

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

Chang Su<sup>1</sup>, Massimo Bollasina<sup>1</sup>, James Weber<sup>2</sup>, David Stevenson<sup>1</sup>

<sup>1</sup>School of GeoSciences, University of Edinburgh, Edinburgh, UK

<sup>2</sup>Department of Meteorology, University of Reading, Reading, UK

Correspondence to: Chang Su (Chang.Su@ed.ac.uk)

**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°C 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, 2023), quantifying how  $O_3$  responds to hot conditions is becoming increasingly critical for policymakers (Ebi et al., 2021). In China, summertime  $O_3$  has

30 remained elevated despite recent controls on nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ), underscoring the need to diagnose the meteorological and chemical drivers of  $\text{O}_3$  during hot periods (Wang et al., 2022b).

Ozone is a significant air pollutant that adversely affects human health, particularly respiratory functions. Exposure to elevated  $\text{O}_3$  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 fatalities were attributed to  $\text{O}_3$  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  $\text{O}_3$  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,  $\text{O}_3$  is also a significant greenhouse gas that further enhances surface warming (Szopa et al., 2021), with positive feedbacks on  $\text{O}_3$  levels (Meng et al., 2023).

The underlying relationship between high temperatures and the resultant increase in surface  $\text{O}_3$  concentration can be modulated by four primary mechanisms: (i) emissions of  $\text{O}_3$  precursors ( $\text{NO}_x$  and VOCs), (ii) rates of chemical reaction, (iii) transport and entrainment from the free troposphere, and (iv) deposition of  $\text{O}_3$  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  $\text{O}_3$  response.

**(i) Emissions.** The production and destruction of  $\text{O}_3$  are highly dependent on its precursors, particularly  $\text{NO}_x$  and volatile organic compounds (VOCs) (Liu et al., 2021b; Solberg et al., 2008). Biogenic VOC (BVOC) emissions, especially isoprene ( $\text{C}_5\text{H}_8$ ), increase exponentially with leaf temperature and light intensity, amplifying  $\text{O}_3$  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  $\text{NO}_x$ -hydrogen oxides ( $\text{HO}_x = \text{OH} + \text{HO}_2$ )-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  $\text{O}_3$ , although the reaction rates of several important processes are negatively correlated with increasing temperature (Archibald et al., 2020a; Gu et al., 2020). Thermal decomposition of peroxyacyl nitrate (PAN) type reservoirs (e.g.,  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$  (PAN)  $\rightarrow$   $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$  (PA) +  $\text{NO}_2$ ) at high temperatures further shifts reactive nitrogen toward  $\text{NO}_x$ , enriching  $\text{O}_3$  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  $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$ , thus favouring net  $\text{O}_3$  production (Li et al., 2021).

**(iii) Transport.** High-temperature extremes like HWs frequently coincide with synoptic stagnation, weak circulation and ventilation, and a deeper planetary boundary layer (PBL) (Archibald et al., 2020a; Duc et al., 2022; Utembe et al., 2018; Wu et al., 2019). Stagnation and weak ventilation consistently concentrate O<sub>3</sub> 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 O<sub>3</sub>, thereby making it harder for ground-level O<sub>3</sub> to build up (Pfister et al., 2014). The impact of a deeper boundary layer ventilation at high temperatures is partly offset by O<sub>3</sub> entrained from the residual layer aloft (Bloomer et al., 2010).

**(iv) Deposition.** The deposition velocity ( $V_d$ ) of O<sub>3</sub> and its precursors is often parameterised as  $V_d = (R_a + R_b + R_c)^{-1}$ , which represents O<sub>3</sub> 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., 2020a; 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 (O<sub>3</sub>, NO<sub>2</sub>) (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., 2020a). In contrast, dry soils tend to exhibit lower soil resistance than moist soils, so soil/litter uptake of O<sub>3</sub> strengthens as surfaces dry—partly offsetting the stomatal signal. (Clifton et al., 2020b; Stella et al., 2011).

Complicating this picture are spatial variations in precursor-sensitivity regimes. In NO<sub>x</sub>-limited (VOC-rich) environments—typically found in rural and regions downwind of ozone precursor emissions—O<sub>3</sub> production increases nearly linearly with NO<sub>x</sub> 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<sub>x</sub>/VOC ratios (VOC-limited regime), additional NO<sub>x</sub> (mainly emitted in the form of NO) can suppress O<sub>3</sub> by titrating ozone back to NO<sub>2</sub> ( $O_3 + NO \rightarrow NO_2 + O_2$ ), and O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> levels as a result of the combined effects of O<sub>3</sub>'s temperature responses, while some reported a non-monotonic relationship between temperature and climate penalty factor (O<sub>3</sub>-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<sub>3</sub>-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 (Meduffie 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<sub>3</sub> 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<sub>3</sub> dynamics.

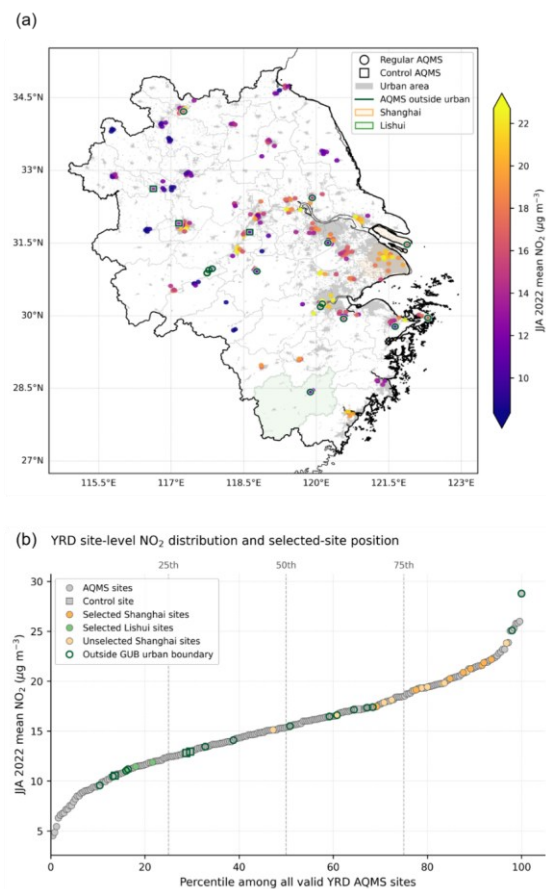
In this study, we investigate the mechanisms of surface O<sub>3</sub>'s chemical response to high temperatures in two contrasting environments within the Yangtze River Delta (YRD) in China: urban Shanghai and rural (forest-influenced) Lishui. Focusing on summer 2022, we combine surface observations with 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<sub>3</sub> response to be attributed to local chemical and emission-related processes under prescribed environmental conditions. By quantifying O<sub>3</sub> 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<sub>3</sub>-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<sub>2</sub> gradient are shown in Fig. 1.



**Figure 1.** (a) Spatial distribution of Air Quality Monitoring Sites (AQMS) across the YRD in summer 2022, coloured by JJA 2022 mean NO<sub>2</sub>. 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 NO<sub>2</sub> 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 ([www.gadm.org](http://www.gadm.org)).

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<sub>x</sub> environment with stronger influence from surrounding vegetated areas. These two cases are used to examine how O<sub>3</sub>-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<sub>2</sub> part of the YRD AQMS distribution, with a mean NO<sub>2</sub> concentration of 20.58 µg m<sup>-3</sup>, corresponding to approximately the 87<sup>th</sup> percentile among valid YRD sites.

The selected Lishui sites occupy a lower-NO<sub>2</sub> part of the YRD AQMS distribution, with a mean NO<sub>2</sub> concentration of 11.46 µg m<sup>-3</sup>, corresponding to approximately the 18<sup>th</sup> 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<sub>x</sub> 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 3,900/km<sup>2</sup> (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<sup>2</sup>, and the urban district accounts for about 8.6% of its total area (Lishui Municipal Statistics Bureau, 2025).

We collected ground-level hourly O<sub>3</sub> observation data from the China National Environmental Monitoring Center (CNEMC). The AQMS are in the busiest areas of Shanghai (30.67°N-31.88°N, 120.85°E-122.2°E) and in the populated centre area of Lishui (27.44°N-28.78°N, 118.70°E-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 O<sub>3</sub> measurements from the national monitoring network. Earlier major heatwave summers in the region, such as 2003 and 2013, predate the availability of constant O<sub>3</sub> observations

(see <https://soft.net/air/>). The 2022 data are therefore used to examine O<sub>3</sub>-temperature sensitivity under a heat extreme setting.

We assessed O<sub>3</sub> and meteorological data for June-August 2022 (JJA 2022). Eight AQMS and two Meteorological Monitoring Sites (MMS) in Shanghai, and three AQMSs and one MMS in Lishui met this criterion (spatial distribution see Fig. 1). For each retained site, we extracted hourly surface O<sub>3</sub> 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.

