderating influence of sea-land thermal and moisture exchanges on coastal boundary-layer conditions, whereas the steeper slope in Lishui reflects a greater propensity for hot-dry excursions in a forested inland setting. The RH– T co-variation is much tighter in Shanghai ($R^2 = 0.83$) than in Lishui ($R^2 = 0.57$): in Shanghai the highest-density region (Fig. 5c) and the strongest O₃ increases (Fig. 5a) lie close to the regression line, implying that the linear T –RH relationship provides a good description of typical warm-season daytime conditions and of the pathway along which O₃ responds to combined warming and drying. In Lishui, by contrast, the main density maximum lies above the regression

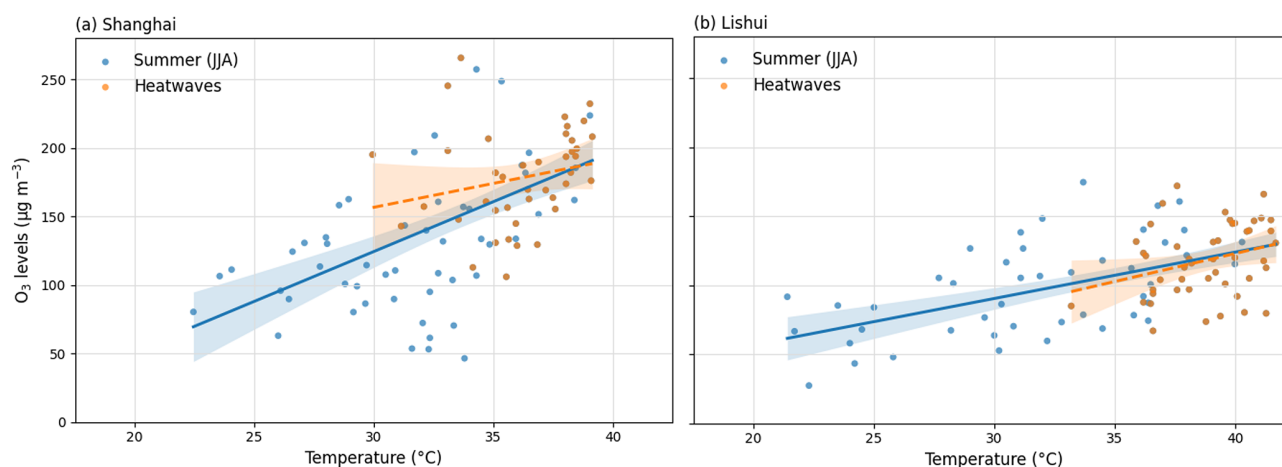


Figure 4. Relationship between observed daily maximum surface ozone concentration and air temperature (based on hourly data) during the summer of 2022 (JJA; blue) and heatwave days (orange; definition see Sect. 2.1) for (a) Shanghai and (b) Lishui. Points are the daily maximum values (average values for sites; spatial distribution shown in Fig. 1); solid (JJA) and dashed (heatwave) lines are ordinary-least-squares fits. Shaded envelopes show the 95 % confidence intervals for the fitted lines.

line and does not coincide with the dominant O_3 -increase pathway, indicating that the fitted slope is influenced by a smaller number of hot, anomalously dry episodes. This behaviour is consistent with previous studies reporting that Lishui RH conditions are dominated by strong evapotranspiration from vegetation and soils, which is negatively correlated with temperature over the YRD in summer (Wang et al., 2023). In addition, stomatal closure under low-humidity conditions, which always corresponds to high-temperature conditions, would reduce O_3 dry deposition and further enhance O_3 levels (Kavassalis and Murphy, 2017), contributing to the high- O_3 tail at the hot, dry end of the Lishui distribution.

In Fig. 5c and d, we compare relative humidity from the VRH model configuration used in the subsequent simulations – defined by a conserved absolute humidity equal to the regional JJA 2022 mean ($q = 0.0184 \text{ kg kg}^{-1}$) – with the observed T -RH distribution. The VRH curve follows the locus of highest observational density in both Shanghai and Lishui, indicating that this configuration provides a realistic representation of the humidity-temperature conditions sampled in 2022 and is therefore suitable as the baseline humidity scenario for the box-model experiments.

Overall, Fig. 5 demonstrates that hot, dry conditions are favourable for elevated O_3 at both sites, but that the joint T -RH- O_3 variability differs between the coastal megacity and the forest-surrounded inland region: Shanghai exhibits a stronger, more coherent O_3 - T -RH relationship in summer 2022 than Lishui, reflecting differences in local meteorology, surface characteristics, precursor emissions and chemical regime.

To interpret these observed O_3 -temperature-humidity relationships in terms of process contributions and mechanisms, we next use an observation-constrained box model to quantify the extent to which the observed high-temperature O_3

response can be explained by changes in local chemical kinetics, precursor abundances, temperature diurnal cycles, and humidity conditions. Furthermore, the mechanisms underlying process contributions will be explored through budget-level simulations.

3.2 Chemical-regime diagnosis and process consistency of the box model

This section evaluates whether the UKCA Box model provides chemically plausible Shanghai-like and Lishui-like environments for the subsequent temperature-sensitivity experiments. The purpose is not to perform a formal model evaluation against observations or to use UKESM as an observational benchmark. Instead, we use three complementary diagnostics: (i) local O_3 responses to perturbations in NO_x and VOC emissions, (ii) contextual comparison of selected short-lived chemical species with available observations, and (iii) comparison of O_x production and loss pathways between the box model and the same-chemistry UKESM-AMIP simulation.

To establish the precursor-sensitivity regimes underlying the subsequent O_3 -temperature analysis, Fig. 6 examines the O_3 response to NO_x and VOC changes using O_3 - NO_x -isoprene response surfaces at 30°C and $\pm 10\%$ precursor perturbations across 25 to 40°C .

Figure 6 summarises the box-model sensitivity experiments used to diagnose precursor regimes in Shanghai (Fig. 6a and c) and Lishui (Fig. 6b and d). The baseline experiments, where there are no other processes but chemical reaction rates and pathways changing with temperature (marked as Ori), are consistent with the observed conditions in the 28.75 – 31.25°C temperature bin. In Shanghai, the daily-mean O_3 is $63.7 \mu\text{g m}^{-3}$ in the model versus

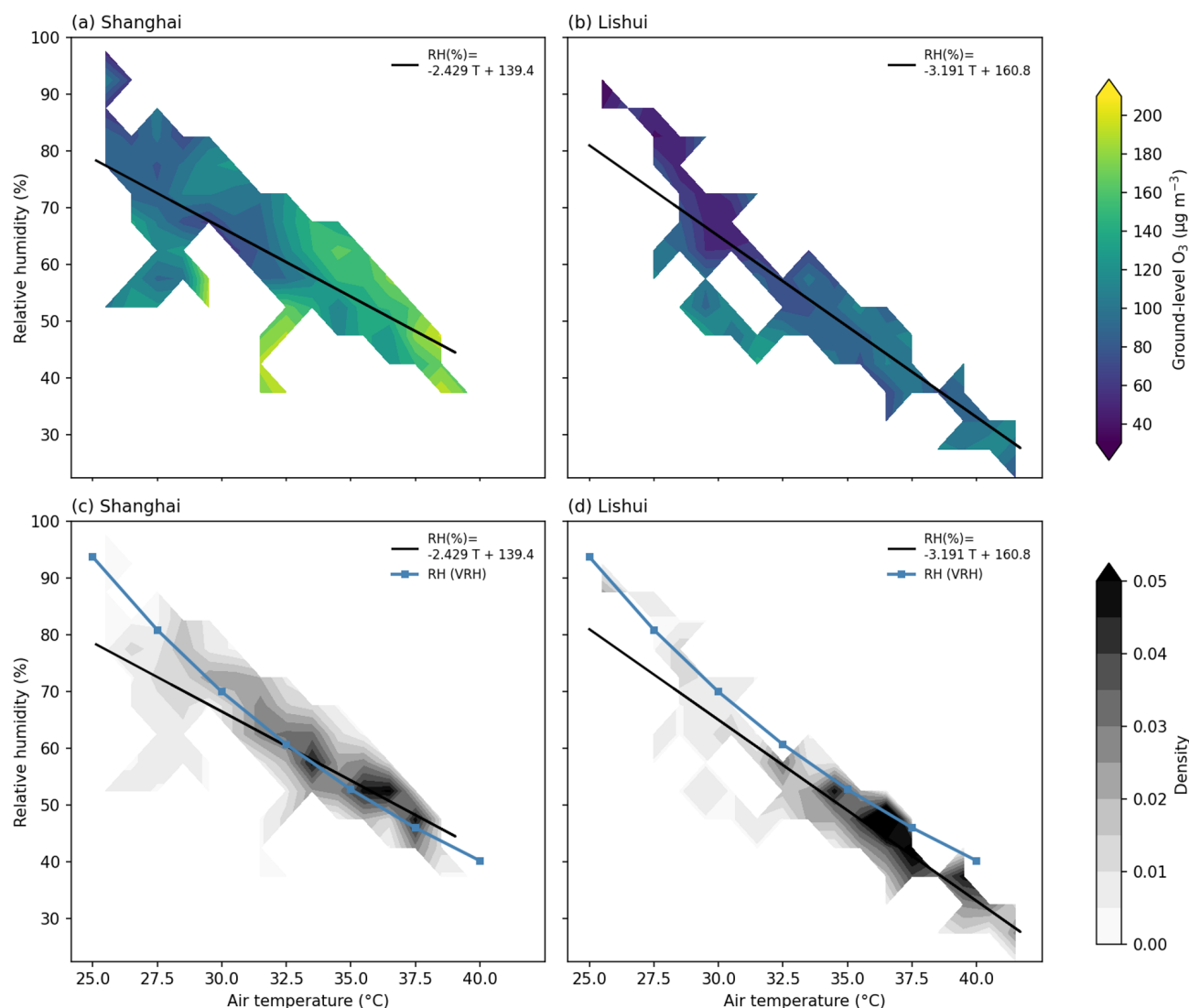


Figure 5. Observed air temperature–relative humidity space for (a, c) Shanghai and (b, d) Lishui (daytime, $T \geq 25^\circ\text{C}$). Panels (a)–(b) show the ground-level O₃ ($\mu\text{g m}^{-3}$) binned on a $1^\circ\text{C} \times 5\%$ RH grid; panels (c)–(d) show the data density (fraction of site samples per bin) on the same grid. The solid black line in each panel is the ordinary-least-squares fit of RH to T from the unbinned 3-hourly records. Ozone: hourly observations averaged from 8 AQMS (Shanghai) and 3 AQMS (Lishui); meteorology: three-hourly MMS data; all aggregated to 3 h means. The blue solid line with square markers in panels (c)–(d) is the RH curve with conserved absolute humidity ($q = 0.0184 \text{ kg kg}^{-1}$) used in the VRH model scenario.

$69.5 \mu\text{g m}^{-3}$ in the observations. In Lishui, the corresponding values are $35.8 \mu\text{g m}^{-3}$ (model) and $52.5 \mu\text{g m}^{-3}$ (observations), a low bias that is consistent with Lishui being NO_x-limited (see below) and suggests that the grid-cell-average NO_x levels in the box configuration are lower than those sampled by the monitoring site.

Panels (a) and (b) show the simulated O₃ response surfaces in NO_x–isoprene concentration space at 30°C for Shanghai and Lishui, respectively. The Shanghai baseline lies within a VOC-limited regime, where O₃ increases with isoprene and decreases with increasing NO_x. In contrast, the Lishui base-

line lies within a NO_x-limited regime, where O₃ responds positively to NO_x and only weakly to additional isoprene.

The local $\pm 10\%$ perturbations show consistent precursor responses across the investigated temperature range. In Shanghai (Fig. 6c), O₃ decreases with higher NO_x emissions and increases with higher VOC emissions from 25 to 40°C , indicating a VOC-limited regime (Pusede et al., 2015). This VOC-limited behaviour is consistent with the high-NO_x, anthropogenically dominated environment of Shanghai and agrees with Liu et al. (2021b)'s study on the effectiveness of emission control strategies in China's major urban areas. In contrast, Lishui (Fig. 6d) exhibits the opposite

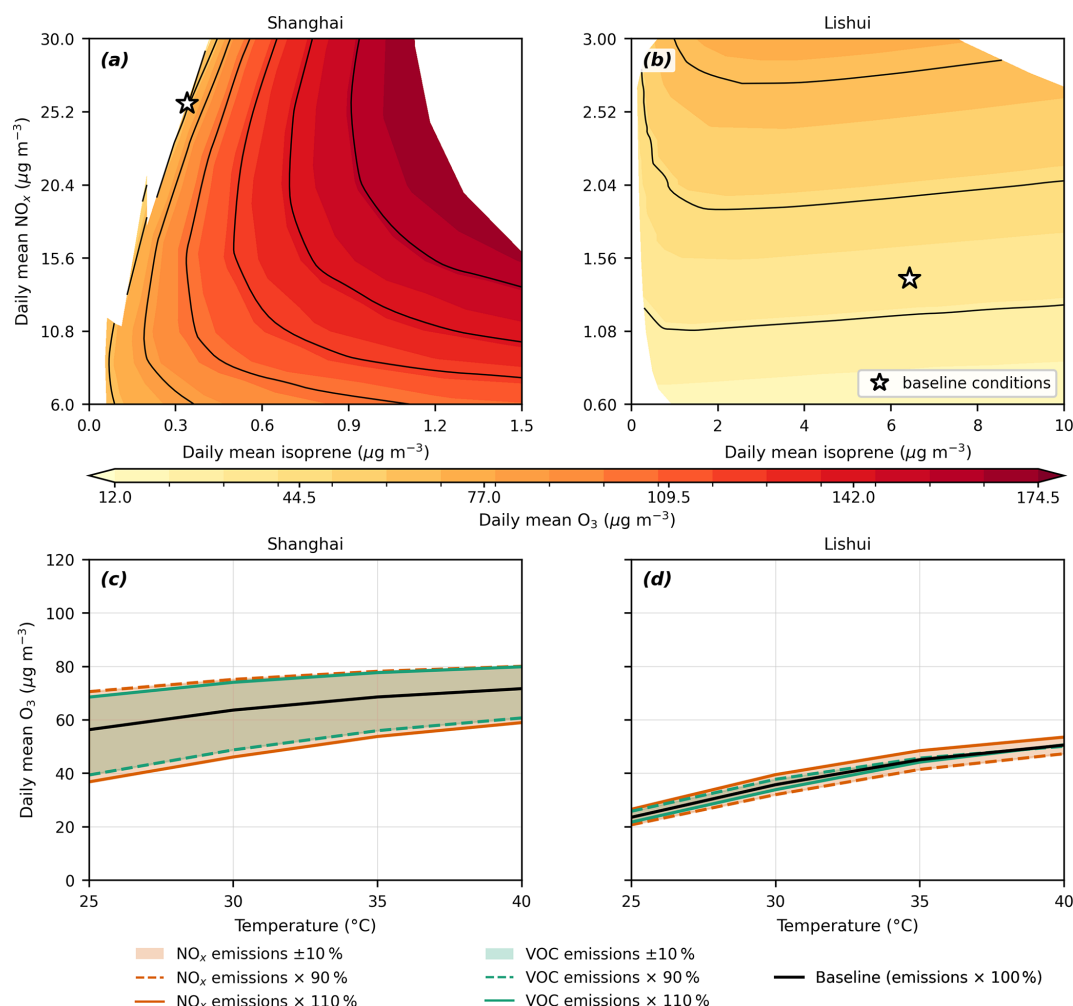


Figure 6. Simulated precursor sensitivity of daily mean surface O_3 in Shanghai and Lishui using the UKCA Box Model under the VRH_Ori baseline configuration with emission changes. Panels (a) and (b) show box model simulations of the evolution of ozone as a function of NO_x ($NO + NO_2$) and isoprene at $30^{\circ}C$. Colours indicate daily mean O_3 , black lines denote O_3 contours, and white stars mark the baseline conditions. Panels (c) and (d) show the temperature dependence of O_3 under $\pm 10\%$ perturbations in NO_x and VOC emissions at 25, 30, 35, and $40^{\circ}C$.

tendency: O_3 increases with NO_x enhancement and is only weakly affected by VOC perturbations, signifying a NO_x -limited regime (Utembe et al., 2018). This behaviour is characteristic of rural or suburban photochemical environments influenced by regional BVOC emissions and relatively low NO_x levels (Sillman, 1999).

The signs of these responses remain unchanged between 25 and $40^{\circ}C$, indicating no regime reversal within the tested perturbation range. These experiments therefore establish contrasting VOC-limited and NO_x -limited baseline environments for interpreting the subsequent O_3 -temperature and O_x budget analyses.

The simulated PAN, OH, HO_2 , and C_5H_8 concentrations are compared with the available observational references in Table 4.