**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 | 1h                  | Jun-Aug 2022 |
| BS        | Baoshan              | 31.24, 121.27        | Shanghai | Urban       | Temperature & Dew-point temperature | 3h                  | Jun-Aug 2022 |
| LS        | Lishui               | 28.27, 119.55        | Lishui   | Rural       | Temperature & Dew-point temperature | 3h                  | Jun-Aug 2022 |
| 1142A     | Shiwuchang           | 31.20, 121.48        | Shanghai | Urban       | O <sub>3</sub>                      | 1h                  | Jun-Aug 2022 |
| 1143A     | Hongkou              | 31.30, 121.47        | Shanghai | Urban       | O <sub>3</sub>                      | 1h                  | Jun-Aug 2022 |
| 1144A     | Xuhui Shangshida     | 31.17, 121.41        | Shanghai | Urban       | O <sub>3</sub>                      | 1h                  | Jun-Aug 2022 |
| 1145A     | Yangpu Sipiao        | 31.27, 121.54        | Shanghai | Urban       | O <sub>3</sub>                      | 1h                  | Jun-Aug 2022 |
| 1147A     | Jing'an Station      | 31.23, 121.43        | Shanghai | Urban       | O <sub>3</sub>                      | 1h                  | Jun-Aug 2022 |
| 1148A     | Pudong Chuansha      | 31.19, 121.70        | Shanghai | Urban       | O <sub>3</sub>                      | 1h                  | Jun-Aug 2022 |
| 1149A     | Pudong Xinqu Station | 31.23, 121.53        | Shanghai | Urban       | O <sub>3</sub>                      | 1h                  | Jun-Aug 2022 |

|       |                         |               |          |                |                |    |              |
|-------|-------------------------|---------------|----------|----------------|----------------|----|--------------|
| 1150A | Pudong<br>Zhangjiang    | 31.21, 121.58 | Shanghai | Urban          | O <sub>3</sub> | 1h | Jun-Aug 2022 |
| 1267A | Jiancezhan Dalou        | 28.45, 119.91 | Lishui   | Urban/Suburban | O <sub>3</sub> | 1h | Jun-Aug 2022 |
| 1268A | Dandu Primary<br>School | 28.46, 119.93 | Lishui   | Urban/Suburban | O <sub>3</sub> | 1h | Jun-Aug 2022 |
| 1269A | Yuzhuang Qian           | 28.42, 119.88 | Lishui   | Urban/Suburban | O <sub>3</sub> | 1h | Jun-Aug 2022 |

185 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<sub>x</sub> 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.

190 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-day 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.

200 For the ozone-temperature analysis, we use daily maximum surface O<sub>3</sub> (O<sub>3max</sub>) and daily maximum air temperature (T<sub>max</sub>) because climate-penalty assessments are conventionally based on daily peak metrics (e.g. daily max 1-h O<sub>3</sub> versus daily T<sub>max</sub>), 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 period (all JJA days vs. heatwave days), thus yielding four subsets of ozone-temperature analysis: urban-all, urban-HW, rural-all, and rural-HW.

205 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 O<sub>3</sub>, we aligned the temporal resolution by applying a 3-hour mean to the hourly O<sub>3</sub> series, ensuring that O<sub>3</sub>, temperature, and humidity share the same 3-hourly meteorological sampling times.

## 210 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 ( $1.25^\circ \times 1.9^\circ$ ; 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., 2020b; 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  $O_3$  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  $O_3$  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,  $O_3$  budget calculations were carried out by configuring 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  $30^\circ\text{C}$ , 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).

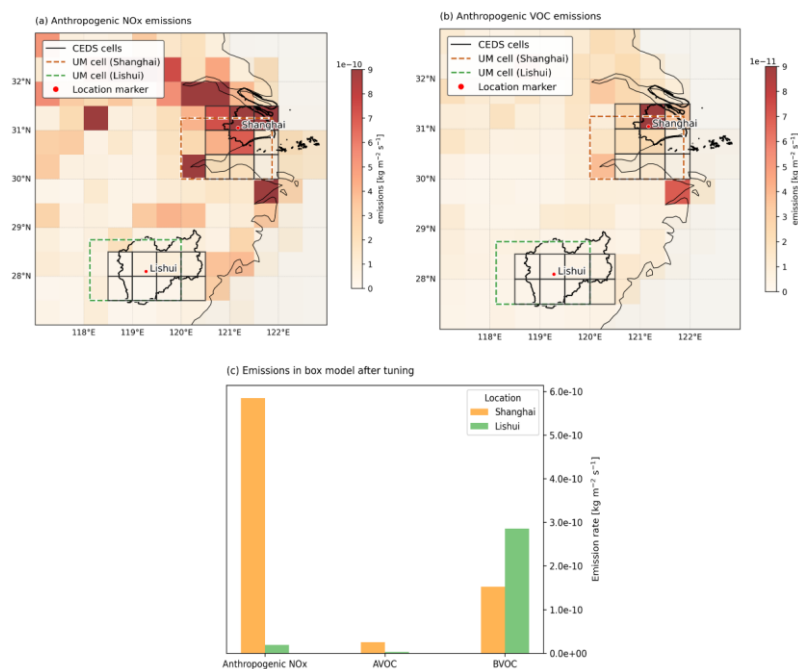
We repeat a representative summer-day radiation cycle until the system attains a steady state (defined as a state in which the variation in the output daily mean values of key chemical species is within  $\pm 0.1\%$  of the previous day). To avoid analysing

relatively unimportant partitioning between O<sub>3</sub> and closely related odd-oxygen species, we focus our analysis on the wider odd-oxygen family (O<sub>x</sub>) (using UKCA definition as O<sub>x</sub> = O<sub>3</sub> + O(<sup>1</sup>D) + O(<sup>3</sup>P) + NO<sub>2</sub> + 2NO<sub>3</sub> + 3N<sub>2</sub>O<sub>5</sub> + HNO<sub>4</sub> + HNO<sub>3</sub> + PANs) (Bates and Jacob, 2020; Hu et al., 2017). The model time resolution is 10 minutes. Initial trace-gas fields follow the standard ST\_urban UKCA box initial-condition set, except the initial concentrations of key O<sub>3</sub> precursors, the concentrations of which are consistent with observations where available (See NO<sub>2</sub>, CO, and C<sub>5</sub>H<sub>8</sub> in Table 2; see other observations in Table S1). Localised adjustments to emissions, deposition, and selected baseline species are described below and in Supplement Tables S1 and S3.

**Table 2.** Observational NO<sub>2</sub>, CO, and C<sub>5</sub>H<sub>8</sub> 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 <sub>2</sub>               | 20.6 ug/m <sup>3</sup>                     | 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 ug/m <sup>3</sup>                      | CNEMC, summer 2022, Shanghai         | 438 ug/m <sup>3</sup>                    | CNEMC, summer 2022, Lishui                                                             |
| C <sub>5</sub> H <sub>8</sub> | 0.3 ppbv                                   | Gu et al. (2022), Jul 2018, Shanghai | 1 to 3 ppbv                              | Geng et al. (2011), Sep 2009, Lishui                                                   |

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.



**Figure 2.** Anthropogenic and biogenic emission fields and box-model emission inputs. (a) CEDS anthropogenic NO<sub>x</sub> emissions over the study region for JJA 2022 (kg NO m<sup>-2</sup> s<sup>-1</sup>). (b) CEDS anthropogenic VOC species included in the box-model emission input, calculated as the sum of C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and HCHO emissions (kg VOC m<sup>-2</sup> s<sup>-1</sup>). (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<sub>x</sub>, sum of AVOC species included in the box-model input, and BVOCs (units: kg m<sup>-2</sup> s<sup>-1</sup>). Coastlines from Natural Earth (naturalearthdata.com). Administrative boundaries from the GADM database (www.gadm.org).

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<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and HCHO, and therefore represents an effective subset rather than the complete urban AVOC mixture. Biogenic emissions of C<sub>5</sub>H<sub>8</sub> 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<sub>3</sub>, CO, HCHO, NO<sub>2</sub>, and the deposited NO<sub>y</sub> species (include NO, NO<sub>2</sub>, NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HO<sub>2</sub>NO<sub>2</sub>, HNO<sub>2</sub>, PAN, PPAN, 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 ±20 % or the observed order of magnitude, prevent unrealistic build-up or over-removal, and retain the intended precursor regime at each site. O<sub>3</sub> was not tuned directly, and its deposition was not adjusted to force agreement with observed O<sub>3</sub>.

The remaining constraints were applied according to the chemical role of each species. CO was constrained to within ±20 % of the available observations. Where suitable observations were unavailable, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> 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 ±20 % of observations shows that the model reproduces the overall reactive VOC environment well and supports the adopted effective AVOC representation. O<sub>3</sub>, 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<sub>x</sub>, VOC-limited environment. NO<sub>2</sub> deposition was increased to represent unresolved NO<sub>x</sub> 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<sub>2</sub> level within ±20 %. C<sub>5</sub>H<sub>8</sub> 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<sub>5</sub>H<sub>8</sub> 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<sub>5</sub>H<sub>8</sub> and monoterpene concentrations remained within the observed order of magnitude.

For Lishui, the adjustment was designed to establish a clean, low-NO<sub>x</sub>, NO<sub>x</sub>-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<sub>2</sub> targets for the regional box environment. Instead, forest-canopy and mountain-background observations  
305 provided order-of-magnitude references for NO<sub>2</sub> (see Table 2). The original NO<sub>2</sub> deposition was retained, and the NO source was reduced only when NO accumulated. C<sub>5</sub>H<sub>8</sub> emissions were reduced to represent export and dilution from the vegetation-rich source region, producing a daytime C<sub>5</sub>H<sub>8</sub> concentration within  $\pm 20$  % of the available Lishui observation. Monoterpene emissions were retained at their inventory value because suitable observations were unavailable.

310 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 O<sub>3</sub> 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  
315 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),  
320 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., 2020b), 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  
325 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 (Pacífico et al., 2011).

Temperature and horizontal wind fields were nudged (Telford et al., 2013) in the model run to the ECMWF ERA5 reanalyses  
330 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.

335 A 6-month run from March 1 2022, to August 31 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

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

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

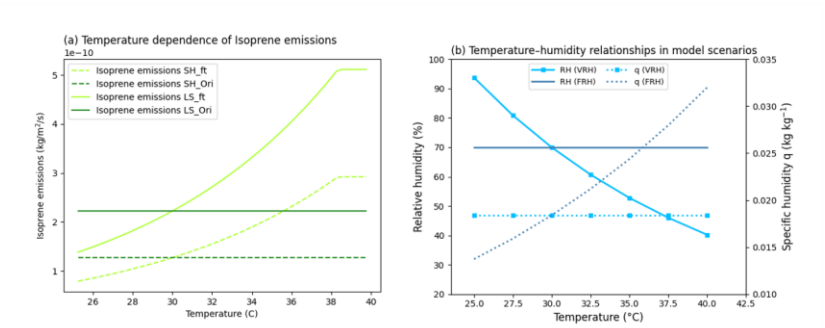
| Index                                 | Experiment | RH            | Diurnal cycle (D) | T-dependent isoprene emission (ft) | Environmental background |
|---------------------------------------|------------|---------------|-------------------|------------------------------------|--------------------------|
| <b>Shanghai - Variable RH (VRH)</b>   |            |               |                   |                                    | <b>Urban</b>             |
| 1                                     | SH_VRH_Ori | Change with T | No                | No                                 | Urban                    |
| 2                                     | SH_VRH_D   | Change with T | Yes               | No                                 | Urban                    |
| 3                                     | SH_VRH_ft  | Change with T | No                | Yes                                | Urban                    |
| 4                                     | SH_VRH_Dft | Change with T | Yes               | Yes                                | Urban                    |
| <b>Lishui - Variable RH (VRH)</b>     |            |               |                   |                                    | <b>Rural</b>             |
| 5                                     | LS_VRH_Ori | Change with T | No                | No                                 | Rural                    |
| 6                                     | LS_VRH_D   | Change with T | Yes               | No                                 | Rural                    |
| 7                                     | LS_VRH_ft  | Change with T | No                | Yes                                | Rural                    |
| 8                                     | LS_VRH_Dft | Change with T | Yes               | Yes                                | Rural                    |
| <b>Shanghai - Fixed RH (RH = 70%)</b> |            |               |                   |                                    | <b>Urban</b>             |
| 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                    |
| <b>Lishui - Fixed RH (RH = 70%)</b>   |            |               |                   |                                    | <b>Rural</b>             |
| 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 |

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 Appendix Table S2).
- 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.



**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<sup>-2</sup> d<sup>-1</sup> (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<sup>-1</sup>) on the right.

365 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.

370 The temperature response of isoprene followed the equations below:

$$\text{isoprene emissions} = \text{local summer average emissions} * ft$$

The ft is the isoprene temperature dependence factor (Pacifico et al., 2011):

375

$$ft = e^{0.1*(T-30)} \text{ when } e^{0.1*(T-30)} < 2.3 \text{ (T in } ^\circ\text{C)} \\ ft = 2.3 \text{ when } e^{0.1*(T-30)} \geq 2.3 \text{ (T in } ^\circ\text{C)}$$

Where T is temperature in centigrade.

380

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

385 The reference conditions were set at 30 °C and 70% RH (mass mixing ratio of water (q) = 0.0184 kg/kg), 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.

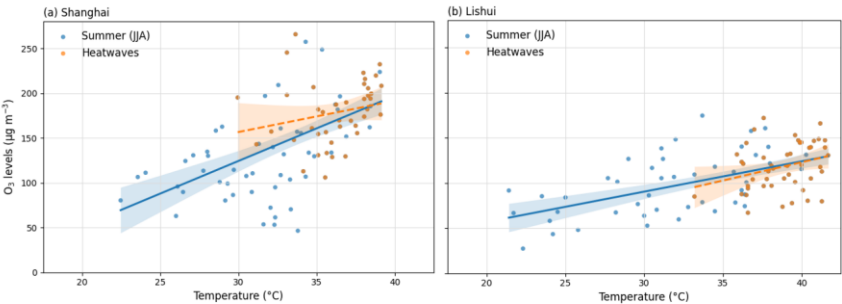
390

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 O<sub>3</sub>-temperature relationship.

395 **3 Results**

**3.1 Observed O<sub>3</sub> response to temperature and humidity variations**

The observed relationships between daily maximum O<sub>3</sub> and daily maximum temperature in Shanghai and Lishui are shown in Fig. 4.



400 **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 Section 2.1) for (a) Shanghai and (b) Lishui. Points are the daily maximum values (average values for sites; spatial distribution shown in Figure 1); solid (JJA) and dashed (heatwave) lines are ordinary-least-squares fits. Shaded envelopes show the 95% confidence intervals for the fitted lines.

405

Across both data subsets (JJA and HW days), and at both locations (Shanghai and Lishui), O<sub>3max</sub> increases with T<sub>max</sub>, resulting in positive correlations. Averaged over eight Shanghai sites, the summertime O<sub>3</sub> fractional change per unit temperature change is 7.27 µg m<sup>-3</sup> °C<sup>-1</sup> 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<sup>-3</sup> °C<sup>-1</sup> (95 % CI [2.30, 4.41], p < 0.01).

410

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 O<sub>3</sub> formation, where temperature increases enhance BVOC emissions while NO<sub>x</sub> 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 O<sub>3</sub> sensitivity to temperature in Shanghai compared

415

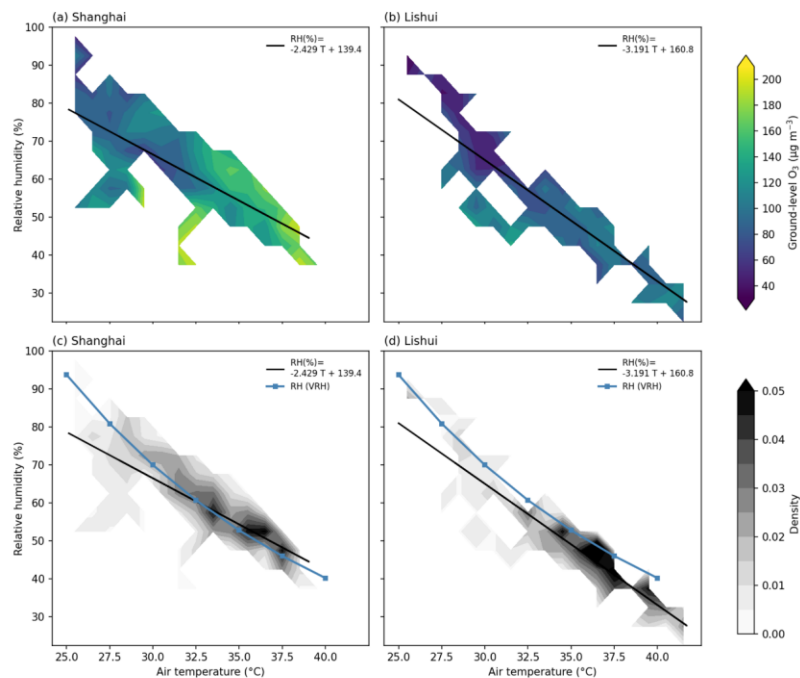
to Lishui is consistent with stronger  $\text{NO}_x$  availability and generally higher pollution levels in Shanghai, and may relate to the capacity for PAN thermal decomposition in the YRD (detailed PAN analysis see Fig. 10) (Steiner et al., 2010).

420 Regressions during HWs indicate a different behaviour at the two locations. In Lishui, the heatwave-period  $\text{O}_{3\text{max}}\text{-T}_{\text{max}}$  sensitivity is  $4.05 \mu\text{g m}^{-3} \text{ }^\circ\text{C}^{-1}$  (95% CI [0.203, 7.899],  $p < 0.05$ ), indicating a significant positive association between  $\text{O}_{3\text{max}}$  and  $\text{T}_{\text{max}}$  during HW periods. By contrast, in Shanghai, the Ordinary Least Squares (OLS) slope estimated from heatwave days is  $3.49 \mu\text{g m}^{-3} \text{ }^\circ\text{C}^{-1}$  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

425 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  $\text{O}_3\text{-T}$  linkage in Shanghai.

To examine the joint influence of temperature and humidity, Fig. 5 shows the observed daytime  $\text{O}_3$  distribution across T-RH

430 space in Shanghai and Lishui.



**Figure 5.** Observed air temperature-relative humidity space for (a, c) Shanghai and (b, d) Lishui (daytime,  $T \geq 25$  °C). Panels (a-b) show the ground-level O<sub>3</sub> (µg m<sup>-3</sup>) binned on a 1 °C × 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 ( $q=0.0184$  kg kg<sup>-1</sup>) used in the VRH model scenario.

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, O<sub>3</sub> increases with temperature and decreases with RH, indicating a preference for warm, dry conditions.

445 Linear regression of RH on T yields slopes of  $-2.429\% \text{ } ^\circ\text{C}^{-1}$  for Shanghai and  $-3.191\% \text{ } ^\circ\text{C}^{-1}$  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  $\text{O}_3$  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  $\text{O}_3$  responds to combined warming and drying. In Lishui, by contrast, the main density maximum lies above the regression line and does not coincide with the dominant  $\text{O}_3$ -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, 455 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  $\text{O}_3$  dry deposition and further enhance  $\text{O}_3$  levels (Kavassalis and Murphy, 2017), contributing to the high- $\text{O}_3$  tail at the hot, dry end of the Lishui distribution.