The model values in Table 4 are from baseline experiments (Ori) at $30^{\circ}C$. The simulated PAN and C_5H_8 concentrations are consistent in order of magnitude with the reported observations. Direct summertime OH and HO_2 measurements are not available for urban Shanghai, so the winter Shanghai measurements provide the closest direct urban reference. Same-site measurements in other cities show that daytime OH is approximately 2–5 times higher in summer than in winter, while the summer-to-winter difference in HO_2 ranges from little seasonal change to a factor of approximately 5 (Heard et al., 2004; Kanaya et al., 2007; Ren et al., 2006). The Shanghai observations therefore provide a well-defined urban reference for the magnitude of HO_x , while the Taizhou measurements provide the corresponding warm-season YRD comparison.

Table 4. Comparison of PAN, OH, HO₂, and C₅H₈ levels in observation and UKCA Box Model.

Species	Environment	Location	Year	Period	Value type	Value (µg m ⁻³)	Source type	Reference
PAN	Urban	Shanghai	2017	Summer	Seasonal mean	4.4	Observation	Zhang et al. (2021)
	Urban	Shanghai	2022	Summer	Daily mean	7.1	UKCA Box	This study
	Suburban	Hangzhou	2021	Summer	Daily mean	6.7	Observation	Wu et al. (2023)
	Background	Nanjing	2020	Summer	Daily mean	2	Observation	Xu et al. (2024)
	Rural	Lishui	2022	Summer	Daily mean	3.6	UKCA Box	This study
OH	Urban	Shanghai	2019	Nov–Dec	Noon mean (11:00–13:00)	7.6×10^{-5}	Observation	Zhang et al. (2022)
	Urban	Shanghai	2022	Summer	Noon mean (11:00–13:00)	2.6×10^{-4}	UKCA Box	This study
	Suburban	Taizhou	2018	May–Jun	Daily maximum	3.0×10^{-4}	Observation	Ma et al. (2022b)
	Rural	Lishui	2022	Summer	Daily mean	1.4×10^{-5}	UKCA Box	This study
HO ₂	Urban	Shanghai	2019	Nov–Dec	Noon mean (11:00–13:00)	4.4×10^{-3}	Observation	Zhang et al. (2022)
	Urban	Shanghai	2022	Summer	Noon mean (11:00–13:00)	1.0×10^{-2}	UKCA Box	This study
	Suburban	Taizhou	2018	May–Jun	Daily maximum	6.2×10^{-2}	Observation	Ma et al. (2022b)
	Rural	Lishui	2022	summer	Daily mean	2.9×10^{-2}	UKCA Box	This study
C ₅ H ₈	Urban	Shanghai	2018	July	Daily mean	0.8	Observation	Gu et al. (2022)
	Urban	Shanghai	2022	summer	Daily mean	0.3	UKCA Box	This study
	Rural	Lishui	2009	September	Daytime average	8.3	Observation	Geng et al. (2011)
	Rural	Lishui	2022	summer	Daytime average	7.4	UKCA Box	This study

The corresponding O_x production and loss pathways in the UKCA Box model and UKESM-AMIP are compared in Fig. 7.

Figure 7 compares the fractional O_x production and loss pathways in the UKCA Box model with those simulated by UKESM-AMIP using the same UKCA chemical mechanism. The UKESM-AMIP simulation is used as a three-dimensional context for interpreting the box-model O_x budget, because it includes physical processes that are absent from the 0-D box configuration, such as transport, boundary-layer mixing, convection, and meteorological variability.

The Box Model reproduces the rank order of production pathways in the nudged UKESM-AMIP model. In Shanghai, the total O_x production flux is $1.62 \times 10^{-9} \text{ kg m}^{-2} \text{ s}^{-1}$ in the Box model versus $2.03 \times 10^{-9} \text{ kg m}^{-2} \text{ s}^{-1}$ in the UKESM model. And in Lishui, this O_x production flux is $4.10 \times 10^{-10} \text{ kg m}^{-2} \text{ s}^{-1}$ in the Box model, while this value is $8.40 \times 10^{-10} \text{ kg m}^{-2} \text{ s}^{-1}$ in the UKESM.

In both cities, peroxy-NO reactions (HO₂ + NO and RO₂/CH₃O₂ + NO) dominate the chemical production fraction in the box model, matching the pattern in UKESM and consistent with summertime O₃ photochemistry described by Ma et al. (2022b). This agreement in fractional chemistry indicates that the box model captures the regime (NO_x-VOC-OH coupling) rather than simply tuning totals. Chemical loss through O(¹D) + H₂O → 2OH and radical-ozone reactions (HO₂ + O₃, OH + O₃) is represented with similar sign and relative importance in both frameworks.

The UKCA Box simulation shows a larger fractional contribution from dry deposition to the O_x sink (Fig. 7a–b). In the 3-D UKESM simulations, this sink is explicitly divided into deposition and dynamical export (dynamical export refers to physical transport and mixing, including horizon-

tal advection, vertical entrainment with the growing boundary layer, shallow/deep convection, and ventilating outflow; not included in Fig. 7). In contrast, the box model treats the air parcel as a closed, well-mixed volume with no transport, so all non-chemical removal must appear as a lower-boundary deposition term. According to the monthly mean O₃ levels from June to August (UKESM) and the trend of daily mean O₃ levels (UKCA box model), both UKESM and UKCA Box produce nearly constant surface O₃, indicating that the net O_x tendency is close to zero. In UKESM, this large residual (“UKESM sum”) reflects the contribution of dynamical export. In the box model, the production-loss balance is achieved by having chemical production intentionally offset by the parameterised dry-deposition term, leaving only a small net production or loss. The larger deposition fraction in UKCA Box should therefore be interpreted as representing the combined effect of true surface uptake and the export processes, which are explicitly resolved in UKESM.

Overall, Fig. 6, Table 4, and Fig. 7 support the use of the UKCA Box model as a controlled chemical-process diagnostic. The model reproduces the expected contrast between a VOC-sensitive Shanghai-like environment and a NO_x-sensitive Lishui-like environment, and its dominant O_x production and loss pathways are broadly consistent with the same-chemistry UKESM simulation, while the differences illustrate the impact of absent physical drivers in the Box model. At the same time, the comparison does not constitute a formal validation of absolute O₃ concentrations, especially for Lishui, where monitoring-site observations and the regional box-model environment represent different spatial scales. The following sections therefore interpret the box-model experiments primarily in terms of relative process sen-

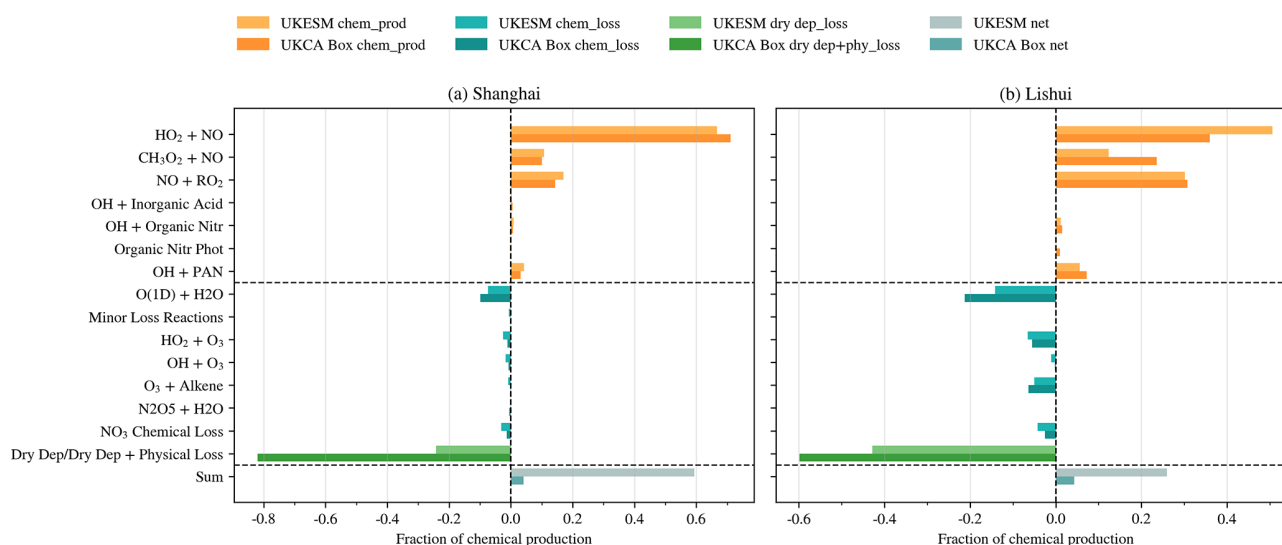


Figure 7. O_x production-loss budget by process category for two models at two sites. Panels (a)–(b) show the fractional contribution to total chemical production (unitless) from each reaction class. Positive bars denote chemical production (orange tones), negative bars denote chemical loss (teal tones) and dry deposition (UKESM) / dry deposition + physical transport (UKCA Box) loss (green tones); the grey bar at the far right gives the net sum. Darker shades represent UKESM and lighter shades the UKCA Box. Reaction classes on the y axis include major O_x production and loss pathways. (a) Shanghai; (b) Lishui. Box model simulations were conducted under baseline conditions (Ori settings, 30 °C, and 70 % RH). The JJA averaged temperature and humidity in UKESM are 27.1 °C and 71.9 % RH.

sitivity and chemical-regime behaviour, rather than as direct simulations of monitored O_3 concentrations.

3.3 Temperature responses of ozone in the box model and observations

The observed and simulated $O_{3\max}-T_{\max}$ relationships are compared in Fig. 8.

Figure 8 compares observed JJA $O_{3\max}-T_{\max}$ relationships in the VRH set of experiments with the UKCA Box Model: Ori (reference – fixed temperature and isoprene emissions across all hours of day), D (diurnal temperature cycle only), ft (temperature-dependent isoprene only), and Dft (both). The main purpose of these sensitivity experiments is to evaluate the impact of those processes on O_3 's temperature responses. In the box model simulations, the VRH experiments exhibit a trend in RH-temperature that resembles reality; thus, these experiments are considered reasonably good evaluators of the box model's performance when compared with observations.

Shanghai (urban; Fig. 8a). Above 30 °C, the ft and Dft simulations exhibit significant coordination in both ozone concentrations and trend, indicating that the temperature dependence of isoprene emissions explains most of the observed sensitivity in this regime. Relative to Ori and D, both ft and Dft lift O_3 by about 20 to 40 $\mu\text{g m}^{-3}$ at 32.5–37.5 °C and reproduce the monotonic increase with temperature. At $T < 30$ °C, observations align more closely with Ori/D, whereas ft/Dft are low-biased. Two factors likely contribute: (i) wider uncertainty at the cool end (grey 95 %

CI band) owing to fewer low-temperature days in summer 2022, and (ii) meteorological controls (e.g., mixing depth, advection, cloudiness) that covary with temperature but are not explicitly represented in the box model, which isolates chemical responses. At the upper tail, the simulated slope weakens because the applied isoprene function saturates at ~ 38.3 °C, reducing the Dft (and ft) response from 9.3 $\mu\text{g m}^{-3} \text{ °C}^{-1}$ between 35–37.5 °C to 2.1 $\mu\text{g m}^{-3} \text{ °C}^{-1}$ between 37.5–40 °C; the observations maintain a steeper gradient ($\approx 12 \mu\text{g m}^{-3} \text{ °C}^{-1}$). The different isoprene emission threshold might be the cause, since suppression of isoprene emissions was not observed in the 10–40 °C range in Shanghai (Gu et al., 2022). And additional heat-linked processes (e.g., boundary-layer dynamics, anthropogenic VOCs, or NO_x variability) may continue to amplify O_3 at extreme temperatures.

Lishui (rural; Fig. 8b). The simulations reproduce the shape of the observed O_3-T curve, but the simulated O_3 is systematically low-biased by about 50 $\mu\text{g m}^{-3}$. This offset is consistent with site representativeness (i.e. the observations exhibit a populated area in Lishui where NO_x emissions are higher than the box model simulations, which cover the whole Lishui region, most of which are rural areas). Importantly, introducing temperature-dependent isoprene (ft/Dft) yields only minor changes relative to Ori/D, indicating that Lishui operates largely in a NO_x -limited regime where additional VOC reactivity produces only modest O_3 increases, i.e. including T -dependence for isoprene leads to higher VOC levels, but this doesn't increase O_3 in Lishui, whereas

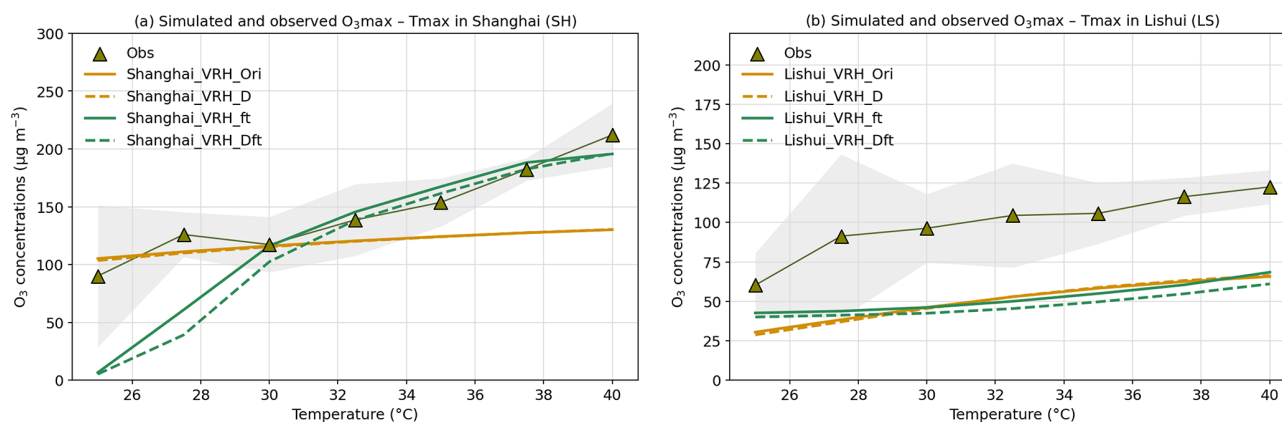


Figure 8. Comparison of observed and simulated O_3 _{max}– T_{max} relationships for (a) Shanghai and (b) Lishui (summer, JJA). Observations are shown as olive triangles connected by a line; the grey envelope denotes the 95 % confidence interval of the observed bin means (2.5 $^{\circ}\text{C}$ T_{max} bins; e.g., the 25 $^{\circ}\text{C}$ bin denotes summer days with T_{max} 23.75–26.25 $^{\circ}\text{C}$). Colored solid/dashed lines show the four model configurations (VRH_Ori, VRH_D, VRH_ft, VRH_Dft; see Table 3).

it does in Shanghai. The small influence of the D option confirms that, after binning by T_{max} , imposing a diurnal temperature cycle alone does not substantially alter daily O_3 _{max} in this case.

Overall, the VRH experiments show that the UKCA Box captures the observed temperature sensitivity of O_3 when the isoprene-temperature coupling is represented (Shanghai), while the weak ft/Dft effect at Lishui is consistent with NO_x limitation. Discrepancies at low temperatures and in the highest bins highlight the role of meteorology and extreme-heat processes that lie outside the box configuration, motivating targeted sensitivity tests (e.g., boundary-layer depth, deposition, NO_x variability) in future work.

The resulting changes in O_3 _{max} between 30 and 40 $^{\circ}\text{C}$ are quantified in Table 5.

Table 5 presents the increase in O_3 _{max} from 30 to 40 $^{\circ}\text{C}$ for the observations and the box model experiments. Because the experiments differ only in the process switched on, we quantify each process's contribution to the O_3 warming response by comparing the simulated 30 to 40 $^{\circ}\text{C}$ change. For each experiment X , we define $\Delta O_3^X = O_3^X(40^{\circ}\text{C}) - O_3^X(30^{\circ}\text{C})$, and similarly, ΔO_3^{obs} from the observations. All metrics below are expressed as fractions of ΔO_3^{obs} and therefore dimensionless. The net chemical response is $f_{\text{chem}} = \Delta O_3^{\text{VRH_Ori}} / \Delta O_3^{\text{obs}}$, i.e., the fraction of the observed 30 to 40 $^{\circ}\text{C}$ increase that can be explained by temperature-dependent gas-phase chemistry alone under VRH conditions. The additional effect of each process is then quantified as the incremental fraction of ΔO_3^{obs} gained when that process is switched on: for the diurnal cycle, $f_{\text{diurnal}} = (\Delta O_3^{\text{VRH_D}} - \Delta O_3^{\text{VRH_Ori}}) / \Delta O_3^{\text{obs}}$; for the isoprene temperature dependence, $f_{\text{iso}} = (\Delta O_3^{\text{VRH_ft}} - \Delta O_3^{\text{VRH_Ori}}) / \Delta O_3^{\text{obs}}$; and for humidity, $f_{\text{humid}} = (\Delta O_3^{\text{FRH}} - \Delta O_3^{\text{VRH}}) / \Delta O_3^{\text{obs}}$. Positive values indicate that the process amplifies the increase in O_3 with temperature, whereas negative values indicate damping.