460 In Figs. 5c and 5d, 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.

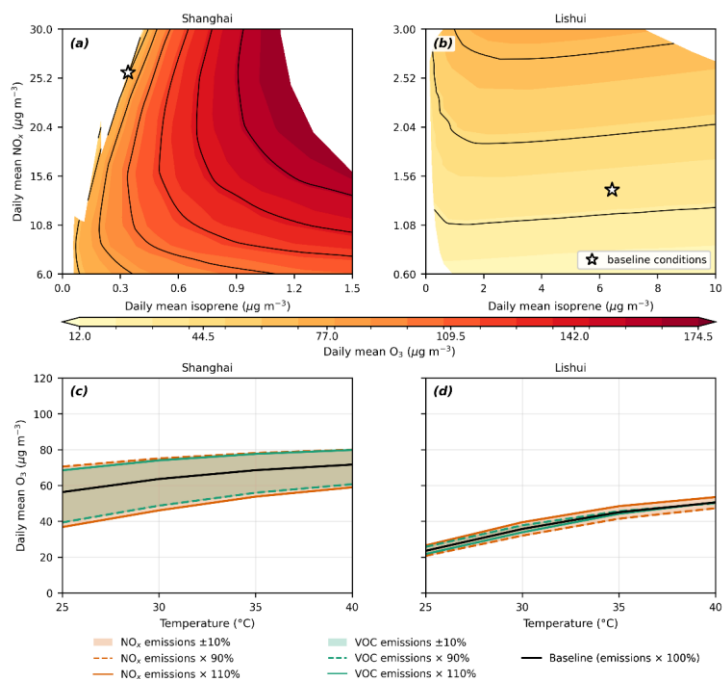
465 Overall, Figure 5 demonstrates that hot, dry conditions are favourable for elevated  $\text{O}_3$  at both sites, but that the joint T-RH- $\text{O}_3$  variability differs between the coastal megacity and the forest-surrounded inland region: Shanghai exhibits a stronger, more coherent  $\text{O}_3$ -T-RH relationship in summer 2022 than Lishui, reflecting differences in local meteorology, surface characteristics, precursor emissions and chemical regime.

470 To interpret these observed  $\text{O}_3$ -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  $\text{O}_3$  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.

### 475 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<sub>3</sub> responses to perturbations in NO<sub>x</sub> and VOC emissions, (ii) contextual comparison of selected short-lived chemical  
480 species with available observations, and (iii) comparison of O<sub>x</sub> 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<sub>3</sub>-temperature analysis, Fig. 6 examines the O<sub>3</sub> response to NO<sub>x</sub> and VOC changes using O<sub>3</sub>-NO<sub>x</sub>-isoprene response surfaces at 30 °C and ±10 % precursor perturbations  
485 across 25 to 40 °C.



**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 °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 °C.

Figure 6 summarises the box-model sensitivity experiments used to diagnose precursor regimes in Shanghai (Fig. 6a and 6c) and Lishui (Fig. 6b and 6d). 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  $\mu g m^{-3}$  in the model versus 69.5  $\mu g m^{-3}$  in the observations. In Lishui, the corresponding values are 35.8  $\mu g m^{-3}$  (model) and 52.5  $\mu g m^{-3}$  (observations), a low bias that is consistent with Lishui

being NO<sub>x</sub>-limited (see below) and suggests that the grid-cell-average NO<sub>x</sub> levels in the box configuration are lower than those sampled by the monitoring site.

Panels (a) and (b) show the simulated O<sub>3</sub> response surfaces in NO<sub>x</sub>-isoprene concentration space at 30 °C for Shanghai and Lishui, respectively. The Shanghai baseline lies within a VOC-limited regime, where O<sub>3</sub> increases with isoprene and decreases with increasing NO<sub>x</sub>. In contrast, the Lishui baseline lies within a NO<sub>x</sub>-limited regime, where O<sub>3</sub> responds positively to NO<sub>x</sub> and only weakly to additional isoprene.

The local ±10 % perturbations show consistent precursor responses across the investigated temperature range. In Shanghai (Fig. 6c), O<sub>3</sub> decreases with higher NO<sub>x</sub> 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<sub>x</sub>, 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 tendency: O<sub>3</sub> increases with NO<sub>x</sub> enhancement and is only weakly affected by VOC perturbations, signifying a NO<sub>x</sub>-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<sub>x</sub> levels (Sillman, 1999).

The signs of these responses remain unchanged between 25 and 40 °C, indicating no regime reversal within the tested perturbation range. These experiments therefore establish contrasting VOC-limited and NO<sub>x</sub>-limited baseline environments for interpreting the subsequent O<sub>3</sub>-temperature and O<sub>x</sub> budget analyses.

The simulated PAN, OH, HO<sub>2</sub>, and C<sub>5</sub>H<sub>8</sub> concentrations are compared with the available observational references in Table 4.

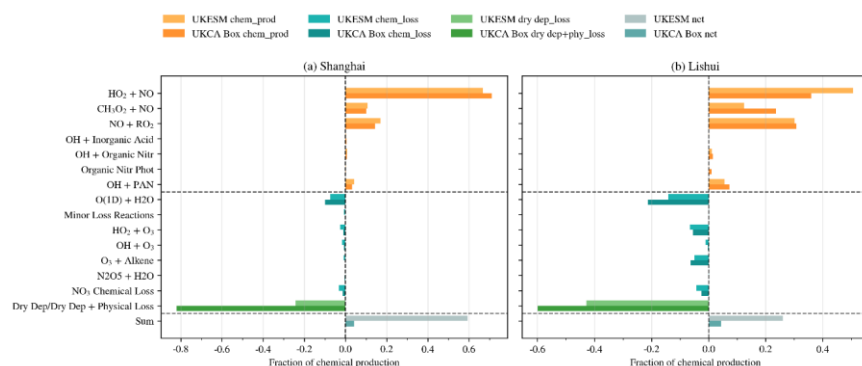
**Table 4.** Comparison of PAN, OH, HO<sub>2</sub>, and C<sub>5</sub>H<sub>8</sub> levels in observation and UKCA Box Model

| Species | Environment | Location | Year | Period  | Value type              | Value (ug/m <sup>3</sup> ) | 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 <sup>-5</sup>     | Observation | Zhang et al. (2022) |
|         | Urban       | Shanghai | 2022 | Summer  | Noon mean (11:00-13:00) | 2.6 × 10 <sup>-4</sup>     | UKCA Box    | This study          |
|         | Suburban    | Taizhou  | 2018 | May-Jun | Daily maximum           | 3.0 × 10 <sup>-4</sup>     | Observation | Ma et al. (2022b)   |
|         | Rural       | Lishui   | 2022 | Summer  | Daily mean              | 1.4 × 10 <sup>-5</sup>     | UKCA Box    | This study          |

|                               |          |          |      |           |                            |                      |             |                     |
|-------------------------------|----------|----------|------|-----------|----------------------------|----------------------|-------------|---------------------|
| HO <sub>2</sub>               | Urban    | Shanghai | 2019 | Nov-Dec   | Noon mean<br>(11:00-13:00) | $4.4 \times 10^{-3}$ | Observation | Zhang et al. (2022) |
|                               | Urban    | Shanghai | 2022 | Summer    | Noon mean<br>(11:00-13:00) | $1.0 \times 10^{-2}$ | UKCA Box    | This study          |
|                               | Suburban | Taizhou  | 2018 | May-Jun   | Daily maximum              | $6.2 \times 10^{-2}$ | Observation | Ma et al. (2022b)   |
|                               | Rural    | Lishui   | 2022 | summer    | Daily mean                 | $2.9 \times 10^{-2}$ | UKCA Box    | This study          |
| C <sub>5</sub> H <sub>8</sub> | 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<br>average         | 8.3                  | Observation | Geng et al. (2011)  |
|                               | Rural    | Lishui   | 2022 | summer    | Daytime<br>average         | 7.4                  | UKCA Box    | This study          |

The model values in Table 4 are from baseline experiments (Ori) at 30 °C. The simulated PAN and C<sub>5</sub>H<sub>8</sub> concentrations are consistent in order of magnitude with the reported observations. Direct summertime OH and HO<sub>2</sub> 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<sub>2</sub> 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<sub>x</sub>, while the Taizhou measurements provide the corresponding warm-season YRD comparison.

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



**Figure 7.** O<sub>x</sub> 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<sub>x</sub> 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.

Figure 7 compares the fractional O<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> 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 (HO<sub>2</sub> + NO and RO<sub>2</sub>/CH<sub>3</sub>O<sub>2</sub> + NO) dominate the chemical production fraction in the box model, matching the pattern in UKESM and consistent with summertime O<sub>3</sub> photochemistry described by Ma et al. (2022b). This agreement in fractional chemistry indicates that the box model captures the regime (NO<sub>x</sub>-VOC-OH coupling) rather than

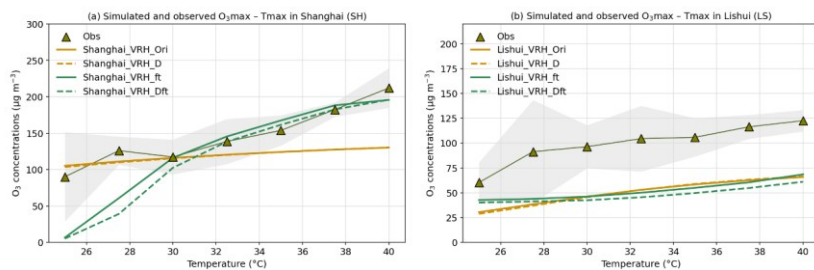
simply tuning totals. Chemical loss through  $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$  and radical-ozone reactions ( $\text{HO}_2 + \text{O}_3$ ,  $\text{OH} + \text{O}_3$ ) is represented with similar sign and relative importance in both frameworks.

The UKCA Box simulation shows a larger fractional contribution from dry deposition to the  $\text{O}_x$  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 horizontal 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  $\text{O}_3$  levels from June to August (UKESM) and the trend of daily mean  $\text{O}_3$  levels (UKCA box model), both UKESM and UKCA Box produce nearly constant surface  $\text{O}_3$ , indicating that the net  $\text{O}_x$  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  $\text{NO}_x$ -sensitive Lishui-like environment, and its dominant  $\text{O}_x$  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  $\text{O}_3$  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 sensitivity and chemical-regime behaviour, rather than as direct simulations of monitored  $\text{O}_3$  concentrations.

### 3.3 Temperature responses of ozone in the box model and observations

The observed and simulated  $\text{O}_{3\text{max}}\text{-T}_{\text{max}}$  relationships are compared in Fig. 8.



**Figure 8.** Comparison of observed and simulated  $O_{3max}$ - $T_{max}$  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 °C  $T_{max}$  bins; e.g., the 25 °C bin denotes summer days with  $T_{max}$  23.75-26.25 °C). Colored solid/dashed lines show the four model configurations (VRH\_Ori, VRH\_D, VRH\_ft, VRH\_Dft; see Table 3).