This normalisation allows us to directly compare the extent to which the observed O_3 -temperature sensitivity can be attributed to each process at the two sites. Notably, due to the nature of the 0-D box-model (no transport, clouds, or physical feedbacks), this attribution should be interpreted as under a controlled chemical framework instead of a full decomposition of all meteorological controls.

In Shanghai, decomposition of the O_x budget shows that the net chemical term accounts for 18.7 % of the observed 30 to 40 $^{\circ}\text{C}$ increase, while the diurnal temperature cycle alone has a negligible effect on the net chemistry. By contrast, the temperature dependence of isoprene emissions explains 69.1 % of the observed O_3 rise, identifying this pathway as the dominant driver of the warm-season O_3 - T slope in urban Shanghai. When isoprene's temperature sensitivity is enabled, the diurnal cycle yields an additional 14.3 % O_3 increment, consistent with enhanced photolysis and radical propagation during warmer, sunnier hours reported in YRD (Xia et al., 2022).

Humidity acts as an important modulator of the O_3 -temperature response. In our experiments, increasing RH by about 30 % at 40 $^{\circ}\text{C}$ (FRH: $q = 0.0320 \text{ kg kg}^{-1}$, RH = 70 %; VRH: $q = 0.0184 \text{ kg kg}^{-1}$, RH = 40.2 %), while keeping the temperature diurnal cycle and isoprene temperature dependence switched on (VRH_Dft settings), leads to a $21.9 \mu\text{g m}^{-3}$ reduction in O_3 _{max} at 40 $^{\circ}\text{C}$. Expressed as a fraction of the observed 30 to 40 $^{\circ}\text{C}$ change, this contribution is $(\Delta O_3^{\text{FRH_Dft}} - \Delta O_3^{\text{VRH_Dft}}) / \Delta O_3^{\text{obs}}$. This humidity-driven decrease reflects the role of water vapour in enhancing O_x loss via $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ pathway: in the FRH case, the vertically integrated $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ flux ($\text{kg m}^{-2} \text{ s}^{-1}$) increases by about 42 %, strengthening the O_3 decomposition pathway and offsetting part of the thermally driven O_3 enhancement.

In the NO_x -limited regime (i.e. Lishui), the process attribution gives different results. The chemical response itself

Table 5. Changes in daily maximum O₃ ($\Delta O_{3\max}$) from 30 to 40 °C. Unit: $\mu\text{g m}^{-3}$.

Scenario	Observation	FRH_Ori	VRH_Ori	FRH_D	VRH_D	FRH_ft	VRH_ft	FRH_Dft	VRH_Dft
ΔO_3 in Shanghai	94.77	14.05	17.75	14.63	18.68	62.02	83.26	74.96	96.83
ΔO_3 in Lishui	26.21	11.66	21.08	13.04	22.4	14.43	23.81	12.43	21.57

explains 80.4 % of the observed 30 $\rightarrow$ 40 °C change, implying that enhanced photochemistry at higher temperatures – through faster reaction rates and stronger actinic flux – dominates the O₃ increase (Archibald et al., 2020b). The isoprene temperature dependence contributes only 10.4 %, consistent with a NO_x-limited environment where additional VOC reactivity produces comparatively small changes in O₃ production (Steiner et al., 2006). The diurnal temperature cycle makes only a minor contribution to the 30 $\rightarrow$ 40 °C O₃ increase, whereas the humidity perturbation is non-negligible. When RH is raised from 40.2 % to 70 % at 40 °C (VRH: $q = 0.0184 \text{ kg kg}^{-1}$; FRH: $q = 0.0320 \text{ kg kg}^{-1}$) under the VRH_Dft settings, the resulting change in humidity accounts for $9.1 \mu\text{g m}^{-3}$ of O_{3max} reduction. O_x budget diagnostics show that this damping arises from two linked effects of higher water vapour: a reduction in O_x production via the HO₂ + NO channel (≈ 15.3 % reduction in FRH scenarios compared with that in VRH scenarios), and an enhancement of O_x loss via O₃ photolysis followed by O(¹D) + H₂O (≈ 36.9 % compared with VRH scenarios). Both mechanisms are consistent with Li et al. (2021), who showed that elevated relative humidity suppresses O₃ generation by inhibiting the OH/HO₂-NO₂ chain and promotes O₃ loss through the O(¹D) + H₂O pathway.

Taken together, Fig. 8 and Table 5 demonstrate that the UKCA Box model produces a physically interpretable decomposition of the O₃-temperature relationship: isoprene-temperature coupling is decisive in Shanghai, while baseline chemical partitioning and humidity dominate in Lishui. These site-specific attributions align with the contrasting chemical regimes and underscore the need to represent both biogenic VOC responses and meteorologically linked processes when projecting O₃ extremes under warming.

3.4 Temperature response on O_x, PAN, and HO_x diurnal cycles

The temperature dependence of the O_x budget is examined through its diurnal evolution in Fig. 9 and the corresponding daily integrated production and loss terms in Table 6.

Figure 9, Tables 6 and 7 summarise how O_x production and loss terms from the UKCA Box Model respond to temperature. In Shanghai (Fig. 9a–d; Table 6), all major production pathways increase with temperature, except for organic-nitrate photolysis (labelled ORG NITR PHOT in Table 6), which has a minor impact on total production. From Fig. 9a–d, the reaction HO₂ + NO $\rightarrow$ OH + NO₂ is the dom-

inant and most temperature-sensitive source of O_x production. Although its marginal sensitivity (change in O_x production per °C) weakens from 25 $\rightarrow$ 40 °C, it remains the single largest contributor. The second key source, RO₂ + NO $\rightarrow$ RO + NO₂, displays the opposite behaviour – its temperature sensitivity strengthens with warming. From 35 to 40 °C, the contribution of RO₂ + NO to total O_x production increases by $207.7 \text{ t O}_x \text{ d}^{-1}$ in Shanghai, nearly doubling the increase from 25 to 30 °C, underscoring the growing role of peroxy-radical chemistry at high temperatures. This growth is consistent with high-temperature partitioning of the OH-HO₂-RO₂ cycle – most notably the HO₂ + NO channel – and with the well-documented increase in effective VOC reactivity under hot conditions due to both faster kinetics and temperature-sensitive VOC emissions (e.g. isoprene) (Meng et al., 2023). Even with reduced temperature sensitivity, the HO₂ + NO reaction accounted for more than 50.1 % of total chemical production, confirming the importance of the HO₂-NO pathway in the urban regime.

For chemical loss in Shanghai, O(¹D) + H₂O $\rightarrow$ 2OH is the leading term. Its temperature sensitivity is $55.01 \text{ t O}_x \text{ d}^{-1} \text{ °C}^{-1}$ between 25–35 °C, decreasing to $\sim 36.74 \text{ t O}_x \text{ d}^{-1} \text{ °C}^{-1}$ from 35–40 °C, consistent with partial saturation of midday photolysis at the hottest conditions. In the total budget, however, deposition dominates loss. O₃ dry deposition exhibits the stronger temperature sensitivity, which maximises between 25–35 °C, whereas NO_y deposition varies less with temperature but remains the largest absolute sink at all temperatures, controlling the sign of the net O_x tendency. As deposition in the UKCA Box Model serves both as deposition and as physical loss, the magnitude comparison is not so useful.

In Lishui (Fig. 9e–h; Table 7), both production and loss magnitudes are substantially smaller than in Shanghai, consistent with lower precursor loadings in rural southwestern Zhejiang and the prevalence of NO_x-limited chemistry outside urban cores in the YRD (An et al., 2021; Ren et al., 2022). HO₂ + NO is still the largest single production term, but at $T > 30$ °C its strength becomes comparable to CH₃O₂ + NO and RO₂ + NO, indicating a more distributed peroxy-NO contribution in the regional background. For chemical loss, O(¹D) + H₂O dominates from 25–30 °C. At temperatures higher than 30 °C, O₃ + ALKENE reactions' contribution grows rapidly with temperature and becomes comparable in magnitude to O(¹D) + H₂O, highlighting the role of thermally enhanced VOC-ozone chemistry outside the urban core where the O₃ + C₅H₈ reaction plays a crucial role.

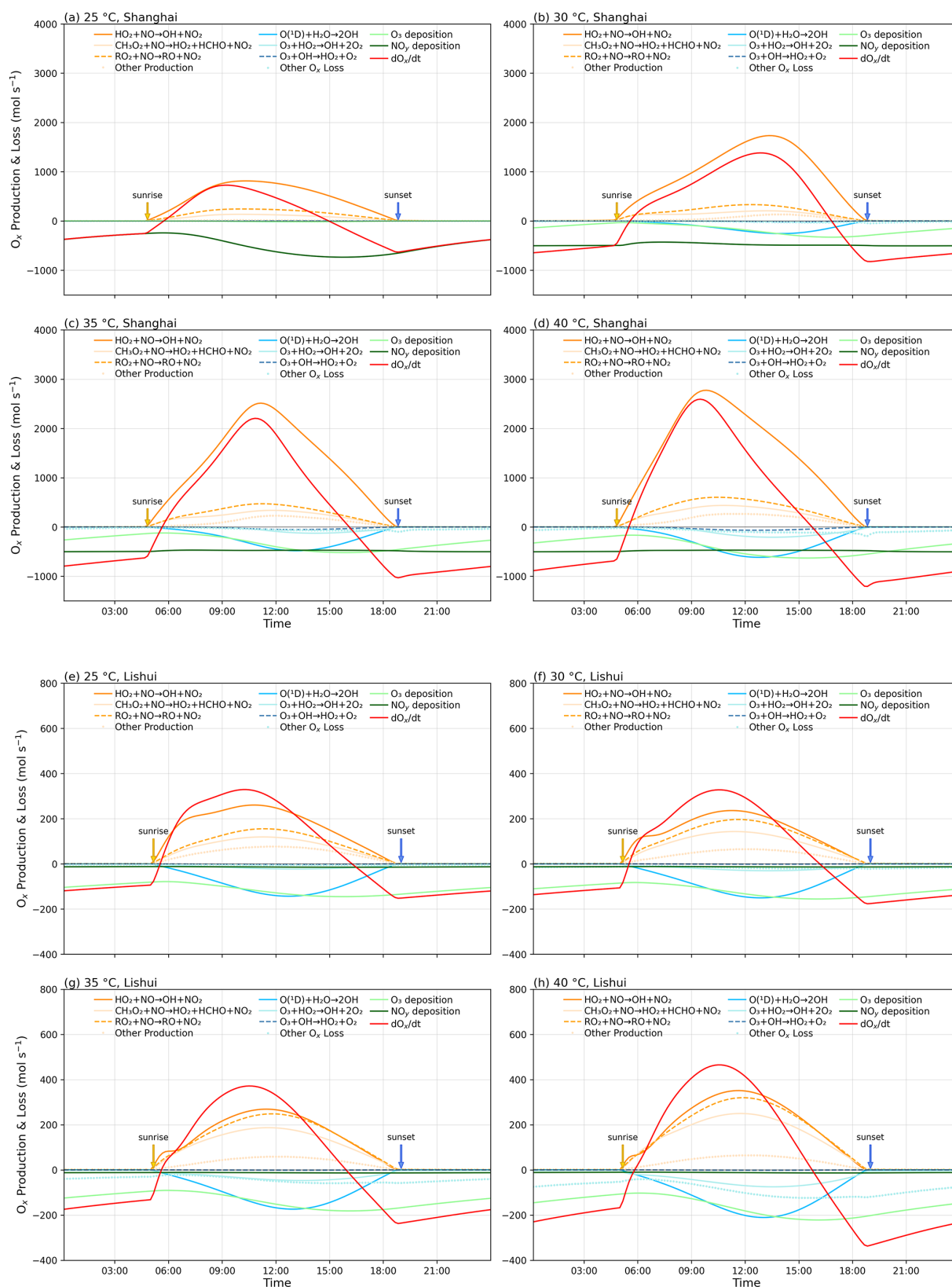


Figure 9. Diurnal O_x budget in the Dft configuration for Shanghai at $T_{\max}$ of (a) 25 °C, (b) 30 °C, (c) 35 °C, (d) 40 °C, and for Lishui at $T_{\max}$ of (e) 25 °C, (f) 30 °C, (g) 35 °C, (h) 40 °C. Curves show major chemical production pathways (orange), chemical loss terms (blue), deposition loss terms (green), and the net tendency dO_x/dt (red). Arrows indicate local sunrise and sunset. Time is local, and budget terms are expressed in mol s^{-1} . The y axis scale is consistent within each site but differs between Shanghai and Lishui.

Table 6. Daily contribution of main production and loss pathways to the O_x budget at 25, 30, 35, and 40 °C in Shanghai (unit: metric tonnes of O_x per day ($tO_x d^{-1}$; O_x counted as O_3)).

Process path	Temperature (°C)			
	25	30	35	40
Chemical Production				
HO ₂ + NO	1150.5	2305.7	3100.6	3559.9
CH ₃ O ₂ + NO	193.8	322	489	640.2
RO ₂ + NO	357.4	476.9	649.1	856.8
OH + INORG ACID	7.6	17.3	28.9	28.4
OH + ORG NITR	9.5	22.9	37.1	57.1
ORG NITR PHOT	4.1	3.2	3.8	5.3
OH + PAN REACT	3.7	96.2	193.8	271.9
Total Chem Prod	1726.7	3244.3	4502.3	5419.7
Chemical loss				
O(¹ D) + H ₂ O	17.4	292.8	567.5	751.2
MINOR LOSS REACTIONS	11	4.5	4.2	4.8
O ₃ + HO ₂	0	23.2	132.8	256.2
O ₃ + OH	0.2	19.9	58.7	80.8
O ₃ + ALKENE	0.5	5.2	12	26.4
N ₂ O ₅ + H ₂ O	0	17.7	41.5	53.6
NO ₃ Chemical loss	0.1	32.7	103.9	214.9
Total Chem Loss	29.3	395.9	920.7	1387.9
Deposition (& transport) loss				
O ₃ dry Deposition	21.8	711.7	1323.3	1688.8
NO _y Deposition	2013.7	2006.9	2011.2	2012.5
Total Dep (& trans) Loss	2035.4	2718.5	3334.5	3701.3

In the depositional budget, O₃ dry deposition is relatively more important in Lishui than in Shanghai, consistent with the much larger vegetated land fraction – which elevates deposition velocity of O₃ via stomatal and surface uptake – and with weaker in-situ NO_y production under rural low-NO_x conditions (Clifton et al., 2020a).

Overall, the Box model yields a coherent, process-level explanation for the observed O₃-temperature behaviour. In Shanghai, warming amplifies O_x primarily through HO₂ + NO chemistry while deposition – especially NO_y deposition – limits the net build-up. In Lishui, the warming response is shared more evenly among peroxy-NO sources, and O₃ deposition plays a larger role in the sink, with O₃-alkene loss emerging at the hottest conditions.

To identify the role of PAN-mediated NO_x recycling, Fig. 10 shows the temperature dependence of PAN concentration and thermal decomposition at both sites.

Figure 10 contrasts the diurnal evolution of peroxyacetyl nitrate (PAN) concentrations (dashed curves, right axis) with the thermal decomposition flux PAN → CH₃C(O)O₂ (PA) + NO₂ (solid curves, left axis) at four imposed temperatures in Shanghai (panel a) and Lishui (panel b). In both

locations, the decomposition flux increases monotonically with temperature and peaks around local noon-early afternoon, with daytime values far exceeding nighttime values. This behaviour is consistent with the strong temperature dependence of the PAN stability (PAN thermally decomposes rapidly at higher temperatures) and with daytime heating that accelerates the decomposition reaction (Fischer et al., 2014).

Despite the broadly similar flux patterns, concentration responses differ by site. In Lishui (Fig. 10c–d), PAN concentrations decrease with warming across the full range. As the temperature rises, thermal loss outpaces daytime production (due to low ambient NO_x), so the reservoir is progressively depleted. The result is a clean negative PAN-*T* relationship.

In Shanghai, the response is non-monotonic. In Fig. 10b, from 25 to 35 °C, the PAN concentration increases, even as the thermal decomposition of PAN accelerates as shown in Fig. 10a. This implies that, over this range, enhanced PAN production – via larger peroxyacetyl radical supply and abundant NO₂ – offsets the faster loss, allowing concentrations to rise. However, at 40 °C, the pattern reverses after mid-day: the decomposition flux jumps sharply relative to 35 °C, while the PAN concentration drops in the afternoon. Two ex-

Table 7. Daily contribution of main production and loss pathways to the O_x budget at 25, 30, 35, and 40 °C in Lishui (unit: metric tonnes of O_x per day ($t O_x d^{-1}$; O_x counted as O_3)).