Figure 8 compares observed JJA  $O_{3max}$ - $T_{max}$  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. 8(a)). 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  $\mu g m^{-3}$  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  $\mu g m^{-3} °C^{-1}$  between 35-37.5 °C to 2.1  $\mu g m^{-3} °C^{-1}$  between 37.5-40 °C; the observations maintain a steeper gradient (~12  $\mu g m^{-3} °C^{-1}$ ). 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<sub>x</sub> variability) may continue to amplify O<sub>3</sub> at extreme temperatures.

Lishui (rural; Fig. 8(b)). The simulations reproduce the shape of the observed O<sub>3</sub>-T curve, but the simulated O<sub>3</sub> is systematically low-biased by about 50 µg m<sup>-3</sup>. This offset is consistent with site representativeness (i.e. the observations exhibit a populated area in Lishui where NO<sub>x</sub> 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<sub>x</sub>-limited regime where additional VOC reactivity produces only modest O<sub>3</sub> increases, i.e. including T-dependence for isoprene leads to higher VOC levels, but this doesn't increase O<sub>3</sub> in Lishui, whereas it does in Shanghai. The small influence of the D option confirms that, after binning by T<sub>max</sub>, imposing a diurnal temperature cycle alone does not substantially alter daily O<sub>3max</sub> in this case.

Overall, the VRH experiments show that the UKCA Box captures the observed temperature sensitivity of O<sub>3</sub> when the isoprene-temperature coupling is represented (Shanghai), while the weak ft/Dft effect at Lishui is consistent with NO<sub>x</sub> 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<sub>x</sub> variability) in future work.

The resulting changes in O<sub>3max</sub> between 30 and 40 °C are quantified in Table 5.

**Table 5.** Changes in daily maximum O<sub>3</sub> (ΔO<sub>3max</sub>) 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 |
| $\Delta\text{O}_3$ in Shanghai | 94.77       | 14.05   | 17.75   | 14.63 | 18.68 | 62.02  | 83.26  | 74.96   | 96.83   |
| $\Delta\text{O}_3$ in Lishui   | 26.21       | 11.66   | 21.08   | 13.04 | 22.4  | 14.43  | 23.81  | 12.43   | 21.57   |

Table 5 presents the increase in O<sub>3max</sub> from 30 to 40 °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<sub>3</sub> warming response by comparing the simulated 30 to 40 °C change. For each experiment X, we define ΔO<sub>3</sub><sup>X</sup> = O<sub>3</sub><sup>X</sup> (40 °C) – O<sub>3</sub><sup>X</sup> (30 °C), and similarly, ΔO<sub>3</sub><sup>obs</sup> from the observations. All metrics below are expressed as fractions of ΔO<sub>3</sub><sup>obs</sup> and therefore dimensionless. The net chemical response is f<sub>chem</sub> = ΔO<sub>3</sub><sup>VRH\_Ori</sup> / ΔO<sub>3</sub><sup>obs</sup>, i.e., the fraction of the observed 30 to 40 °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<sub>3</sub><sup>obs</sup> gained when that process is switched on: for the diurnal cycle, f<sub>diurnal</sub> =

630  $(\Delta O_3^{VRH\_D} - \Delta O_3^{VRH\_Ori}) / \Delta O_3^{obs}$ ; for the isoprene temperature dependence,  $f_{iso} = (\Delta O_3^{VRH\_ft} - \Delta O_3^{VRH\_Ori}) / \Delta O_3^{obs}$ ; and for humidity,  $f_{humid} = (\Delta O_3^{FRH} - \Delta O_3^{VRH}) / \Delta O_3^{obs}$ . 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 °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 °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  $O_{3max}$  at 40 °C. Expressed as a fraction of the observed 30 to 40 °C change, this contribution is  $(\Delta O_3^{FRH\_Dft} - \Delta O_3^{VRH\_Dft}) / \Delta O_3^{obs}$ . This humidity-driven decrease reflects the role of water vapour in enhancing  $O_x$  loss via  $O(^1D) + H_2O$  pathway: in the FRH case, the vertically integrated  $O(^1D) + H_2O$  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.

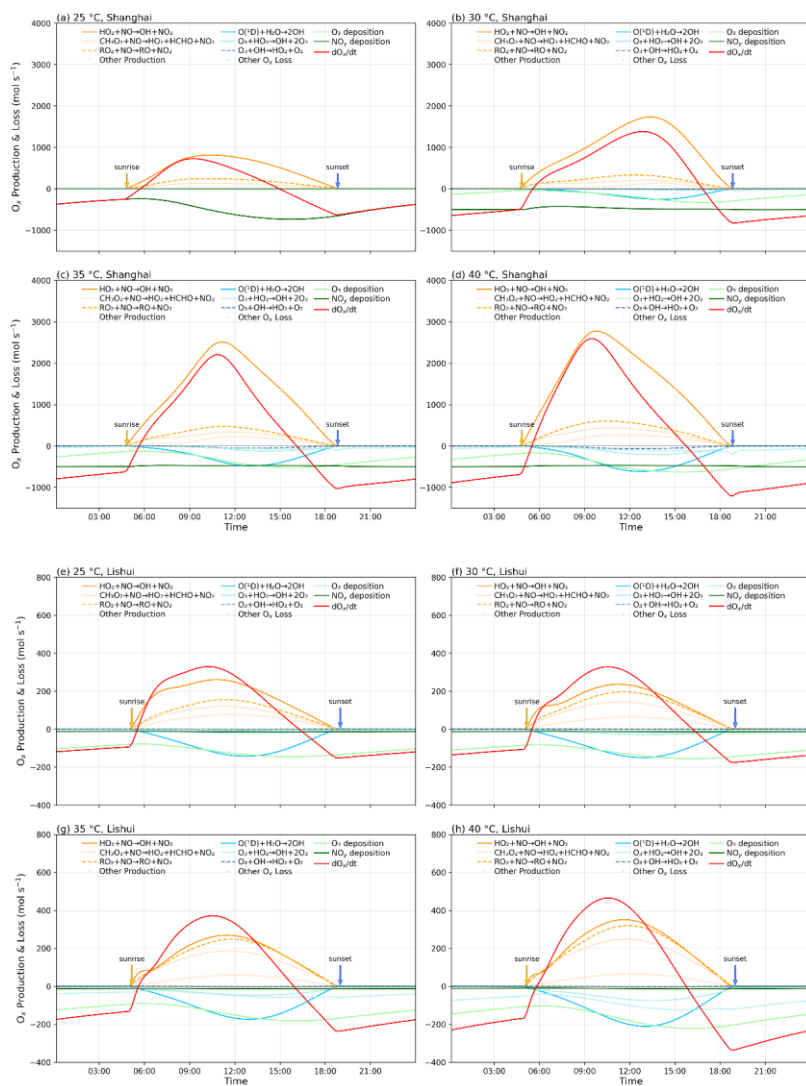
In the  $NO_x$ -limited regime (i.e. Lishui), the process attribution gives different results. The chemical response itself explains 80.4% of the observed 30→40 °C change, implying that enhanced photochemistry at higher temperatures—through faster reaction rates and stronger actinic flux—dominates the  $O_3$  increase (Archibald et al., 2020a). The isoprene temperature dependence contributes only 10.4 %, consistent with a  $NO_x$ -limited environment where additional VOC reactivity produces comparatively small changes in  $O_3$  production (Steiner et al., 2006). The diurnal temperature cycle makes only a minor contribution to the 30→40 °C  $O_3$  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  $HO_2 + NO$  channel ( $\approx 15.3$  % reduction in FRH scenarios compared with that in VRH scenarios), and an enhancement of  $O_x$  loss via  $O_3$  photolysis followed by  $O(^1D) + H_2O$  ( $\approx 36.9$  % compared with VRH scenarios). Both mechanisms are consistent with Li et al. (2021), who showed that elevated relative

humidity suppresses O<sub>3</sub> generation by inhibiting the OH/HO<sub>2</sub>-NO<sub>2</sub> chain and promotes O<sub>3</sub> loss through the O(<sup>1</sup>D) + H<sub>2</sub>O pathway.

Taken together, Figure 8 and Table 5 demonstrate that the UKCA Box model produces a physically interpretable decomposition of the O<sub>3</sub>-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 O<sub>3</sub> extremes under warming.

### 3.4 Temperature response on O<sub>x</sub>, PAN, and HO<sub>x</sub> diurnal cycles

The temperature dependence of the O<sub>x</sub> budget is examined through its diurnal evolution in Fig. 9 and the corresponding daily integrated production and loss terms in Table 6.



675 **Figure 9.** Diurnal O<sub>x</sub> budget in the Dft configuration for Shanghai at T<sub>max</sub> of (a) 25 °C, (b) 30 °C, (c) 35 °C, (d) 40 °C, and  
for Lishui at T<sub>max</sub> 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<sub>x</sub>/dt (red). Arrows indicate local sunrise and  
sunset. Time is local, and budget terms are expressed in mol s<sup>-1</sup>. The y-axis scale is consistent within each site but differs  
between Shanghai and Lishui.