Process path	Temperature (°C)			
	25	30	35	40
Chemical Production				
$HO_2 + NO$	380	334.7	371.2	475.5
$CH_3O_2 + NO$	173.4	209.3	275.1	365.9
$RO_2 + NO$	217.8	275.9	348	444.5
$OH + INORG ACID$	0.1	0	0	0
$OH + ORG NITR$	9.5	11.6	16.2	25.3
$ORG NITR PHOT$	3	7.1	14.2	24.3
$OH + PAN REACT$	99.9	74.5	53.1	42.5
Total Chem Prod	883.7	913.2	1077.8	1377.9
Chemical loss				
$O(^1D) + H_2O$	187.8	196.6	224.8	269.3
MINOR LOSS REACTIONS	0	0.1	0.1	0.1
$O_3 + HO_2$	35.6	48.3	74.5	117.2
$O_3 + OH$	4	2	1.6	1.9
$O_3 + ALKENE$	11.7	46.9	132.7	267.8
$N_2O_5 + H_2O$	0.1	0	0	0
NO_3 Chemical loss	6.5	15.9	35.8	69.5
Total Chem Loss	245.8	309.6	469.6	725.8
Deposition (& transport) loss				
O_3 dry Deposition	470.7	496.7	564.9	669.5
NO_y Deposition	56.2	54.1	52.2	49.3
Total Dep (& trans) Loss	526.9	550.8	617.1	718.8

planations, which are not mutually exclusive, are consistent with the curves. First, PAN's thermal instability means the $PA + NO_2 \rightleftharpoons PAN$ equilibrium shifts strongly toward PAN dissociation at high temperature (Cleary et al., 2007); thermal loss is the primary PAN sink in the lower troposphere and accelerates through the warmest hours, producing the observed afternoon drawdown in Fig. 10a. Second, extreme heat coincides with lower afternoon PAN production efficiency, e.g. due to the reduction in biogenic precursor supply, e.g., C_5H_8 as an indirect source of PA encountered its threshold at 38.3 °C, or enhanced radical competition (Liu et al., 2021a; Ma et al., 2022a; Phillips et al., 2013), so low peroxyacetyl radical (PA) levels limit the reaction between $PA + NO_2$ to form PAN. This PAN concentration drop may imply a threshold of PAN thermal decomposition above 40 °C in Shanghai, which occurs above 39 °C in California as described by Steiner et al. (2010).

A further notable contrast is the lower temperature behaviour (25 °C). Both the thermal decomposition flux and the PAN concentration are lower in Shanghai than in Lishui at this temperature, indicating that, under cooler conditions, PAN acts as a less effective NO_x reservoir near the urban site.

Overall, Fig. 10 shows that warming consistently strengthens PAN thermal decomposition at both sites, but the net concentration response is site-specific: monotonic decreases in Lishui, and increases followed by depletion in Shanghai at the highest temperature. These distinctions have practical implications: during heat extremes, PAN-mediated transport of NO_x is likely reduced because rapid afternoon decomposition limits PAN lifetime in VOC-limited urban areas like Shanghai, and the effect can be less significant in Lishui.

The associated temperature responses of HO_x cycling and the $HO_2 + NO$ pathway are shown in Fig. 11.

Figure 11 presents the diurnal evolution of the $HO_2 + NO$ production flux (solid orange), the aggregate HO_x -termination ("sink") flux (green dashed; e.g. $OH + NO_2 + M$, $HO_2 + RO_2/HO_2$), and the HO_x concentration (blue dotted; right axis) at four imposed temperatures. As shown in Fig. 9, the HO_2 and NO reaction is the dominant O_3 chemical production pathway in both environments. HO_x sink reactions terminate O_3 formation, while HO_x is widely used as a proxy for the atmosphere's oxidising capacity, with OH controlling daytime oxidative processing (Feng et al., 2021); moreover, net ozone formation scales with the peroxy- NO

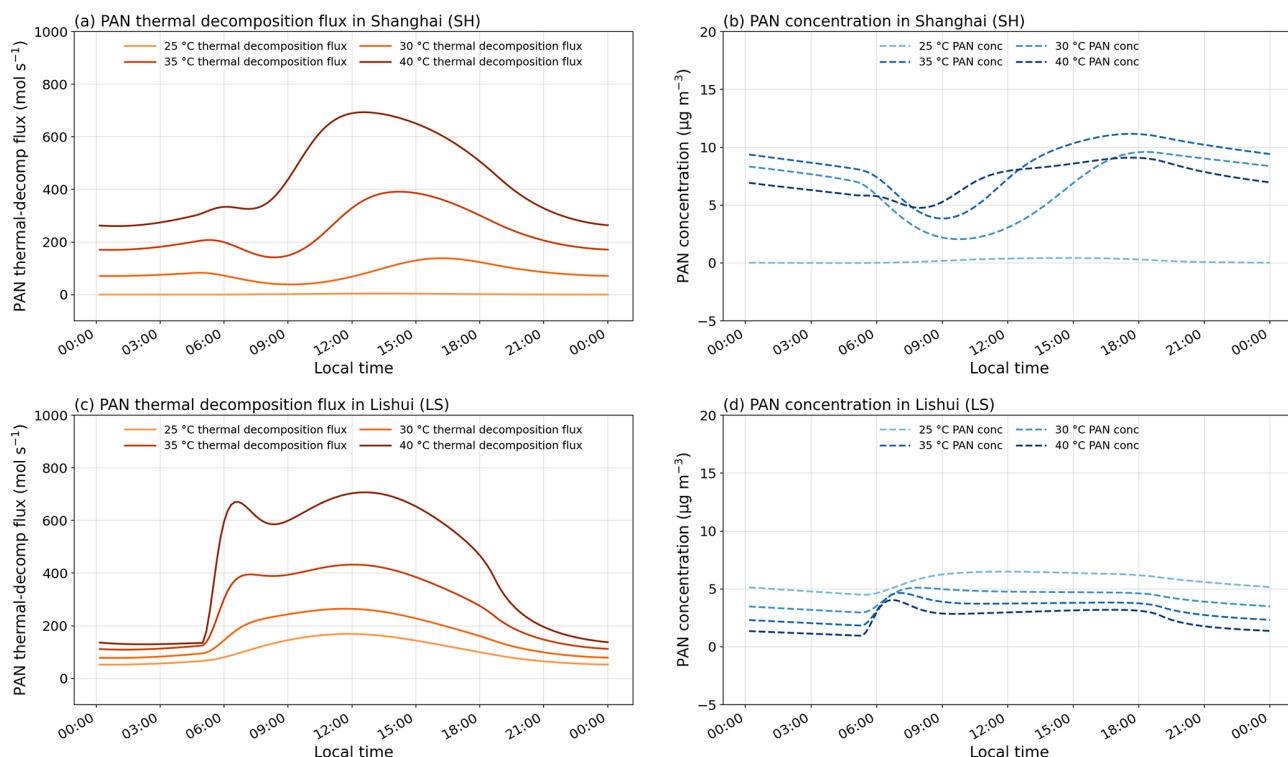


Figure 10. Diurnal peroxyacetyl nitrate (PAN) budget at four temperatures. (a–b) Shanghai and (c–d) Lishui. Solid orange curves show the PAN thermal-decomposition flux (left axis, mol s^{-1}); dashed blue curves show PAN concentration (right axis, $\mu\text{g m}^{-3}$). Each pair corresponds to a temperature scenario (25, 30, 35, 40 °C; lighter → darker with increasing temperature). Local time on the x axis.

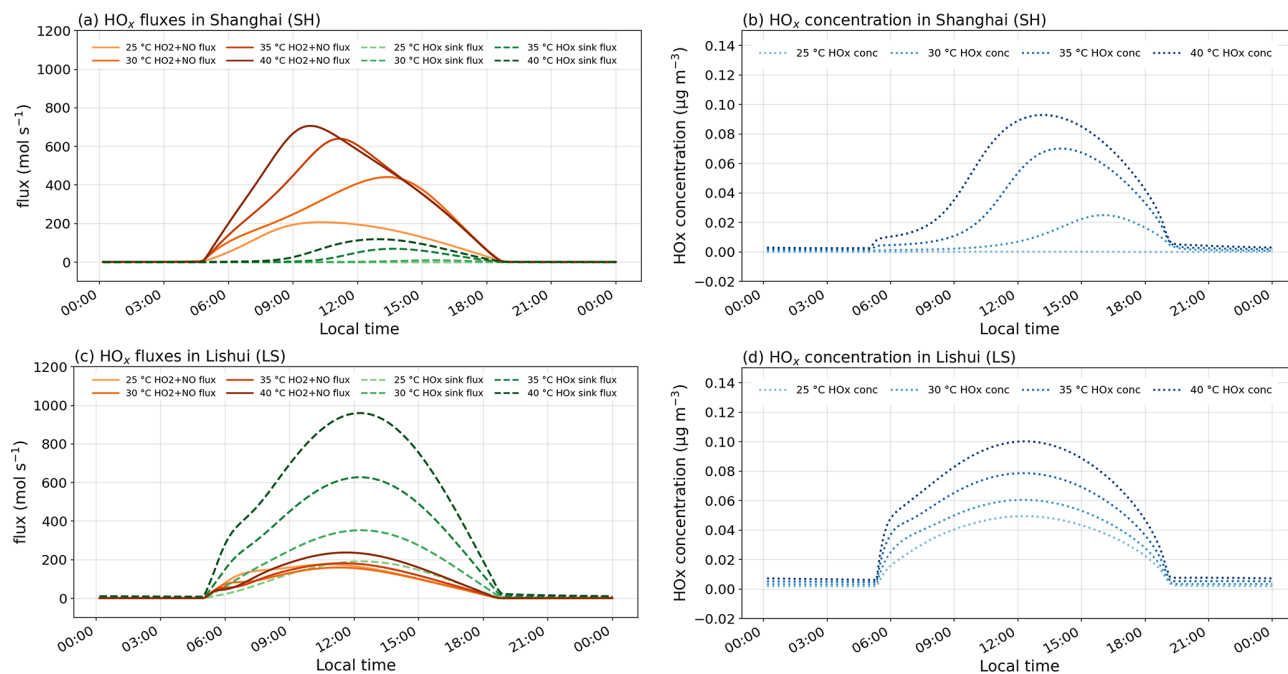


Figure 11. Diurnal $\text{HO}_2 + \text{NO}$ reaction, HO_x sink, and HO_x concentration at four temperatures. (a–b) Shanghai and (c–d) Lishui. Solid orange lines show the $\text{HO}_2 + \text{NO}$ reaction flux (left axis, mol s^{-1}); dashed green lines show the total HO_x sink flux (left axis); dotted blue lines show HO_x concentration (right axis, $\mu\text{g m}^{-3}$). Each trio corresponds to a temperature scenario (25, 30, 35, 40 °C; lighter → darker with increasing temperature). Local time on the x axis.

reactions, so higher HO_x – especially HO_2 – correlates with stronger photochemical O_3 production (Archibald et al., 2020b; Pusede et al., 2015).

In both panels, chemical activity is tightly bound to daylight: fluxes are negligible at night, rise sharply after sunrise, peak near local noon-early afternoon, and collapse after sunset, reflecting the photochemical control of radical production.

In Shanghai (Fig. 11a–b), warming mainly strengthens the HO_x -driven O_x production. With increasing temperature, the daytime $\text{HO}_2 + \text{NO}$ production flux (solid curves) increases strongly, and the peak HO_x concentrations (blue dotted curves, right axis) also increase, indicating more efficient radical recycling and a faster O_3 production cycle at higher T . The HO_x termination flux (green dashed curves) also grows with temperature, but the enhancement remains much smaller than the $\text{HO}_2 + \text{NO}$ pathway throughout the day, so the temperature increase shows a more substantial impact on including more HO_x in O_x formation instead of facilitating the HO_x sink pathway. At $T < 30^\circ\text{C}$, both HO_x levels and the sink are low, implying that primary radical production is weak and the O_3 production cycle can be slow.

In Lishui (Fig. 11c–d), the behaviour is significantly different. Across the temperature range, the HO_x sink plays a much larger role, and at $T \geq 30^\circ\text{C}$, its magnitude exceeds the $\text{HO}_2 + \text{NO}$ flux. Interpreted in the context of the O_3 chemical cycle, this means a larger fraction of the available HO_x is channelled into termination rather than propagation. Even so, HO_x concentrations remain high from 25 to 40°C , indicating efficient radical production; the high sink simply prevents those radicals from translating into proportionally larger $\text{HO}_2 + \text{NO}$ rates.

Together, the panels show that warming enhances radical activity in both environments, but the partitioning between propagation and termination is site dependent: Shanghai exhibits production-dominated HO_x cycling that favours O_3 formation at high temperature, whereas Lishui exhibits sink-dominated cycling, consistent with background conditions where O_3 production is constrained by NO_x rather than HO_x availability.

4 Discussion

4.1 Potential influence of temperature-dependent AVOC emissions

The present UKCA Box configuration represents only a limited subset of emitted AVOCs. In particular, some alkanes, alkenes, and aromatic compounds associated with temperature-dependent evaporative emissions are not available as explicit emitted tracers in the current chemical mechanism. Incorporating the full range of temperature-dependent AVOCs would therefore require an extension of both the chemical mechanism and the emission mapping, and these

species could not be included directly in the present box-model experiments.

To assess the potential importance of temperature-dependent AVOC emissions, we reproduced the temperature-dependent emission-scaling framework of Qin et al. (2025) using the JJA 2022 CEDS emissions for Shanghai. The calculation included selected AVOC categories associated with volatile chemical products (VCPs), including industrial and residential solvent use, and gasoline evaporation. Both temperature functions were normalised to 30°C , which represents the average baseline condition used in the box-model experiments. From 30 to 40°C , the selected VCP-related emission flux increased by 58.6 %, from 4.83×10^{-10} to $7.66 \times 10^{-10} \text{ kg m}^{-2} \text{ s}^{-1}$, while the gasoline-evaporation flux increased by 33.3 %, from 4.17×10^{-11} to 5.56×10^{-11} . The combined selected temperature-dependent AVOC flux consequently increased from 5.25×10^{-10} to $8.22 \times 10^{-10} \text{ kg m}^{-2} \text{ s}^{-1}$, corresponding to an additional 56.6 % increase.

We further examined whether this estimated AVOC enhancement could be represented explicitly in the UKCA Box experiments by applying the CEDS-to-StratTrop lumping approach of Archer-Nicholls et al. (2021). Comparison of the relevant CEDS species and sectors with the emitted StratTrop AVOC tracers showed that the overlap is very limited. On the source-species mass basis used in the mapping, these species account for only 3.56 % of the selected gasoline-evaporation emissions, while none of the selected VCP-related solvent emissions is represented. Most of the temperature-dependent butanes, pentanes, higher alkanes, other alkenes and aromatics are therefore absent from the emitted-tracer mapping.

Qin et al. (2025) found that temperature-driven AVOC emission enhancements increased MDA8 O_3 by 4.6 ppb and peak O_3 by 7.5 ppb during a Shanghai heatwave. Their results indicate that an AVOC enhancement of the magnitude estimated here can produce a measurable additional O_3 increase under hot urban conditions. Temperature-dependent AVOCs can therefore increase anthropogenic VOC availability under hot urban conditions, and their resulting O_3 contribution will be examined using an expanded VOC mechanism in future work.

4.2 Influence of the isoprene temperature-response parameterisation

Because temperature-dependent isoprene emissions strongly amplify simulated O_3 in Shanghai, we examined how this effect depends on the emission scheme. We compared the JULES iBVOC formulation used in the main experiments with the temperature activity factor implemented in MEGAN v2.1. The iBVOC scheme used with JULES represents the short-term temperature response as $fT = \min[\exp(0.1(T - 303.15)), 2.3]$. The response therefore increases exponentially above the 30°C reference condition until reaching a fixed upper limit of 2.3 at approximately 38.3°C , after which

the emission factor remains constant (Pacífico et al., 2011). By contrast, the MEGAN temperature activity factor accounts for both the instantaneous temperature and thermal acclimation through the mean temperatures over the preceding 24 and 240 h, T24 and T240. These prior-temperature terms determine the magnitude and temperature of the emission maximum rather than imposing a fixed threshold (Guenther et al., 2012).

We examined the influence of these formulations in Shanghai by normalising both temperature factors to the same isoprene emission at 30 °C and applying them over the 30–40 °C experimental range. The JULES temperature factor increased from 1.0 at 30 °C to its maximum value of 2.3 above 38.3 °C. The MEGAN factor increased continuously throughout the investigated range, reaching 2.68 at 40 °C; under the T24 and T240 conditions (30 °C; assumed from JJA YRD conditions and model setting) applied here, its emission maximum therefore occurred above 40 °C and outside the experimental range. The corresponding isoprene flux at 40 °C was $2.92 \times 10^{-10} \text{ kg m}^{-2} \text{ s}^{-1}$ using JULES and $3.40 \times 10^{-10} \text{ kg m}^{-2} \text{ s}^{-1}$ using MEGAN, compared with the common value of $1.27 \times 10^{-10} \text{ kg m}^{-2} \text{ s}^{-1}$ at 30 °C. These values correspond to increases of 130.0 % and 167.9 %, respectively.

The differences in calculated isoprene emissions propagated directly into the simulated evolution of daily maximum O_3 . At 30 °C, both schemes produced the same daily maximum O_3 of $116.1 \mu\text{g m}^{-3}$. At 40 °C, daily maximum O_3 reached $199.3 \mu\text{g m}^{-3}$ with JULES and $212.3 \mu\text{g m}^{-3}$ with MEGAN. The resulting 30–40 °C increases were therefore 83.3 and $96.2 \mu\text{g m}^{-3}$, respectively. Differences between the schemes remained relatively small between 32.5 and 37.5 °C, but became more pronounced once the JULES temperature factor approached its fixed upper limit. At 40 °C, MEGAN produced $12.9 \mu\text{g m}^{-3}$ more O_3 than JULES. Thus, both schemes confirm a large isoprene-driven amplification of urban O_3 at high temperature, while the greater high-temperature response in MEGAN indicates that the fixed JULES threshold provides a more conservative estimate near and above 40 °C.

5 Summary and conclusions

This study quantitatively evaluated the summertime temperature responses of ground-level ozone (O_3) across the Yangtze River Delta (YRD) and diagnosed how temperature-dependent O_x chemistry modulates surface O_3 using targeted UKCA Box experiments. We combined site observations from the 2022 summer in an urban megacity (Shanghai) and a rural region (Lishui) with a suite of experiments that separated the roles of chemical kinetics, temperature-dependent biogenic emissions, diurnal thermal structure, and humidity. Furthermore, we examined the O_x budget, PAN thermolysis, and the HO_x cycle to identify the mechanisms underlying the

observed temperature sensitivities. We highlight that urban-rural differences largely exist in the intensity, process, and mechanism of ground-level O_3 temperature responses. The conclusions are based on controlled 0-D box-model experiments, so the quantitative process fractions represent local chemical and emission-related sensitivities rather than a full meteorological attribution of the observed O_3 -temperature relationship.

The principal regime-specific mechanisms identified by these analyses are summarised in Fig. 12, which contrasts typical summer (30 °C) and heat extreme (40 °C) conditions in Shanghai and Lishui. The conceptual comparison highlights the stronger temperature-amplified BVOC contribution in the Shanghai-like VOC-limited environment and the greater importance of radical- NO_x chemistry in the Lishui-like lower- NO_x environment, together with the modulation of both responses by humidity and diurnal temperature structure.

Summertime daily maximum observations showed robust, positive O_3 -temperature relationships in both regions, stronger in Shanghai than in Lishui (mean JJA $\Delta\text{O}_{3\text{max}} - \Delta T_{\text{max}} = 7.27$ vs. $3.36 \mu\text{g m}^{-3} \text{ }^\circ\text{C}^{-1}$). Heatwave slopes remained positive in Lishui, but were statistically uncertain in Shanghai due to the limited number of events and larger variance at the low tail. Two-dimensional T -RH maps revealed that O_3 increases with temperature and decreases with relative humidity (RH). Because RH falls by $\sim 2.4 \text{ \%}$ – $3.2 \text{ \%}$ RH per $^\circ\text{C}$, part of the apparent temperature signal is mediated by drying.

Factorial experiments isolated (i) net temperature-dependent chemical effects (Ori), (ii) the diurnal temperature cycle (D), (iii) temperature-dependent isoprene emissions (ft), and (iv) their combination (Dft), under fixed- and variable-RH assumptions (FRH/VRH). Under the adopted isoprene-temperature parameterisation and Shanghai baseline emission setting, the temperature-dependent isoprene term accounts for $\sim 70 \text{ \%}$ of the observed $\Delta\text{O}_{3\text{max}}$ from 30 to 40 °C, with the diurnal cycle contributing $\sim 10 \text{ \%}$ (allowing isoprene emissions to change with temperature) and residual kinetics accounting for $\sim 20 \text{ \%}$. Below 30 °C, observations aligned more closely with Ori/D, suggesting that unresolved meteorological controls (in the box model) (e.g., diurnal and day-to-day variation in boundary layer depth, transport/mixing into and out of the box) can offset the temperature sensitivity of isoprene emissions at lower temperatures. In Lishui, chemical temperature responses, i.e. peroxy-radical chemistry ($\text{HO}_2/\text{RO}_2 + \text{NO}$), accounted for $\sim 80 \text{ \%}$ of the 30 to 40 °C increase, while isoprene's temperature dependence contributed only $\sim 10 \text{ \%}$, consistent with a NO_x -limited rural regime. Allowing RH to decrease with temperature increased the apparent “thermal chemistry” contribution by $\sim 35 \text{ \%}$ in Lishui and $\sim 20 \text{ \%}$ in Shanghai, underscoring the need to treat T and RH jointly when diagnosing or projecting the climate penalty.

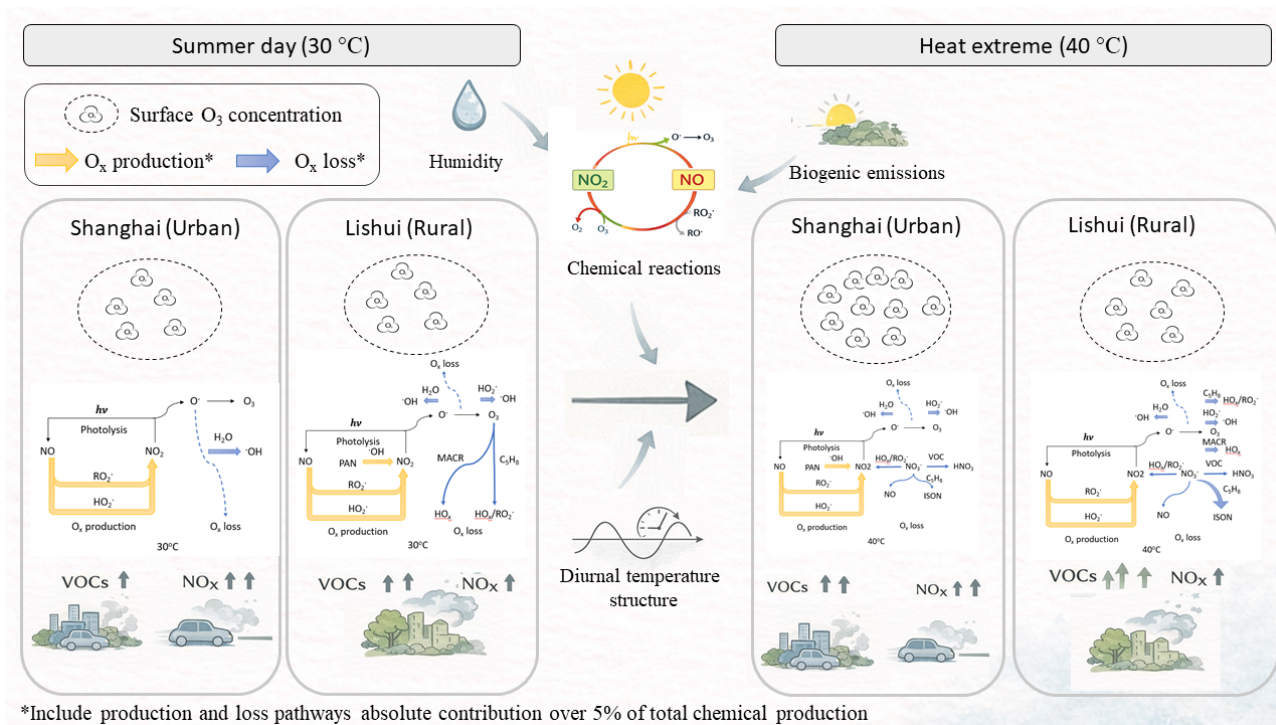


Figure 12. Conceptual summary of the mechanisms controlling surface ozone under typical summer conditions (30 °C; left) and heat extremes (40 °C; right) in Shanghai (urban) and Lishui (rural).

O_x budgets showed $HO_2 + NO$ as the leading production pathway in Shanghai, with $RO_2 + NO$ gaining importance toward 40 °C. In Lishui, the daily contribution of $RO_2 + NO$ (including CH_3O_2 and other RO_2 species) to O_x production exceeds $HO_2 + NO$, and the value doubles from 25 to 40 °C. On the loss side, $O(^1D) + H_2O$ dominates chemical destruction at both sites at temperatures from 25 to 35 °C, whereas $O_3 + \text{alkene}$ reactions dominate O_3 's temperature response at temperatures above 35 °C in Lishui. Deposition and physical transport remain the largest total O_x sink except at 40 °C, where the chemical loss dominates the O_x sink. For PAN, its thermolysis increased monotonically with temperature at both sites, implying stronger thermal NO_x recycling on hot afternoons; PAN concentrations declined with temperature in Lishui (loss outpaces production) but rose from 25 to 35 °C then fell at 40 °C in Shanghai, indicating that urban production can sustain PAN until very high temperatures when thermolysis and oxidant constraints dominate and imply potential threshold of PAN as NO_x source above 40 °C. HO_x diagnostics showed production-dominated cycling in Shanghai ($HO_2 + NO$ and $[HO_x]$ increase with T ; sink modest) versus sink-dominated cycling in Lishui above ~ 30 °C (high HO_x sink), reinforcing the regime contrast.

Our site-scale attribution complements recent global UKCA applications with enhanced VOC chemistry over China that reproduced peak O_3 in industrial regions, identified VOC-limited behaviour in most megacity clusters, and

demonstrated that NO_x -only controls can increase O_3 in VOC-limited environments. In contrast, VOC controls (or combined controls) are effective in reducing O_3 . Read in that context, our findings sharpen the process basis for the YRD:

1. In Shanghai-like urban conditions, temperature-amplified BVOC reactivity is a first-order lever of O_3 on hot days; mitigating the climate penalty therefore requires simultaneous NO_x reductions and targeted VOC management, which corresponds to previous urban O_3 formation studies (Gu et al., 2020; Liu et al., 2021b). Particularly, thoughtful urban greening (species selection/placement – i.e., low VOC emitters) is especially emphasised in this study, alongside improved representation of RH-stomata coupling in deposition schemes.
2. In Lishui-like rural conditions, O_3 sensitivity is governed primarily by radical- NO_x chemistry and thermal PAN- NO_x cycling; NO_x reductions remain the most robust pathway to limit warming-induced O_3 amplification, while VOC reductions have a smaller marginal benefit.
3. Because RH and T co-vary, evaluations that ignore RH changes are likely to over-attribute the temperature effect to kinetic partitioning and understate deposition-mediated sinks. Multi-city analyses have reported a robust negative correlation between RH (or absolute hu-

midity) and surface O_3 , indicating that moist conditions systematically suppress O_3 compared with dry, hot weather (Li et al., 2021). In the present work, even with dry-deposition parameterisations held fixed, we find that changes in humidity alone substantially modify the O_x budget through $O(^1D) + H_2O$ loss and HO_x - NO_x cycling, implying that humidity-driven chemical effects can be a major contributor to the apparent climate penalty, independent of any RH influence on stomatal or surface uptake.

Our conclusions are based on one exceptionally hot summer (2022) and inherit limitations from the heatwave sample size and the 0-D nature of the box model, which does not resolve transport, clouds, or meteorological feedbacks. Nevertheless, agreement across independent diagnostics – JJA and heatwave regressions, binned ΔO_3 comparisons, and O_x /PAN/ HO_x budgets – builds a consistent mechanistic picture. In summary, summertime O_3 in the YRD increases with temperature for regime-specific reasons: BVOC-driven in the urban core, radical- NO_x -driven in the rural area, and materially modulated by humidity conditions. Although the quantitative sensitivities documented here are specific to the 2022 YRD emissions-meteorology setting, the underlying mechanisms, such as temperature-enhanced BVOC reactivity in VOC-limited urban air, radical- NO_x control and PAN-mediated NO_x recycling in rural air, and the damping role of high humidity, are consistent with process-based analyses for other polluted mid-latitude regions (e.g. eastern North America and Europe) and are therefore expected to be qualitatively applicable in similar regimes and climate settings.

The UKCA Box provides a transparent, observation-constrained framework for attributing the chemical component of O_3 temperature responses within O_x chemistry, offering actionable guidance for heat-resilient emission controls and serving as a bridge to regional policy analyses informed by broader UKCA simulations. Priorities for future work include (a) evaluating the performance of the UKCA model on reproducing the meteorological contribution to surface O_3 in different types of summer days, and (b) the contribution of meteorological fields and precursor emissions during heatwaves, non-heatwave hot days and summer days.

Data availability. The data used in this study are available from the corresponding author upon request (chang.su@ed.ac.uk).

Supplement. The supplement related to this article is available online at <https://doi.org/10.5194/acp-26-14439-2026-supplement>.

Author contributions. CS prepared the dataset, performed UKCA Box Model simulations, specified the corresponding model settings, conducted the analysis, and wrote the paper. DS and MB helped design the research, guided the data analysis, contributed to

the scientific discussions, and helped with the final version of the paper. JW performed the UKESM-AMIP simulations, contributed to the corresponding model configuration, and commented on the final version of the paper.

Competing interests. The contact author has declared that none of the authors has any competing interests.

Disclaimer. Publisher's note: Copernicus Publications remains neutral with regard to jurisdictional claims made in the text, published maps, institutional affiliations, or any other geographical representation in this paper. The authors bear the ultimate responsibility for providing appropriate place names. Views expressed in the text are those of the authors and do not necessarily reflect the views of the publisher.

Acknowledgements. We acknowledge the guidance during setting up the UKCA Box Model from N. Luke Abraham, National Centre for Atmospheric Science.

Financial support. This research has been supported by the Natural Environment Research Council (UKRI/NERC) and the UK Department for Energy Security and Net Zero (grant no. NE/X012735/1).

Review statement. This paper was edited by Samara Carbone and reviewed by three anonymous referees.

References

- An, J., Huang, Y., Huang, C., Wang, X., Yan, R., Wang, Q., Wang, H., Jing, S., Zhang, Y., Liu, Y., Chen, Y., Xu, C., Qiao, L., Zhou, M., Zhu, S., Hu, Q., Lu, J., and Chen, C.: Emission inventory of air pollutants and chemical speciation for specific anthropogenic sources based on local measurements in the Yangtze River Delta region, China, *Atmos. Chem. Phys.*, 21, 2003–2025, <https://doi.org/10.5194/acp-21-2003-2021>, 2021.
- Archer-Nicholls, S., Abraham, N. L., Shin, Y. M., Weber, J., Russo, M. R., Lowe, D., Utembe, S. R., O'Connor, F. M., Kerridge, B., Latter, B., Siddans, R., Jenkin, M., Wild, O., and Archibald, A. T.: The Common Representative Intermediates Mechanism Version 2 in the United Kingdom Chemistry and Aerosols Model, *J. Adv. Model. Earth Sy.*, 13, e2020MS002420, <https://doi.org/10.1029/2020MS002420>, 2021.
- Archibald, A. T., O'Connor, F. M., Abraham, N. L., Archer-Nicholls, S., Chipperfield, M. P., Dalvi, M., Folberth, G. A., Denison, F., Dhomse, S. S., Griffiths, P. T., Hardacre, C., Hewitt, A. J., Hill, R. S., Johnson, C. E., Keeble, J., Köhler, M. O., Morgenstern, O., Mulcahy, J. P., Ordóñez, C., Pope, R. J., Rumbold, S. T., Russo, M. R., Savage, N. H., Sellar, A., Stringer, M., Turnock, S. T., Wild, O., and Zeng, G.: Description and evaluation of the UKCA stratosphere–troposphere chemistry scheme (Strat-