680

**Table 6.** ~~O<sub>x</sub> budget sensitivity to temperature in urban and rural areas~~**Daily contribution of main production and loss pathways**  
~~to the O<sub>x</sub> budget at 25, 30, 35, and 40 °C in Shanghai~~ (unit: tO<sub>x</sub> day<sup>-1</sup>; O<sub>x</sub> counted as O<sub>3</sub>)  
**Table 6(a).** ~~Daily contribution of main production and loss pathways to the O<sub>x</sub> budget at 25, 30, 35, and 40 °C in Shanghai~~

Formatted: Page break before

| Temperature<br>(°C )<br><br>Process              |  | Unit: tO <sub>x</sub> day <sup>-1</sup> |               |               |               |
|--------------------------------------------------|--|-----------------------------------------|---------------|---------------|---------------|
|                                                  |  | 25                                      | 30            | 35            | 40            |
| <b>Chemical Production</b>                       |  |                                         |               |               |               |
| HO <sub>2</sub> +NO                              |  | 1150.5                                  | 2305.7        | 3100.6        | 3559.9        |
| CH <sub>3</sub> O <sub>2</sub> +NO               |  | 193.8                                   | 322           | 489           | 640.2         |
| RO <sub>2</sub> +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         |
| <b>Total Chem Prod</b>                           |  | <b>1726.7</b>                           | <b>3244.3</b> | <b>4502.3</b> | <b>5419.7</b> |
| <b>Chemical loss</b>                             |  |                                         |               |               |               |
| O( <sup>1</sup> D)+H <sub>2</sub> O              |  | 17.4                                    | 292.8         | 567.5         | 751.2         |
| MINOR LOSS REACTIONS                             |  | 11                                      | 4.5           | 4.2           | 4.8           |
| O <sub>3</sub> +HO <sub>2</sub>                  |  | 0                                       | 23.2          | 132.8         | 256.2         |
| O <sub>3</sub> +OH                               |  | 0.2                                     | 19.9          | 58.7          | 80.8          |
| O <sub>3</sub> + ALKENE                          |  | 0.5                                     | 5.2           | 12            | 26.4          |
| N <sub>2</sub> O <sub>5</sub> + H <sub>2</sub> O |  | 0                                       | 17.7          | 41.5          | 53.6          |
| NO <sub>3</sub> Chemical loss                    |  | 0.1                                     | 32.7          | 103.9         | 214.9         |
| <b>Total Chem Loss</b>                           |  | <b>29.3</b>                             | <b>395.9</b>  | <b>920.7</b>  | <b>1387.9</b> |
| <b>Deposition (&amp; transport) loss</b>         |  |                                         |               |               |               |
| O <sub>3</sub> dry Deposition                    |  | 21.8                                    | 711.7         | 1323.3        | 1688.8        |
| NO <sub>y</sub> Deposition                       |  | 2013.7                                  | 2006.9        | 2011.2        | 2012.5        |

685 **Table 6(b).7.** Daily contribution of main production and loss pathways to the O<sub>x</sub> budget at 25, 30, 35, and 40 °C in Lishui  
 (unit: tO<sub>x</sub> day<sup>-1</sup>; O<sub>x</sub> counted as O<sub>3</sub>)

| Total Dep (& trans) Loss                         |                  | 2035.4                                  | 2718.5       | 3334.5        | 3701.3        |
|--------------------------------------------------|------------------|-----------------------------------------|--------------|---------------|---------------|
|                                                  |                  | Unit: tO <sub>x</sub> day <sup>-1</sup> |              |               |               |
| Process                                          | Temperature (°C) | 25                                      | 30           | 35            | 40            |
|                                                  |                  |                                         |              |               |               |
| <b>Chemical Production</b>                       |                  |                                         |              |               |               |
| HO <sub>2</sub> +NO                              |                  | 380                                     | 334.7        | 371.2         | 475.5         |
| CH <sub>3</sub> O <sub>2</sub> +NO               |                  | 173.4                                   | 209.3        | 275.1         | 365.9         |
| RO <sub>2</sub> +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          |
| <b>Total Chem Prod</b>                           |                  | <b>883.7</b>                            | <b>913.2</b> | <b>1077.8</b> | <b>1377.9</b> |
| <b>Chemical loss</b>                             |                  |                                         |              |               |               |
| O( <sup>1</sup> D)+H <sub>2</sub> O              |                  | 187.8                                   | 196.6        | 224.8         | 269.3         |
| MINOR LOSS REACTIONS                             |                  | 0                                       | 0.1          | 0.1           | 0.1           |
| O <sub>3</sub> +HO <sub>2</sub>                  |                  | 35.6                                    | 48.3         | 74.5          | 117.2         |
| O <sub>3</sub> +OH                               |                  | 4                                       | 2            | 1.6           | 1.9           |
| O <sub>3</sub> + ALKENE                          |                  | 11.7                                    | 46.9         | 132.7         | 267.8         |
| N <sub>2</sub> O <sub>5</sub> + H <sub>2</sub> O |                  | 0.1                                     | 0            | 0             | 0             |
| NO <sub>3</sub> Chemical loss                    |                  | 6.5                                     | 15.9         | 35.8          | 69.5          |
| <b>Total Chem Loss</b>                           |                  | <b>245.8</b>                            | <b>309.6</b> | <b>469.6</b>  | <b>725.8</b>  |
| <b>Deposition (&amp; transport) loss</b>         |                  |                                         |              |               |               |
| O <sub>3</sub> dry Deposition                    |                  | 470.7                                   | 496.7        | 564.9         | 669.5         |

|                                     |              |              |              |              |
|-------------------------------------|--------------|--------------|--------------|--------------|
| NO <sub>y</sub> Deposition          | 56.2         | 54.1         | 52.2         | 49.3         |
| <b>Total Dep (&amp; trans) Loss</b> | <b>526.9</b> | <b>550.8</b> | <b>617.1</b> | <b>718.8</b> |

Figure 9, Table 6, and Table 67 summarise how O<sub>x</sub> production and loss terms from the UKCA Box Model respond to temperature. In Shanghai (Fig. 9a-d; Table 6a6), all major production pathways increase with temperature, except for organic-nitrate photolysis (labelled ORG NITR PHOT in Table 6a6), which has a minor impact on total production. From Fig. 9a-d, the reaction HO<sub>2</sub> + NO → OH + NO<sub>2</sub> is the dominant and most temperature-sensitive source of O<sub>x</sub> production. Although its marginal sensitivity (change in O<sub>x</sub> production per °C) weakens from 25→40 °C, it remains the single largest contributor. The second key source, RO<sub>2</sub> + NO → RO + NO<sub>2</sub>, displays the opposite behaviour—its temperature sensitivity strengthens with warming. From 35 to 40 °C, the contribution of RO<sub>2</sub> + NO to total O<sub>x</sub> production increases by 207.7 tO<sub>x</sub> day<sup>-1</sup> 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-HO<sub>2</sub>-RO<sub>2</sub> cycle—most notably the HO<sub>2</sub>+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 HO<sub>2</sub> + NO reaction accounted for more than 50.1 % of total chemical production, confirming the importance of the HO<sub>2</sub>-NO pathway in the urban regime.

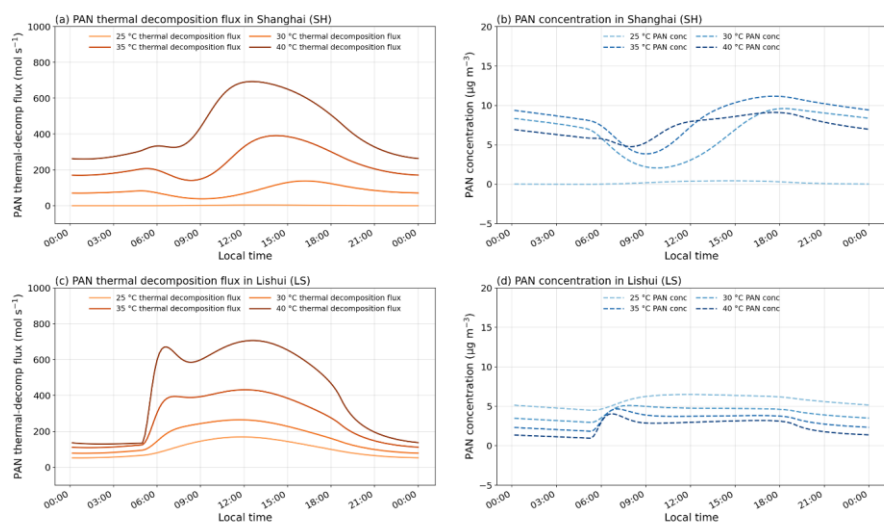
For chemical loss in Shanghai, O(<sup>1</sup>D) + H<sub>2</sub>O → 2OH is the leading term. Its temperature sensitivity is 55.01 tO<sub>x</sub> day<sup>-1</sup> °C<sup>-1</sup> between 25-35 °C, decreasing to ~36.74 tO<sub>x</sub> day<sup>-1</sup> °C<sup>-1</sup> from 35-40 °C, consistent with partial saturation of midday photolysis at the hottest conditions. In the total budget, however, deposition dominates loss. O<sub>3</sub> dry deposition exhibits the stronger temperature sensitivity, which maximises between 25-35 °C, whereas NO<sub>y</sub> deposition varies less with temperature but remains the largest absolute sink at all temperatures, controlling the sign of the net O<sub>x</sub> 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 6b7), 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<sub>x</sub>-limited chemistry outside urban cores in the YRD (An et al., 2021; Ren et al., 2022). HO<sub>2</sub> + NO is still the largest single production term, but at T > 30 °C its strength becomes comparable to CH<sub>3</sub>O<sub>2</sub> + NO and RO<sub>2</sub> + NO, indicating a more distributed peroxy-NO contribution in the regional background. For chemical loss, O(<sup>1</sup>D) + H<sub>2</sub>O dominates from 25-30 °C. At temperatures higher than 30 °C, O<sub>3</sub> + ALKENE reactions' contribution grows rapidly with temperature and becomes comparable in magnitude to O(<sup>1</sup>D) + H<sub>2</sub>O, highlighting the role of thermally enhanced VOC-ozone chemistry outside the urban core where the O<sub>3</sub> + C<sub>5</sub>H<sub>8</sub> reaction plays a crucial role. In the depositional budget, O<sub>3</sub> dry deposition is relatively more important in Lishui than in Shanghai, consistent with the much

larger vegetated land fraction—which elevates deposition velocity of  $O_3$  via stomatal and surface uptake—and with weaker in-situ  $NO_y$  production under rural low- $NO_x$  conditions (Clifton et al., 2020b).