- Trop v1.0) implemented in UKESM1, *Geosci. Model Dev.*, 13, 1223–1266, <https://doi.org/10.5194/gmd-13-1223-2020>, 2020a.
- Archibald, A. T., Turnock, S. T., Griffiths, P. T., Cox, T., Derwent, R. G., Knote, C., and Shin, M.: On the changes in surface ozone over the twenty-first century: sensitivity to changes in surface temperature and chemical mechanisms, *Philos. T. R. Soc. A*, 378, 20190329, <https://doi.org/10.1098/rsta.2019.0329>, 2020b.
- Bates, K. H. and Jacob, D. J.: An Expanded Definition of the Odd Oxygen Family for Tropospheric Ozone Budgets: Implications for Ozone Lifetime and Stratospheric Influence, *Geophys. Res. Lett.*, 47, e2019GL084486, <https://doi.org/10.1029/2019GL084486>, 2020.
- Bloomer, B. J., Vinnikov, K. Y., and Dickerson, R. R.: Changes in seasonal and diurnal cycles of ozone and temperature in the eastern U.S., *Atmos. Environ.*, 44, 2543–2551, <https://doi.org/10.1016/j.atmosenv.2010.04.031>, 2010.
- Chen, P., Zhao, X., Wang, O., Shao, M., Xiao, X., Wang, S., and Wang, Q. g.: Characteristics of VOCs and their Potentials for O₃ and SOA Formation in a Medium-sized City in Eastern China, *Aerosol Air Qual. Res.*, 22, 210239, <https://doi.org/10.4209/aaqr.210239>, 2022.
- Cleary, P. A., Wooldridge, P. J., Millet, D. B., McKay, M., Goldstein, A. H., and Cohen, R. C.: Observations of total peroxy nitrates and aldehydes: measurement interpretation and inference of OH radical concentrations, *Atmos. Chem. Phys.*, 7, 1947–1960, <https://doi.org/10.5194/acp-7-1947-2007>, 2007.
- Clifton, O. E., Fiore, A. M., Massman, W. J., Baublitz, C. B., Coyle, M., Emberson, L., Fares, S., Farmer, D. K., Gentine, P., Gerosa, G., Guenther, A. B., Helmig, D., Lombardozzi, D. L., Munger, J. W., Patton, E. G., Pusede, S. E., Schwede, D. B., Silva, S. J., Sörgel, M., Steiner, A. L., and Tai, A. P. K.: Dry Deposition of Ozone Over Land: Processes, Measurement, and Modeling, *Rev. Geophys.*, 58, e2019RG000670, <https://doi.org/10.1029/2019RG000670>, 2020a.
- Clifton, O. E., Paulot, F., Fiore, A. M., Horowitz, L. W., Correa, G., Baublitz, C. B., Fares, S., Goded, I., Goldstein, A. H., Gruening, C., Hogg, A. J., Loubet, B., Mammarella, I., Munger, J. W., Neil, L., Stella, P., Uddling, J., Vesala, T., and Weng, E.: Influence of Dynamic Ozone Dry Deposition on Ozone Pollution, *J. Geophys. Res.-Atmos.*, 125, e2020JD032398, <https://doi.org/10.1029/2020JD032398>, 2020b.
- Cohen, A. J., Brauer, M., Burnett, R., Anderson, H. R., Frostad, J., Estep, K., Balakrishnan, K., Brunekreef, B., Dandona, L., Dandona, R., Feigin, V., Freedman, G., Hubbell, B., Jobling, A., Kan, H., Knibbs, L., Liu, Y., Martin, R., Morawska, L., Pope III, C. A., Shin, H., Straif, K., Shaddick, G., Thomas, M., van Dingenen, R., van Donkelaar, A., Vos, T., Murray, C. J. L., and Forouzanfar, M. H.: Estimates and 25-year trends of the global burden of disease attributable to ambient air pollution: an analysis of data from the Global Burden of Diseases Study 2015, *The Lancet*, 389, 1907–1918, [https://doi.org/10.1016/S0140-6736\(17\)30505-6](https://doi.org/10.1016/S0140-6736(17)30505-6), 2017.
- Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmasada, M. A., Balsamo, G., Bauer, P., Bechtold, P., Beljaars, A. C. M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., Fuentes, M., Geer, A. J., Haimberger, L., Healy, S. B., Hersbach, H., Hólm, E. V., Isaksen, I., Kållberg, P., Köhler, M., Matricardi, M., McNally, A. P., Monge-Sanz, B. M., Morcrette, J. J., Park, B. K., Peubey, C., de Rosnay, P., Tavolato, C., Thépaut, J. N., and Vitart, F.: The ERA-Interim reanalysis: configuration and performance of the data assimilation system, *Q. J. Roy. Meteor. Soc.*, 137, 553–597, <https://doi.org/10.1002/qj.828>, 2011.
- Duc, H. N., Rahman, M. M., Trieu, T., Azzi, M., Riley, M., Koh, T., Liu, S., Bandara, K., Krishnan, V., Yang, Y., Silver, J., Kirley, M., White, S., Capnerhurst, J., and Kirkwood, J.: Study of Planetary Boundary Layer, Air Pollution, Air Quality Models and Aerosol Transport Using Ceilometers in New South Wales (NSW), Australia, *Atmosphere*, 13, 176, <https://doi.org/10.3390/atmos13020176>, 2022.
- Ebi, K. L., Capon, A., Berry, P., Broderick, C., de Dear, R., Havenith, G., Honda, Y., Kovats, R. S., Ma, W., Malik, A., Morris, N. B., Nybo, L., Seneviratne, S. I., Vanos, J., and Jay, O.: Hot weather and heat extremes: health risks, *The Lancet*, 398, 698–708, [https://doi.org/10.1016/S0140-6736\(21\)01208-3](https://doi.org/10.1016/S0140-6736(21)01208-3), 2021.
- Engdow, M. M., Ballinger, A. P., Hegerl, G. C., and Steiner, A. K.: Changes in temperature and heat waves over Africa using observational and reanalysis data sets, *Int. J. Climatol.*, 42, 1165–1180, <https://doi.org/10.1002/joc.7295>, 2022.
- Feng, T., Zhao, S., Hu, B., Bei, N., Zhang, X., Wu, J., Li, X., Liu, L., Wang, R., Tie, X., and Li, G.: Assessment of Atmospheric Oxidizing Capacity Over the Beijing-Tianjin-Hebei (BTH) Area, China, *J. Geophys. Res.-Atmos.*, 126, e2020JD033834, <https://doi.org/10.1029/2020JD033834>, 2021.
- Fischer, E. M. and Schär, C.: Consistent geographical patterns of changes in high-impact European heatwaves, *Nat. Geosci.*, 3, 398–403, <https://doi.org/10.1038/ngeo866>, 2010.
- Fischer, E. V., Jacob, D. J., Yantosca, R. M., Sulprizio, M. P., Millet, D. B., Mao, J., Paulot, F., Singh, H. B., Roiger, A., Ries, L., Talbot, R. W., Dzepina, K., and Pandey Deolal, S.: Atmospheric peroxyacetyl nitrate (PAN): a global budget and source attribution, *Atmos. Chem. Phys.*, 14, 2679–2698, <https://doi.org/10.5194/acp-14-2679-2014>, 2014.
- Forouzanfar, M. H., Alexander, L., Anderson, H. R., Bachman, V. F., Biryukov, S., Brauer, M., Burnett, R., Casey, D., Coates, M. M., Cohen, A., Delwiche, K., Estep, K., Frostad, J. J., Kc, A., Kyu, H. H., Moradi-Lakeh, M., Ng, M., Slepak, E. L., Thomas, B. A., Wagner, J., Aasvang, G. M., Abbafati, C., Ozgoren, A. A., Abd-Allah, F., Abera, S. F., Aboyans, V., Abraham, B., Abraham, J. P., Abubakar, I., Abu-Rmeileh, N. M. E., Aburto, T. C., Achoki, T., Adelekan, A., Adofo, K., Adou, A. K., Adsuar, J. C., Afshin, A., Agardh, E. E., Al Khabouri, M. J., Al Lami, F. H., Alam, S. S., Alasfoor, D., Albittar, M. I., Alegretti, M. A., Aleman, A. V., Alemu, Z. A., Alfonso-Cristancho, R., Alhabib, S., Ali, R., Ali, M. K., Alla, F., Allebeck, P., Allen, P. J., Alsharif, U., Alvarez, E., Alvis-Guzman, N., Amankwaa, A. A., Amare, A. T., Ameh, E. A., Ameli, O., Amini, H., Ammar, W., Anderson, B. O., Antonio, C. A. T., Anwari, P., Cunningham, S. A., Arnlöv, J., Arsenijevic, V. S. A., Artaman, A., Asghar, R. J., Assadi, R., Atkins, L. S., Atkinson, C., Avila, M. A., Awuah, B., Badawi, A., Bahit, M. C., Bakfalouni, T., Balakrishnan, K., Balalla, S., Balu, R. K., Banerjee, A., Barber, R. M., Barker-Collo, S. L., Barquera, S., Barregard, L., Barrero, L. H., Barrientos-Gutierrez, T., Basto-Abreu, A. C., Basu, A., Basu, S., Basulaiman, M. O., Ruvalcaba, C. B., Beardsley, J., Bedi, N., Bekele, T., Bell, M. L., Benjet, C., Bennett, D. A., Benzian, H., Bernabé, E., Beyene, T. J., Bhala, N., Bhalla, A., Bhutta, Z. A., Bikbov, B., Abdulhak, A. A. B., Blore, J. D., Blyth, F. M., Bohensky, M. A., Başara, B. B., Borges, G., Bornstein, N. M., Bose, D., Boufous, S., Bourne,

- R. R., Brainin, M., Brazinova, A., Breitborde, N. J., Brenner, H., Briggs, A. D. M., Broday, D. M., Brooks, P. M., Bruce, N. G., Brugh, T. S., Brunekreef, B., Buchbinder, R., Bui, L. N., Bukhman, G., Bulloch, A. G., Burch, M., Burney, P. G. J., Campos-Nonato, I. R., Campuzano, J. C., Cantoral, A. J., Caravanos, J., Cárdenas, R., Cardis, E., Carpenter, D. O., Caso, V., Castañeda-Orjuela, C. A., Castro, R. E., Catalá-López, F., Cavalleri, F., Çavlin, A., Chadha, V. K., Chang, J.-c., Charlson, F. J., Chen, H., Chen, W., Chen, Z., Chiang, P. P., Chimed-Ochir, O., Chowdhury, R., Christophi, C. A., Chuang, T.-W., Chugh, S. S., Cirillo, M., Claßen, T. K. D., Colistro, V., Colomar, M., Colquhoun, S. M., Contreras, A. G., Cooper, C., Cooperrider, K., Cooper, L. T., Coresh, J., Courville, K. J., Criqui, M. H., Cuevas-Nasu, L., Damsere-Derry, J., Danawi, H., Dandona, L., Dandona, R., Dargan, P. I., Davis, A., Davitoliu, D. V., Dayama, A., de Castro, E. F., De la Cruz-Góngora, V., De Leo, D., de Lima, G., Degenhardt, L., del Pozo-Cruz, B., Dellavalle, R. P., Deribe, K., Derrett, S., Jarlais, D. C. D., Dessalegn, M., deVeber, G. A., Devries, K. M., Dharmaratne, S. D., Dherani, M. K., Dicker, D., Ding, E. L., Dokova, K., Dorsey, E. R., Driscoll, T. R., Duan, L., Durrani, A. M., Ebel, B. E., Ellenbogen, R. G., Elshrek, Y. M., Endres, M., Ermakov, S. P., Erskine, H. E., Eshrati, B., Esteghamati, A., Fahimi, S., Faraon, E. J. A., Farzadfar, F., Fay, D. F. J., Feigin, V. L., Feigl, A. B., Fereshstehnejad, S.-M., Ferrari, A. J., Ferri, C. P., Flaxman, A. D., Fleming, T. D., Foigt, N., Foreman, K. J., Paleo, U. F., Franklin, R. C., Gabbe, B., Gaffikin, L., Gakidou, E., Gamkrelidze, A., Gankpé, F. G., Gansevoort, R. T., García-Guerra, F. A., Gasana, E., Geleijnse, J. M., Gessner, B. D., Gething, P., Gibney, K. B., Gillum, R. F., Ginawi, I. A. M., Giroud, M., Giussani, G., Goenka, S., Goginashvili, K., Dantes, H. G., Gona, P., de Cosio, T. G., González-Castell, D., Gotay, C. C., Goto, A., Gouda, H. N., Guerrant, R. L., Gughani, H. C., Guillemin, F., Gunnell, D., Gupta, R., Gupta, R., Gutiérrez, R. A., Hafezi-Nejad, N., Hagan, H., Hagstromer, M., Halasa, Y. A., Hamadeh, R. R., Hammami, M., Hankey, G. J., Hao, Y., Harb, H. L., Haregu, T. N., Haro, J. M., Havmoeller, R., Hay, S. I., Hedayat, M. T., Heredia-Pi, I. B., Hernandez, L., Heuton, K. R., Heydarpour, P., Hajar, M., Hoek, H. W., Hoffman, H. J., Hornberger, J. C., Hosgood, H. D., Hoy, D. G., Hsairi, M., Hu, G., Hu, H., Huang, C., Huang, J. J., Hubbell, B. J., Huiart, L., Hussein, A., Iannarone, M. L., Iburg, K. M., Idrisov, B. T., Ikeda, N., Innos, K., Inoue, M., Islami, F., Ismayilova, S., Jacobsen, K. H., Jansen, H. A., Jarvis, D. L., Jassal, S. K., Jauregui, A., Jayaraman, S., Jeemon, P., Jensen, P. N., Jha, V., Jiang, F., Jiang, G., Jiang, Y., Jonas, J. B., Juel, K., Kan, H., Roseline, S. S. K., Karam, N. E., Karch, A., Karema, C. K., Karthikeyan, G., Kaul, A., Kawakami, N., Kazi, D. S., Kemp, A. H., Kengne, A. P., Keren, A., Khader, Y. S., Khalifa, S. E. A. H., Khan, E. A., Khang, Y.-H., Khatibzadeh, S., Khonelidze, I., Kielling, C., Kim, D., Kim, S., Kim, Y., Kimokoti, R. W., Kinfu, Y., King, J. M., Kissela, B. M., Kivipelto, M., Knibbs, L. D., Knudsen, A. K., Kokubo, Y., Kose, M. R., Kosen, S., Kraemer, A., Kravchenko, M., Krishnaswami, S., Kromhout, H., Ku, T., Defo, B. K., Bicer, B. K., Kuipers, E. J., Kulkarni, C., Kulkarni, V. S., Kumar, G. A., Kwan, G. F., Lai, T., Balaji, A. L., Laloo, R., Lallukka, T., Lam, H., Lan, Q., Lansingh, V. C., Larson, H. J., Larsson, A., Laryea, D. O., Lavados, P. M., Lawrynowicz, A. E., Leasher, J. L., Lee, J.-T., Leigh, J., Leung, R., Levi, M., Li, Y., Li, Y., Liang, J., Liang, X., Lim, S. S., Lindsay, M. P., Lipshultz, S. E., Liu, S., Liu, Y., Lloyd, B. K., Logroscino, G., London, S. J., Lopez, N., Lortet-Tieulent, J., Lotufo, P. A., Lozano, R., Lunevicius, R., Ma, J., Ma, S., Machado, V. M. P., MacIntyre, M. F., Magis-Rodriguez, C., Mahdi, A. A., Majdan, M., Malekzadeh, R., Mangalam, S., Mapoma, C. C., Marape, M., Marcenés, W., Margolis, D. J., Margono, C., Marks, G. B., Martin, R. V., Marzan, M. B., Mashal, M. T., Masiye, F., Mason-Jones, A. J., Matsushita, K., Matzopoulos, R., Mayosi, B. M., Mazorodze, T. T., McKay, A. C., McKee, M., McLain, A., Meaney, P. A., Medina, C., Mehndiratta, M. M., Mejia-Rodriguez, F., Mekonnen, W., Melaku, Y. A., Meltzer, M., Memish, Z. A., Mendoza, W., Mensah, G. A., Meretoja, A., Mhimbira, F. A., Micha, R., Miller, T. R., Mills, E. J., Misganaw, A., Mishra, S., Ibrahim, N. M., Mohammad, K. A., Mokdad, A. H., Mola, G. L., Monasta, L., Hernandez, J. C. M., Montico, M., Moore, A. R., Morawska, L., Mori, R., Moschandreass, J., Moturi, W. N., Mozaffarian, D., Mueller, U. O., Mukaigawara, M., Mullany, E. C., Murthy, K. S., Naghavi, M., Nahas, Z., Naheed, A., Naidoo, K. S., Naldi, L., Nand, D., Nangia, V., Narayan, K. M. V., Nash, D., Neal, B., Nejjari, C., Neupane, S. P., Newton, C. R., Ngalesoni, F. N., de Dieu Ndirabegga, J., Nguyen, G., Nguyen, N. T., Nieuwenhuijsen, M. J., Nisar, M. I., Nogueira, J. R., Nolla, J. M., Nolte, S., Norheim, O. F., Norman, R. E., Norrving, B., Nyakarahuka, L., Oh, I.-H., Ohkubo, T., Olusanya, B. O., Omer, S. B., Opio, J. N., Orozco, R., Pagcatipunan, R. S., Jr., Pain, A. W., Pandian, J. D., Panelo, C. I. A., Papachristou, C., Park, E.-K., Parry, C. D., Caicedo, A. J. P., Patten, S. B., Paul, V. K., Pavlin, B. I., Pearce, N., Pedraza, L. S., Pedroza, A., Stokic, L. P., Pekerlicli, A., Pereira, D. M., Perez-Padilla, R., Perez-Ruiz, F., Perico, N., Perry, S. A. L., Pervaiz, A., Pesudovs, K., Peterson, C. B., Petzold, M., Phillips, M. R., Phua, H. P., Plass, D., Poenaru, D., Polanczyk, G. V., Polinder, S., Pond, C. D., Pope, C. A., Pope, D., Popova, S., Pourmalek, F., Powles, J., Prabhakaran, D., Prasad, N. M., Qato, D. M., Quezada, A. D., Quistberg, D. A. A., Racapé, L., Rafay, A., Rahimi, K., Rahimi-Movaghar, V., Rahman, S. U., Raju, M., Rakovac, I., Rana, S. M., Rao, M., Razavi, H., Reddy, K. S., Refaat, A. H., Rehm, J., Remuzzi, G., Ribeiro, A. L., Riccio, P. M., Richardson, L., Riederer, A., Robinson, M., Roca, A., Rodriguez, A., Rojas-Rueda, D., Romieu, I., Ronfani, L., Room, R., Roy, N., Ruhago, G. M., Rushton, L., Sabin, N., Sacco, R. L., Saha, S., Sahathevan, R., Sahraian, M. A., Salomon, J. A., Salvo, D., Sampson, U. K., Sanabria, J. R., Sanchez, L. M., Sánchez-Pimienta, T. G., Sanchez-Riera, L., Sandar, L., Santos, I. S., Sapkota, A., Satpathy, M., Saunders, J. E., Sawhney, M., Saylan, M. I., Scarborough, P., Schmidt, J. C., Schneider, I. J. C., Schöttker, B., Schwebel, D. C., Scott, J. G., Seedat, S., Sepanlou, S. G., Serdar, B., Servan-Mori, E. E., Shaddick, G., Shahrzad, S., Levy, T. S., Shangguan, S., She, J., Sheikhbahaei, S., Shibuya, K., Shin, H. H., Shinohara, Y., Shiri, R., Shishani, K., Shiue, I., Sigfusdottir, I. D., Silberberg, D. H., Simard, E. P., Sindi, S., Singh, A., Singh, G. M., Singh, J. A., Skirbekk, V., Sliwa, K., Soljak, M., Soneji, S., Søreide, K., Soshnikov, S., Sposato, L. A., Sreeramreddy, C. T., Stapelberg, N. J. C., Stathopoulou, V., Steckling, N., Stein, D. J., Stein, M. B., Stephens, N., Stöckl, H., Straif, K., Stroumpoulis, K., Sturua, L., Sunguya, B. F., Swaminathan, S., Swaroop, M., Sykes, B. L., Tabb, K. M., Takahashi, K., Talongwa, R. T., Tandon, N., Tanne, D., Tanner, M., Tavakkoli, M., Te Ao, B. J., Teixeira, C. M., Téllez Rojo, M. M., Terkawi, A. S., Texcalac-Sangrador, J. L., Thackway, S. V., Thomson, B., Thorne-Lyman, A. L., Thrift, A. G., Thurston, G. D., Till-

- mann, T., Tobollik, M., Tonelli, M., Topouzis, F., Towbin, J. A., Toyoshima, H., Traebert, J., Tran, B. X., Trasande, L., Trillini, M., Trujillo, U., Dimbuene, Z. T., Tsilimbaris, M., Tuzcu, E. M., Uchendu, U. S., Ukwaja, K. N., Uzun, S. B., van de Vijver, S., Van Dingenen, R., van Gool, C. H., van Os, J., Varakin, Y. Y., Vasankari, T. J., Vasconcelos, A. M. N., Vavilala, M. S., Veerman, L. J., Velasquez-Melendez, G., Venketasubramanian, N., Vijayakumar, L., Villalpando, S., Violante, F. S., Vlassov, V. V., Vollset, S. E., Wagner, G. R., Waller, S. G., Wallin, M. T., Wan, X., Wang, H., Wang, J., Wang, L., Wang, W., Wang, Y., Warouw, T. S., Watts, C. H., Weichenenthal, S., Weiderpass, E., Weintraub, R. G., Werdecker, A., Wessells, K. R., Westerman, R., Whiteford, H. A., Wilkinson, J. D., Williams, H. C., Williams, T. N., Woldeyohannes, S. M., Wolfe, C. D. A., Wong, J. Q., Woolf, A. D., Wright, J. L., Wurtz, B., Xu, G., Yan, L. L., Yang, G., Yano, Y., Ye, P., Yenese, M., Yentür, G. K., Yip, P., Yonemoto, N., Yoon, S.-J., Younis, M. Z., Younoussi, Z., Yu, C., Zaki, M. E., Zhao, Y., Zheng, Y., Zhou, M., Zhu, J., Zhu, S., Zou, X., Zunt, J. R., Lopez, A. D., Vos, T., and Murray, C. J.: Global, regional, and national comparative risk assessment of 79 behavioural, environmental and occupational, and metabolic risks or clusters of risks in 188 countries, 1990–2013: a systematic analysis for the Global Burden of Disease Study 2013, *The Lancet*, 386, 2287–2323, [https://doi.org/10.1016/S0140-6736\(15\)00128-2](https://doi.org/10.1016/S0140-6736(15)00128-2), 2015.
- García-Martínez, I. and Bollasina, M.: Identifying the evolving human imprint on heat wave trends over the United States and Mexico, *Environ. Res. Lett.*, 16, 094039, <https://doi.org/10.1088/1748-9326/ac1edb>, 2021.
- Geng, F., Tie, X., Guenther, A., Li, G., Cao, J., and Harley, P.: Effect of isoprene emissions from major forests on ozone formation in the city of Shanghai, China, *Atmos. Chem. Phys.*, 11, 10449–10459, <https://doi.org/10.5194/acp-11-10449-2011>, 2011.
- Gong, Y., Cai, M., Yao, L., Cheng, L., Hao, C., and Zhao, Z.: Assessing Changes in the Ecosystem Services Value in Response to Land-Use/Land-Cover Dynamics in Shanghai from 2000 to 2020, *Int. J. Environ. Res. Publ. He.*, 19, 12080, <https://doi.org/10.3390/ijerph191912080>, 2022.
- Gu, C., Wang, S., Zhu, J., Wu, S., Duan, Y., Gao, S., and Zhou, B.: Investigation on the urban ambient isoprene and its oxidation processes, *Atmos. Environ.*, 270, 118870, <https://doi.org/10.1016/j.atmosenv.2021.118870>, 2022.
- Gu, Y., Li, K., Xu, J., Liao, H., and Zhou, G.: Observed dependence of surface ozone on increasing temperature in Shanghai, China, *Atmos. Environ.*, 221, 117108, <https://doi.org/10.1016/j.atmosenv.2019.117108>, 2020.
- Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, *Geosci. Model Dev.*, 5, 1471–1492, <https://doi.org/10.5194/gmd-5-1471-2012>, 2012.
- Heard, D. E., Carpenter, L. J., Creasey, D. J., Hopkins, J. R., Lee, J. D., Lewis, A. C., Pilling, M. J., Seakins, P. W., Carslaw, N., and Emmerson, K. M.: High levels of the hydroxyl radical in the winter urban troposphere, *Geophys. Res. Lett.*, 31, <https://doi.org/10.1029/2004GL020544>, 2004.
- Hoesly, R. M., Smith, S. J., Feng, L., Klimont, Z., Janssens-Maenhout, G., Pitkanen, T., Seibert, J. J., Vu, L., Andres, R. J., Bolt, R. M., Bond, T. C., Dawidowski, L., Kholod, N., Kurokawa, J.-I., Li, M., Liu, L., Lu, Z., Moura, M. C. P., O'Rourke, P. R., and Zhang, Q.: Historical (1750–2014) anthropogenic emissions of reactive gases and aerosols from the Community Emissions Data System (CEDS), *Geosci. Model Dev.*, 11, 369–408, <https://doi.org/10.5194/gmd-11-369-2018>, 2018.
- Hu, L., Jacob, D. J., Liu, X., Zhang, Y., Zhang, L., Kim, P. S., Sulprizio, M. P., and Yantosca, R. M.: Global budget of tropospheric ozone: Evaluating recent model advances with satellite (OMI), aircraft (IAGOS), and ozonesonde observations, *Atmos. Environ.*, 167, 323–334, <https://doi.org/10.1016/j.atmosenv.2017.08.036>, 2017.
- Jin, X. and Holloway, T.: Spatial and temporal variability of ozone sensitivity over China observed from the Ozone Monitoring Instrument, *J. Geophys. Res.-Atmos.*, 120, 7229–7246, <https://doi.org/10.1002/2015JD023250>, 2015.
- Kalisa, E., Fadlallah, S., Amani, M., Nahayo, L., and Habiyaemye, G.: Temperature and air pollution relationship during heat-waves in Birmingham, UK, *Sustain. Cities Soc.*, 43, 111–120, <https://doi.org/10.1016/j.scs.2018.08.033>, 2018.
- Kanaya, Y., Cao, R., Akimoto, H., Fukuda, M., Komazaki, Y., Yokouchi, Y., Koike, M., Tanimoto, H., Takegawa, N., and Kondo, Y.: Urban photochemistry in central Tokyo: 1. Observed and modeled OH and HO₂ radical concentrations during the winter and summer of 2004, *J. Geophys. Res.-Atmos.*, 112, <https://doi.org/10.1029/2007JD008670>, 2007.
- Kavassalis, S. C. and Murphy, J. G.: Understanding ozone-meteorology correlations: A role for dry deposition, *Geophys. Res. Lett.*, 44, 2922–2931, <https://doi.org/10.1002/2016GL071791>, 2017.
- Li, M., Yu, S., Chen, X., Li, Z., Zhang, Y., Wang, L., Liu, W., Li, P., Lichtfouse, E., Rosenfeld, D., and Seinfeld, J. H.: Large scale control of surface ozone by relative humidity observed during warm seasons in China, *Environ. Chem. Lett.*, 19, 3981–3989, <https://doi.org/10.1007/s10311-021-01265-0>, 2021.
- Li, X., Gong, P., Zhou, Y., Wang, J., Bai, Y., Chen, B., Hu, T., Xiao, Y., Xu, B., Yang, J., Liu, X., Cai, W., Huang, H., Wu, T., Wang, X., Lin, P., Li, X., Chen, J., He, C., Li, X., Yu, L., Clinton, N., and Zhu, Z.: Mapping global urban boundaries from the global artificial impervious area (GAIA) data, *Environ. Res. Lett.*, 15, 094044, <https://doi.org/10.1088/1748-9326/ab9be3>, 2020.
- Lishui Municipal Statistics Bureau: Introduction of Lishui, <http://tjj.lishui.gov.cn/col/col1229215882/index.html>, last access: 17 September 2025 (in Chinese).
- Liu, H., Liu, S., Xue, B., Lv, Z., Meng, Z., Yang, X., Xue, T., Yu, Q., and He, K.: Ground-level ozone pollution and its health impacts in China, *Atmos. Environ.*, 173, 223–230, <https://doi.org/10.1016/j.atmosenv.2017.11.014>, 2018.
- Liu, P. and Miao, Y.: Biogenic VOCs from Regional Forests Amplify Ozone Pollution in Shanghai Under Extreme Heat Stress Conditions, *B. Environ. Contam. Tox.*, 117, 23, <https://doi.org/10.1007/s00128-026-04303-1>, 2026.
- Liu, Y., Shen, H., Mu, J., Li, H., Chen, T., Yang, J., Jiang, Y., Zhu, Y., Meng, H., Dong, C., Wang, W., and Xue, L.: Formation of peroxyacetyl nitrate (PAN) and its impact on ozone production in the coastal atmosphere of Qingdao, North China, *Sci. Total Environ.*, 778, 146265, <https://doi.org/10.1016/j.scitotenv.2021.146265>, 2021a.
- Liu, Z., Doherty, R. M., Wild, O., Hollaway, M., and O'Connor, F. M.: Contrasting chemical environments in summertime for

- atmospheric ozone across major Chinese industrial regions: the effectiveness of emission control strategies, *Atmos. Chem. Phys.*, 21, 10689–10706, <https://doi.org/10.5194/acp-21-10689-2021>, 2021b.
- Ma, M., Gao, Y., Ding, A., Su, H., Liao, H., Wang, S., Wang, X., Zhao, B., Zhang, S., Fu, P., Guenther, A. B., Wang, M., Li, S., Chu, B., Yao, X., and Gao, H.: Development and Assessment of a High-Resolution Biogenic Emission Inventory from Urban Green Spaces in China, *Environ. Sci. Technol.*, 56, 175–184, <https://doi.org/10.1021/acs.est.1c06170>, 2022a.
- Ma, X., Tan, Z., Lu, K., Yang, X., Chen, X., Wang, H., Chen, S., Fang, X., Li, S., Li, X., Liu, J., Liu, Y., Lou, S., Qiu, W., Wang, H., Zeng, L., and Zhang, Y.: OH and HO₂ radical chemistry at a suburban site during the EXPLORE-YRD campaign in 2018, *Atmos. Chem. Phys.*, 22, 7005–7028, <https://doi.org/10.5194/acp-22-7005-2022>, 2022b.
- McDuffie, E. E., Edwards, P. M., Gilman, J. B., Lerner, B. M., Dubé, W. P., Trainer, M., Wolfe, D. E., Angevine, W. M., de Gouw, J., Williams, E. J., Tevlin, A. G., Murphy, J. G., Fischer, E. V., McKeen, S., Ryerson, T. B., Peischl, J., Holloway, J. S., Aikin, K., Langford, A. O., Senff, C. J., Alvarez Ii, R. J., Hall, S. R., Ullmann, K., Lantz, K. O., and Brown, S. S.: Influence of oil and gas emissions on summertime ozone in the Colorado Northern Front Range, *J. Geophys. Res.-Atmos.*, 121, 8712–8729, <https://doi.org/10.1002/2016JD025265>, 2016.
- Meehl, G. A., Tebaldi, C., Tilmes, S., Lamarque, J.-F., Bates, S., Pendergrass, A., and Lombardozzi, D.: Future heat waves and surface ozone, *Environ. Res. Lett.*, 13, 064004, <https://doi.org/10.1088/1748-9326/aabdc4>, 2018.
- Meng, X., Jiang, J., Chen, T., Zhang, Z., Lu, B., Liu, C., Xue, L., Chen, J., Herrmann, H., and Li, X.: Chemical drivers of ozone change in extreme temperatures in eastern China, *Sci. Total Environ.*, 874, 162424, <https://doi.org/10.1016/j.scitotenv.2023.162424>, 2023.
- Min, K.-E., Pusede, S. E., Browne, E. C., LaFranchi, B. W., and Cohen, R. C.: Eddy covariance fluxes and vertical concentration gradient measurements of NO and NO₂ over a ponderosa pine ecosystem: observational evidence for within-canopy chemical removal of NO_x, *Atmos. Chem. Phys.*, 14, 5495–5512, <https://doi.org/10.5194/acp-14-5495-2014>, 2014.
- Mulcahy, J. P., Johnson, C., Jones, C. G., Povey, A. C., Scott, C. E., Sellar, A., Turnock, S. T., Woodhouse, M. T., Abraham, N. L., Andrews, M. B., Bellouin, N., Browse, J., Carslaw, K. S., Dalvi, M., Folberth, G. A., Glover, M., Grosvenor, D. P., Hardacre, C., Hill, R., Johnson, B., Jones, A., Kipling, Z., Mann, G., Mollard, J., O'Connor, F. M., Palmieri, J., Reddington, C., Rumbold, S. T., Richardson, M., Schutgens, N. A. J., Stier, P., Stringer, M., Tang, Y., Walton, J., Woodward, S., and Yool, A.: Description and evaluation of aerosol in UKESM1 and HadGEM3-GC3.1 CMIP6 historical simulations, *Geosci. Model Dev.*, 13, 6383–6423, <https://doi.org/10.5194/gmd-13-6383-2020>, 2020.
- Nguyen, D.-H., Lin, C., Vu, C.-T., Cheruiyot, N. K., Nguyen, M. K., Le, T. H., Lukkhasorn, W., Vo, T.-D.-H., and Bui, X.-T.: Tropospheric ozone and NO_x: A review of worldwide variation and meteorological influences, *Environ. Technol. Innovation*, 28, 102809, <https://doi.org/10.1016/j.eti.2022.102809>, 2022.
- Ning, G., Wardle, D. A., and Yim, S. H. L.: Suppression of Ozone Formation at High Temperature in China: From Historical Observations to Future Projections, *Geophys. Res. Lett.*, 49, e2021GL097090, <https://doi.org/10.1029/2021GL097090>, 2022.
- Nolte, C. G., Spero, T. L., Bowden, J. H., Sarofim, M. C., Martinich, J., and Mallard, M. S.: Regional temperature-ozone relationships across the U.S. under multiple climate and emissions scenarios, *J. Air Waste Manage. A.*, 71, 1251–1264, <https://doi.org/10.1080/10962247.2021.1970048>, 2021.
- Olivier, J., Peters, J., Granier, C., Pétron, G., Müller, J.-F., and Wallens, S.: Present and future surface emissions of atmospheric compounds (POET Report #2), EU project EVK2-1999-00011 (POET), 2003.
- Otero, N., Rust, H. W., and Butler, T.: Temperature dependence of tropospheric ozone under NO_x reductions over Germany, *Atmos. Environ.*, 253, 118334, <https://doi.org/10.1016/j.atmosenv.2021.118334>, 2021.
- Pacifico, F., Harrison, S. P., Jones, C. D., Arneth, A., Stith, S., Weedon, G. P., Barkley, M. P., Palmer, P. I., Serça, D., Potosnak, M., Fu, T.-M., Goldstein, A., Bai, J., and Schurgers, G.: Evaluation of a photosynthesis-based biogenic isoprene emission scheme in JULES and simulation of isoprene emissions under present-day climate conditions, *Atmos. Chem. Phys.*, 11, 4371–4389, <https://doi.org/10.5194/acp-11-4371-2011>, 2011.
- Pfister, G. G., Walters, S., Lamarque, J. F., Fast, J., Barth, M. C., Wong, J., Done, J., Holland, G., and Bruyère, C. L.: Projections of future summertime ozone over the U.S., *J. Geophys. Res.-Atmos.*, 119, 5559–5582, <https://doi.org/10.1002/2013JD020932>, 2014.
- Phillips, G. J., Pouvesle, N., Thieser, J., Schuster, G., Axinte, R., Fischer, H., Williams, J., Lelieveld, J., and Crowley, J. N.: Peroxyacetyl nitrate (PAN) and peroxyacetic acid (PAA) measurements by iodide chemical ionisation mass spectrometry: first analysis of results in the boreal forest and implications for the measurement of PAN fluxes, *Atmos. Chem. Phys.*, 13, 1129–1139, <https://doi.org/10.5194/acp-13-1129-2013>, 2013.
- Pope, R. J., Kerridge, B. J., Chipperfield, M. P., Siddans, R., Lat-ter, B. G., Ventress, L. J., Pimlott, M. A., Feng, W., Comyn-Platt, E., Hayman, G. D., Arnold, S. R., and Graham, A. M.: Investigation of the summer 2018 European ozone air pollution episodes using novel satellite data and modelling, *Atmos. Chem. Phys.*, 23, 13235–13253, <https://doi.org/10.5194/acp-23-13235-2023>, 2023.
- Pusede, S. E., Steiner, A. L., and Cohen, R. C.: Temperature and Recent Trends in the Chemistry of Continental Surface Ozone, *Chem. Rev.*, 115, 3898–3918, <https://doi.org/10.1021/cr5006815>, 2015.
- Qin, M., She, Y., Wang, M., Wang, H., Chang, Y., Tan, Z., An, J., Huang, J., Yuan, Z., Lu, J., Wang, Q., Liu, C., Liu, Z., Xie, X., Li, J., Liao, H., Pye, H. O. T., Huang, C., Guo, S., Hu, M., Zhang, Y., Jacob, D. J., and Hu, J.: Increased urban ozone in heatwaves due to temperature-induced emissions of anthropogenic volatile organic compounds, *Nat. Geosci.*, 18, 50–56, <https://doi.org/10.1038/s41561-024-01608-w>, 2025.
- Ren, J., Guo, F., and Xie, S.: Diagnosing ozone–NO_x–VOC sensitivity and revealing causes of ozone increases in China based on 2013–2021 satellite retrievals, *Atmos. Chem. Phys.*, 22, 15035–15047, <https://doi.org/10.5194/acp-22-15035-2022>, 2022.
- Ren, X., Brune, W. H., Mao, J., Mitchell, M. J., Leshner, R. L., Simpas, J. B., Metcalf, A. R., Schwab, J. J., Cai, C., Li, Y., Demerjian, K. L., Felton, H. D., Boynton, G., Adams, A., Perry, J., He,