Overall, the Box model yields a coherent, process-level explanation for the observed  $O_3$ -temperature behaviour. In Shanghai, warming amplifies  $O_x$  primarily through  $HO_2 + NO$  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  $O_3$  deposition plays a larger role in the sink, with  $O_3$ -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.** Diurnal peroxyacetyl nitrate (PAN) budget at four temperatures. Panels (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,  $\mu g\ m^{-3}$ ). Each pair corresponds to a temperature scenario (25, 30, 35, 40 °C; lighter→darker with increasing temperature). Local time on the x-axis.

Figure 10 contrasts the diurnal evolution of peroxyacetyl nitrate (PAN) concentrations (dashed curves, right axis) with the thermal decomposition flux  $\text{PAN} \rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2 (\text{PA}) + \text{NO}_2$  (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).

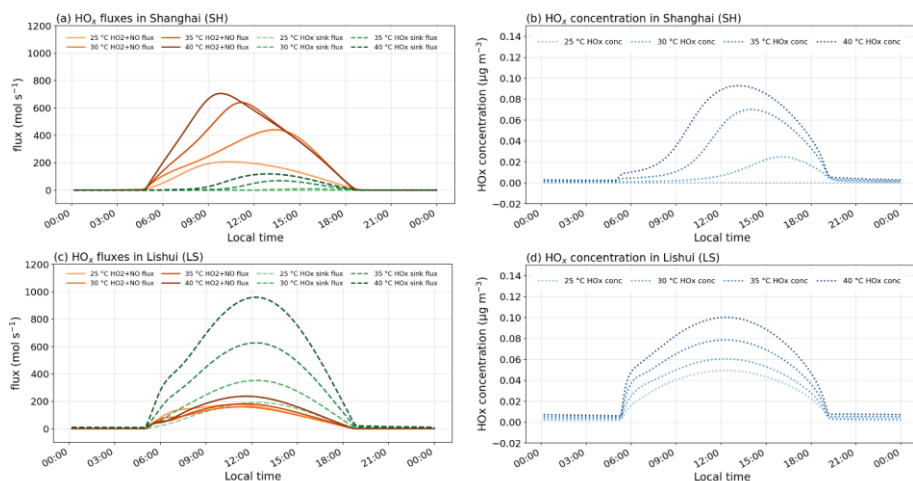
Despite the broadly similar flux patterns, concentration responses differ by site. In Lishui (Fig. 10c-d), PAN concentrations decrease with warming across the full range. As the temperature rises, thermal loss outpaces daytime production (due to low ambient  $\text{NO}_x$ ), so the reservoir is progressively 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  $\text{NO}_2$ —offsets the faster loss, allowing concentrations to rise. However, at 40 °C, the pattern reverses after midday: the decomposition flux jumps sharply relative to 35 °C, while the PAN concentration drops in the afternoon. Two explanations, which are not mutually exclusive, are consistent with the curves. First, PAN's thermal instability means the  $\text{PA} + \text{NO}_2 \rightleftharpoons \text{PAN}$  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.,  $\text{C}_5\text{H}_8$  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 +  $\text{NO}_2$  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  $\text{NO}_x$  reservoir near the urban site.

Overall, Figure 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  $\text{NO}_x$  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<sub>x</sub> cycling and the HO<sub>2</sub> + NO pathway are shown in Fig. 11.



**Figure 11.** Diurnal HO<sub>2</sub>+NO reaction, HO<sub>x</sub> sink, and HO<sub>x</sub> concentration at four temperatures. Panels (a-b) Shanghai and (c-d) Lishui. Solid orange lines show the HO<sub>2</sub>+NO reaction flux (left axis, mol s<sup>-1</sup>); dashed green lines show the total HO<sub>x</sub> sink flux (left axis); dotted blue lines show HO<sub>x</sub> concentration (right axis, µg m<sup>-3</sup>). Each trio corresponds to a temperature scenario (25, 30, 35, 40 °C; lighter→darker with increasing temperature). Local time on the x-axis.

Figure 11 presents the diurnal evolution of the HO<sub>2</sub> + NO production flux (solid orange), the aggregate HO<sub>x</sub>-termination (“sink”) flux (green dashed; e.g. OH + NO<sub>2</sub> + M, HO<sub>2</sub> + RO<sub>2</sub>/HO<sub>2</sub>), and the HO<sub>x</sub> concentration (blue dotted; right axis) at four imposed temperatures. As shown in Fig. 9, the HO<sub>2</sub> and NO reaction is the dominant O<sub>3</sub> chemical production pathway in both environments. HO<sub>x</sub> sink reactions terminate O<sub>3</sub> formation, while HO<sub>x</sub> 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 reactions, so higher HO<sub>x</sub>—especially HO<sub>2</sub>—correlates with stronger photochemical O<sub>3</sub> production (Archibald et al., 2020a; 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.

785 In Shanghai (Fig. 11a-b), warming mainly strengthens the HO<sub>x</sub>-driven O<sub>3</sub> production. With increasing temperature, the daytime  
HO<sub>2</sub> + NO production flux (solid curves) increases strongly, and the peak HO<sub>x</sub> concentrations (blue dotted curves, right axis)  
also increase, indicating more efficient radical recycling and a faster O<sub>3</sub> production cycle at higher T. The HO<sub>x</sub> termination  
flux (green dashed curves) also grows with temperature, but the enhancement remains much smaller than the HO<sub>2</sub> + NO  
790 formation instead of facilitating the HO<sub>x</sub> sink pathway. At T < 30 °C, both HO<sub>x</sub> levels and the sink are low, implying that  
primary radical production is weak and the O<sub>3</sub> production cycle can be slow.

In Lishui (Fig. 11c-d), the behaviour is significantly different. Across the temperature range, the HO<sub>x</sub> sink plays a much larger  
role, and at T ≥ 30 °C, its magnitude exceeds the HO<sub>2</sub> + NO flux. Interpreted in the context of the O<sub>3</sub> chemical cycle, this  
795 means a larger fraction of the available HO<sub>x</sub> is channelled into termination rather than propagation. Even so, HO<sub>x</sub>  
concentrations remain high from 25 to 40 °C, indicating efficient radical production; the high sink simply prevents those  
radicals from translating into proportionally larger HO<sub>2</sub> + NO rates.

Together, the panels show that warming enhances radical activity in both environments, but the partitioning between  
800 propagation and termination is site dependent: Shanghai exhibits production-dominated HO<sub>x</sub> cycling that favours O<sub>3</sub> formation  
at high temperature, whereas Lishui exhibits sink-dominated cycling, consistent with background conditions where O<sub>3</sub>  
production is constrained by NO<sub>x</sub> rather than HO<sub>x</sub> 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  $4.83 \times 10^{-10}$  to  $7.66 \times 10^{-10}$  kg m<sup>-2</sup> s<sup>-1</sup>, while the gasoline-evaporation flux increased by 33.3 %, from  $4.17 \times 10^{-11}$  to  $5.56 \times 10^{-11}$ . The combined selected temperature-dependent AVOC flux consequently increased from  $5.25 \times 10^{-10}$  to  $8.22 \times 10^{-10}$  kg m<sup>-2</sup> s<sup>-1</sup>, 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<sub>3</sub> by 4.6 ppb and peak O<sub>3</sub> 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<sub>3</sub> increase under hot urban conditions. Temperature-dependent AVOCs can therefore increase anthropogenic VOC availability under hot urban conditions, and their resulting O<sub>3</sub> 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<sub>3</sub> 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

835 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 (Pacifico et al., 2011). By contrast, the MEGAN temperature activity factor accounts for both the instantaneous  
840 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  
845 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  
850 167.9 %, respectively.

The differences in calculated isoprene emissions propagated directly into the simulated evolution of daily maximum O<sub>3</sub>. At  
30 °C, both schemes produced the same daily maximum O<sub>3</sub> of 116.1 µg m<sup>-3</sup>. At 40 °C, daily maximum O<sub>3</sub> reached 199.3 µg  
m<sup>-3</sup> with JULES and 212.3 µg m<sup>-3</sup> with MEGAN. The resulting 30-40 °C increases were therefore 83.3 and 96.2 µg m<sup>-3</sup>,  
855 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 µg m<sup>-3</sup>  
more O<sub>3</sub> than JULES. Thus, both schemes confirm a large isoprene-driven amplification of urban O<sub>3</sub> 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.

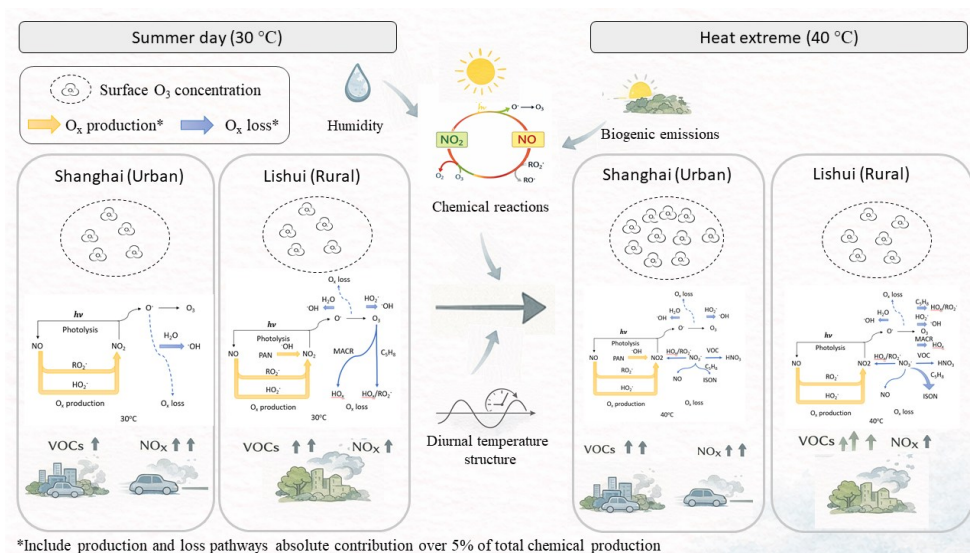
## 860 **5 Summary and conclusions**

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.