- Y., Zhou, X., and Hou, J.: Behavior of OH and HO₂ in the winter atmosphere in New York City, *Atmos. Environ.*, 40, 252–263, <https://doi.org/10.1016/j.atmosenv.2005.11.073>, 2006.
- Shanghai Municipal Statistics Bureau: 2023, Statistical Communiqué of Shanghai on the 2023 National Economic and Social Development, <https://tjj.sh.gov.cn/tjgb/20240321/f66c5b25ce604a1f9af755941d5f454a.html> (last access: 17 September 2025), 2024 (in Chinese).
- Shen, L., Mickley, L. J., and Gilleland, E.: Impact of increasing heat waves on U.S. ozone episodes in the 2050s: Results from a multi-model analysis using extreme value theory, *Geophys. Res. Lett.*, 43, 4017–4025, <https://doi.org/10.1002/2016GL068432>, 2016.
- Sillman, S.: The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments, *Atmos. Environ.*, 33, 1821–1845, [https://doi.org/10.1016/S1352-2310\(98\)00345-8](https://doi.org/10.1016/S1352-2310(98)00345-8), 1999.
- Simon, H., Reff, A., Wells, B., Xing, J., and Frank, N.: Ozone Trends Across the United States over a Period of Decreasing NO_x and VOC Emissions, *Environ. Sci. Technol.*, 49, 186–195, <https://doi.org/10.1021/es504514z>, 2015.
- Solberg, S., Hov, Ø., Søvde, A., Isaksen, I. S. A., Coddeville, P., De Backer, H., Forster, C., Orsolini, Y., and Uhse, K.: European surface ozone in the extreme summer 2003, *J. Geophys. Res.-Atmos.*, 113, <https://doi.org/10.1029/2007JD009098>, 2008.
- Steiner, A. L., Tonse, S., Cohen, R. C., Goldstein, A. H., and Harley, R. A.: Influence of future climate and emissions on regional air quality in California, *J. Geophys. Res.-Atmos.*, 111, <https://doi.org/10.1029/2005JD006935>, 2006.
- Steiner, A. L., Davis, A. J., Sillman, S., Owen, R. C., Michalak, A. M., and Fiore, A. M.: Observed suppression of ozone formation at extremely high temperatures due to chemical and biophysical feedbacks, *P. Natl. Acad. Sci. USA*, 107, 19685–19690, <https://doi.org/10.1073/pnas.1008336107>, 2010.
- Stella, P., Loubet, B., Lamaud, E., Laville, P., and Cellier, P.: Ozone deposition onto bare soil: A new parameterisation, *Agr. Forest Meteorol.*, 151, 669–681, <https://doi.org/10.1016/j.agrformet.2011.01.015>, 2011.
- Sun, W., Hess, P., and Liu, C.: The impact of meteorological persistence on the distribution and extremes of ozone, *Geophys. Res. Lett.*, 44, 1545–1553, <https://doi.org/10.1002/2016GL071731>, 2017.
- Sun, Y., Ilango, S. D., Schwarz, L., Wang, Q., Chen, J.-C., Lawrence, J. M., Wu, J., and Benmarhnia, T.: Examining the joint effects of heatwaves, air pollution, and green space on the risk of preterm birth in California, *Environ. Res. Lett.*, 15, 104099, <https://doi.org/10.1088/1748-9326/abb8a3>, 2020.
- Szopa, S., Naik, V., Adhikary, B., Artaxo, P., Bernsten, T., Collins, W. D., Fuzzi, S., Gallardo, L., Kiendler-Scharr, A., Klimont, Z., Liao, H., Unger, N., and Zanis, P.: Short-Lived Climate Forcers, in: *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by: Masson-Delmotte, V., Zhai, P., Pirani, A., Connors, S. L., Péan, C., Berger, S., Caud, N., Chen, Y., Goldfarb, L., Gomis, M. I., Huang, M., Leitzell, K., Lonnoy, E., Matthews, J. B. R., Maycock, T. K., Waterfield, T., Yelekçi, O., Yu, R., and Zhou, B., Cambridge University Press, Cambridge, UK; New York, NY, USA, 817–922, <https://doi.org/10.1017/9781009157896.008>, 2021.
- Tang, Y., Tang, J., Yu, X., Qiu, L., Wang, J., Hou, X., and Chen, D.: Land ecological protection policies improve ecosystem services: A case study of Lishui, China, *Front. Environ. Sci.*, 10, 973524, <https://doi.org/10.3389/fenvs.2022.973524>, 2022.
- Telford, P. J., Abraham, N. L., Archibald, A. T., Braesicke, P., Dalvi, M., Morgenstern, O., O'Connor, F. M., Richards, N. A. D., and Pyle, J. A.: Implementation of the Fast-JX Photolysis scheme (v6.4) into the UKCA component of the MetUM chemistry-climate model (v7.3), *Geosci. Model Dev.*, 6, 161–177, <https://doi.org/10.5194/gmd-6-161-2013>, 2013.
- UKCA: Box model (UKCA Wiki): https://www.ukca.ac.uk/wiki/index.php/Box_model, last access: 6 October 2025.
- Utembe, S. R., Rayner, P. J., Silver, J. D., Guérette, E.-A., Fisher, J. A., Emmerson, K. M., Cope, M., Paton-Walsh, C., Griffiths, A. D., Duc, H., Monk, K., and Scorgie, Y.: Hot Summers: Effect of Extreme Temperatures on Ozone in Sydney, Australia, *Atmosphere*, 9, 466, <https://doi.org/10.3390/atmos9120466>, 2018.
- Walters, D., Baran, A. J., Boutle, I., Brooks, M., Earnshaw, P., Edwards, J., Furtado, K., Hill, P., Lock, A., Mannes, J., Morcrette, C., Mulcahy, J., Sanchez, C., Smith, C., Stratton, R., Tennant, W., Tomassini, L., Van Weverberg, K., Vosper, S., Willett, M., Browse, J., Bushell, A., Carslaw, K., Dalvi, M., Essery, R., Gedney, N., Hardiman, S., Johnson, B., Johnson, C., Jones, A., Jones, C., Mann, G., Milton, S., Rumbold, H., Sellar, A., Ujiie, M., Whittall, M., Williams, K., and Zerroukat, M.: The Met Office Unified Model Global Atmosphere 7.0/7.1 and JULES Global Land 7.0 configurations, *Geosci. Model Dev.*, 12, 1909–1963, <https://doi.org/10.5194/gmd-12-1909-2019>, 2019.
- Wang, M., Li, M., An, Q., Zhang, Z., and Lu, J.: Investigating the Seasonal Effect of Climatic Factors on Evapotranspiration in the Monsoon Climate Zone: A Case Study of the Yangtze River Basin, *Atmosphere*, 14, 1282, <https://doi.org/10.3390/atmos14081282>, 2023.
- Wang, P., Yang, Y., Li, H., Chen, L., Dang, R., Xue, D., Li, B., Tang, J., Leung, L. R., and Liao, H.: North China Plain as a hot spot of ozone pollution exacerbated by extreme high temperatures, *Atmos. Chem. Phys.*, 22, 4705–4719, <https://doi.org/10.5194/acp-22-4705-2022>, 2022a.
- Wang, W., Parrish, D. D., Wang, S., Bao, F., Ni, R., Li, X., Yang, S., Wang, H., Cheng, Y., and Su, H.: Long-term trend of ozone pollution in China during 2014–2020: distinct seasonal and spatial characteristics and ozone sensitivity, *Atmos. Chem. Phys.*, 22, 8935–8949, <https://doi.org/10.5194/acp-22-8935-2022>, 2022b.
- Wesely, M. L.: Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models, *Atmos. Environ.*, 23, 1293–1304, [https://doi.org/10.1016/0004-6981\(89\)90153-4](https://doi.org/10.1016/0004-6981(89)90153-4), 1989.
- Wilson, B., Pope, M., Porter, J. R., Kearns, E., Shu, E., Bauer, M., Freeman, N., Amodeo, M., Melecio-Vazquez, D., Hsieh, H., and Tarasovitch, M.: Characterizing changes in extreme ozone levels under 2050s climate conditions: An extreme-value analysis in California, *Atmos. Environ.-X*, 16, 100195, <https://doi.org/10.1016/j.aeaoa.2022.100195>, 2022.
- World Meteorological Organization: State of the Climate in 2018 shows accelerating climate change impacts, <https://public.wmo.int/media/news/state-of-climate-2018-shows-accelerating-climate-change-impacts> (last access: 7 October 2026), 2019.

- Wu, K., Yang, X., Chen, D., Gu, S., Lu, Y., Jiang, Q., Wang, K., Ou, Y., Qian, Y., Shao, P., and Lu, S.: Estimation of biogenic VOC emissions and their corresponding impact on ozone and secondary organic aerosol formation in China, *Atmos. Res.*, 231, 104656, <https://doi.org/10.1016/j.atmosres.2019.104656>, 2020.
- Wu, S., Mickley, L. J., Leibensperger, E. M., Jacob, D. J., Rind, D., and Streets, D. G.: Effects of 2000–2050 global change on ozone air quality in the United States, *J. Geophys. Res.-Atmos.*, 113, <https://doi.org/10.1029/2007JD008917>, 2008.
- Wu, W., Fu, T.-M., Arnold, S. R., Spracklen, D. V., Zhang, A., Tao, W., Wang, X., Hou, Y., Mo, J., Chen, J., Li, Y., Feng, X., Lin, H., Huang, Z., Zheng, J., Shen, H., Zhu, L., Wang, C., Ye, J., and Yang, X.: Temperature-Dependent Evaporative Anthropogenic VOC Emissions Significantly Exacerbate Regional Ozone Pollution, *Environ. Sci. Technol.*, 58, 5430–5441, <https://doi.org/10.1021/acs.est.3c09122>, 2024.
- Wu, X., Wang, Y., Xu, K., Han, Y., Li, Q., Liu, Y., Fu, H., Zhang, L., and Chen, J.: Seasonal discrepancies and inter-relationship of peroxyacetyl nitrate (PAN), ozone, and other environmental factors in Hangzhou, East China, *Atmos. Environ.*, 314, 120126, <https://doi.org/10.1016/j.atmosenv.2023.120126>, 2023.
- Wu, Y., Zhao, K., Huang, J., Arend, M., Gross, B., and Moshary, F.: Observation of heat wave effects on the urban air quality and PBL in New York City area, *Atmos. Environ.*, 218, 117024, <https://doi.org/10.1016/j.atmosenv.2019.117024>, 2019.
- Xia, Y., Hu, Y., Huang, Y., Bian, J., Zhao, C., Wei, J., Yan, Y., Xie, F., and Lin, J.: Concurrent hot extremes and high ultraviolet radiation in summer over the Yangtze Plain and their possible impact on surface ozone, *Environ. Res. Lett.*, 17, 064001, <https://doi.org/10.1088/1748-9326/ac6c3c>, 2022.
- Xu, J., Huang, X., Wang, N., Li, Y., and Ding, A.: Understanding ozone pollution in the Yangtze River Delta of eastern China from the perspective of diurnal cycles, *Sci. Total Environ.*, 752, 141928, <https://doi.org/10.1016/j.scitotenv.2020.141928>, 2021.
- Xu, T., Nie, W., Xu, Z., Yan, C., Liu, Y., Zha, Q., Wang, R., Li, Y., Wang, L., Ge, D., Chen, L., Qi, X., Chi, X., and Ding, A.: Investigation on the budget of peroxyacetyl nitrate (PAN) in the Yangtze River Delta: Unravelling local photochemistry and regional impact, *Sci. Total Environ.*, 917, 170373, <https://doi.org/10.1016/j.scitotenv.2024.170373>, 2024.
- Yamada, H.: Contribution of evaporative emissions from gasoline vehicles toward total VOC emissions in Japan, *Sci. Total Environ.*, 449, 143–149, <https://doi.org/10.1016/j.scitotenv.2013.01.045>, 2013.
- Yin, Q., Ma, Q., Lin, W., Xu, X., and Yao, J.: Measurement report: Long-term variations in surface NO_x and SO₂ mixing ratios from 2006 to 2016 at a background site in the Yangtze River Delta region, China, *Atmos. Chem. Phys.*, 22, 1015–1033, <https://doi.org/10.5194/acp-22-1015-2022>, 2022.
- Zhang, G., Jing, S., Xu, W., Gao, Y., Yan, C., Liang, L., Huang, C., and Wang, H.: Simultaneous observation of atmospheric peroxyacetyl nitrate and ozone in the megacity of Shanghai, China: Regional transport and thermal decomposition, *Environ. Pollut.*, 274, 116570, <https://doi.org/10.1016/j.envpol.2021.116570>, 2021.
- Zhang, G., Hu, R., Xie, P., Lou, S., Wang, F., Wang, Y., Qin, M., Li, X., Liu, X., Wang, Y., and Liu, W.: Observation and simulation of HO_x radicals in an urban area in Shanghai, China, *Sci. Total Environ.*, 810, 152275, <https://doi.org/10.1016/j.scitotenv.2021.152275>, 2022.
- Zhang, J., Gao, Y., Luo, K., Leung, L. R., Zhang, Y., Wang, K., and Fan, J.: Impacts of compound extreme weather events on ozone in the present and future, *Atmos. Chem. Phys.*, 18, 9861–9877, <https://doi.org/10.5194/acp-18-9861-2018>, 2018.
- Zhang, L., Brook, J. R., and Vet, R.: A revised parameterization for gaseous dry deposition in air-quality models, *Atmos. Chem. Phys.*, 3, 2067–2082, <https://doi.org/10.5194/acp-3-2067-2003>, 2003.
- Zhao, A., Bollasina, M. A., and Stevenson, D. S.: Strong Influence of Aerosol Reductions on Future Heatwaves, *Geophys. Res. Lett.*, 46, 4913–4923, <https://doi.org/10.1029/2019GL082269>, 2019.