870

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.

875



**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).

Summertime daily maximum observations showed robust, positive  $O_3$ -temperature relationships in both regions, stronger in Shanghai than in Lishui (mean JJA  $\Delta O_{3max} - \Delta T_{max} = 7.27$  vs  $3.36 \mu g m^{-3} ^\circ C^{-1}$ ). 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  $\sim 2.4$ - $3.2\%$  RH per  $^\circ C$ , part of the apparent temperature signal is mediated by drying.

885

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  $\sim 70\%$  of the observed  $\Delta O_{3max}$  from 30 to 40  $^\circ C$ , with the diurnal cycle contributing  $\sim 10\%$  (allowing isoprene emissions to change with temperature) and residual kinetics accounting for  $\sim 20\%$ . Below 30  $^\circ C$ , 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-

890

radical chemistry ( $\text{HO}_2/\text{RO}_2+\text{NO}$ ), accounted for ~80 % of the 30 to 40 °C increase, while isoprene's temperature dependence contributed only ~10 %, consistent with a  $\text{NO}_x$ -limited rural regime. Allowing RH to decrease with temperature increased the apparent "thermal chemistry" contribution by ~35% in Lishui and ~20% in Shanghai, underscoring the need to treat T and RH jointly when diagnosing or projecting the climate penalty.

$\text{O}_x$  budgets showed  $\text{HO}_2+\text{NO}$  as the leading production pathway in Shanghai, with  $\text{RO}_2+\text{NO}$  gaining importance toward 40 °C. In Lishui, the daily contribution of  $\text{RO}_2 + \text{NO}$  (including  $\text{CH}_3\text{O}_2$  and other  $\text{RO}_2$  species) to  $\text{O}_x$  production exceeds  $\text{HO}_2+\text{NO}$ , and the value doubles from 25 to 40 °C. On the loss side,  $\text{O}(^1\text{D})+\text{H}_2\text{O}$  dominates chemical destruction at both sites at temperatures from 25 to 35 °C, whereas  $\text{O}_3 + \text{alkene}$  reactions dominate  $\text{O}_3$ 's temperature response at temperatures above 35 °C in Lishui. Deposition and physical transport remain the largest total  $\text{O}_x$  sink except at 40 °C, where the chemical loss dominate the  $\text{O}_x$  sink. For PAN, its thermolysis increased monotonically with temperature at both sites, implying stronger thermal  $\text{NO}_x$  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  $\text{NO}_x$  source above 40 °C.  $\text{HO}_x$  diagnostics showed production-dominated cycling in Shanghai ( $\text{HO}_2+\text{NO}$  and  $[\text{HO}_x]$  increase with T; sink modest) versus sink-dominated cycling in Lishui above ~30 °C (high  $\text{HO}_x$  sink), reinforcing the regime contrast.

Our site-scale attribution complements recent global UKCA applications with enhanced VOC chemistry over China that reproduced peak  $\text{O}_3$  in industrial regions, identified VOC-limited behaviour in most megacity clusters, and demonstrated that  $\text{NO}_x$ -only controls can increase  $\text{O}_3$  in VOC-limited environments. In contrast, VOC controls (or combined controls) are effective in reducing  $\text{O}_3$ . Read in that context, our findings sharpen the process basis for the YRD:

(i) In Shanghai-like urban conditions, temperature-amplified BVOC reactivity is a first-order lever of  $\text{O}_3$  on hot days; mitigating the climate penalty therefore requires simultaneous  $\text{NO}_x$  reductions and targeted VOC management, which corresponds to previous urban  $\text{O}_3$  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.

(ii) In Lishui-like rural conditions,  $\text{O}_3$  sensitivity is governed primarily by radical- $\text{NO}_x$  chemistry and thermal PAN- $\text{NO}_x$  cycling;  $\text{NO}_x$  reductions remain the most robust pathway to limit warming-induced  $\text{O}_3$  amplification, while VOC reductions have a smaller marginal benefit.

(iii) 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 humidity) and surface O<sub>3</sub>, indicating that moist conditions systematically suppress O<sub>3</sub> 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<sub>x</sub> budget through O(<sup>1</sup>D)+H<sub>2</sub>O loss and HO<sub>x</sub>-NO<sub>x</sub> 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<sub>3</sub> comparisons, and O<sub>x</sub>/PAN/HO<sub>x</sub> budgets—builds a consistent mechanistic picture. In summary, summertime O<sub>3</sub> in the YRD increases with temperature for regime-specific reasons: BVOC-driven in the urban core, radical-NO<sub>x</sub>-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<sub>x</sub> control and PAN-mediated NO<sub>x</sub> 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<sub>3</sub> temperature responses within O<sub>x</sub> 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<sub>3</sub> 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: .

### 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 neither they nor their co-authors have any competing interests.

### Disclaimer

Publisher's note: Copernicus Publications remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

### Acknowledgements

We acknowledge the guidance during setting up the UKCA Box Model from Prof. 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).

### 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, 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, *Journal of Advances in Modeling Earth Systems*, 13, e2020MS002420, <https://doi.org/10.1029/2020MS002420>, 2021.

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, *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 378, 20190329, <https://doi.org/10.1098/rsta.2019.0329>, 2020a.

Archibald, A. T., O'Connor, F. M., Abraham, N. L., Archer-Nicholls, S., Chipperfield, M. P., Dalvi, M., Folberth, G. A., Dennison, 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 (StratTrop v1.0) implemented in UKESM1, *Geosci. Model Dev.*, 13, 1223-1266, 10.5194/gmd-13-1223-2020, 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, *Geophysical Research Letters*, 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, *Atmospheric Environment*, 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 O<sub>3</sub> and SOA Formation in a Medium-sized City in Eastern China, *Aerosol and Air Quality Research*, 22, 210239, <http://dx.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, 10.5194/acp-7-1947-2007, 2007.

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, *Journal of Geophysical Research: Atmospheres*, 125, e2020JD032398, <https://doi.org/10.1029/2020JD032398>, 2020a.

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, *Reviews of Geophysics*, 58, e2019RG000670, <https://doi.org/10.1029/2019RG000670>, 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, C. A., III, 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., Balmaseda, 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, *Quarterly Journal of the Royal Meteorological Society*, 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, 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.

Engdaw, 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, *International Journal of Climatology*, 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, *Journal of Geophysical Research: Atmospheres*, 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, *Nature Geoscience*, 3, 398-403, 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, 10.5194/acp-14-2679-2014, 2014.

Forouzanfar, M. H. and Alexander, L. and Anderson, H. R. and Bachman, V. F. and Biryukov, S. and Brauer, M. and Burnett, R. and Casey, D. and Coates, M. M. and Cohen, A. and Delwiche, K. and Estep, K. and Frostad, J. J. and Kc, A. and Kyu, H. H. and Moradi-Lakeh, M. and Ng, M. and Slepak, E. L. and Thomas, B. A. and Wagner, J. and Aasvang, G. M. and Abbafati, C. and Ozgoren, A. A. and Abd-Allah, F. and Abera, S. F. and Aboyans, V. and Abraham, B. and Abraham, J. P. and Abubakar, I. and Abu-Rmeileh, N. M. E. and Aburto, T. C. and Achoki, T. and Adelekan, A. and Adofo, K. and Adou, A. K. and Adsuar, J. C. and Afshin, A. and Agardh, E. E. and Al Khabouri, M. J. and Al Lami, F. H. and Alam, S. S. and Alasfoor, D. and Albittar, M. I. and Alegretti, M. A. and Aleman, A. V. and Alemu, Z. A. and Alfonso-Cristancho, R. and Alhabib, S. and Ali, R. and Ali, M. K. and Alla, F. and Allebeck, P. and Allen, P. J. and Alsharif, U. and Alvarez, E. and Alvis-Guzman, N. and Amankwaa, A. A. and Amare, A. T. and Ameh, E. A. and Ameli, O. and Amini, H. and Ammar, W. and Anderson, B. O. and Antonio, C. A. T. and Anwar, P. and Cunningham, S. A. and Arnlov, J. and Arsenijevic, V. S. A. and Artaman, A. and Asghar, R. J. and Assadi, R. and Atkins, L. S. and Atkinson, C. and Avila, M. A. and Awuah, B. and Badawi, A. and Bahit, M. C. and Bakfalouni,

T. and Balakrishnan, K. and Balalla, S. and Balu, R. K. and Banerjee, A. and Barber, R. M. and Barker-Collo, S. L. and Barquera, S. and Barregard, L. and Barrero, L. H. and Barrientos-Gutierrez, T. and Basto-Abreu, A. C. and Basu, A. and Basu, S. and Basulaiman, M. O. and Ruvalcaba, C. B. and Beardsley, J. and Bedi, N. and Bekele, T. and Bell, M. L. and Benjet, C. and Bennett, D. A. and Benzian, H. and Bernabé, E. and Beyene, T. J. and Bhala, N. and Bhalla, A. and Bhutta, Z. A. and Bikbov, B. and Abdulhak, A. A. B. and Blore, J. D. and Blyth, F. M. and Bohensky, M. A. and Başara, B. B. and Borges, G. and Bornstein, N. M. and Bose, D. and Boufous, S. and Bourne, R. R. and Brainin, M. and Brazinova, A. and Breitborde, N. J. and Brenner, H. and Briggs, A. D. M. and Broday, D. M. and Brooks, P. M. and Bruce, N. G. and Brugha, T. S. and Brunekreef, B. and Buchbinder, R. and Bui, L. N. and Bukhman, G. and Bulloch, A. G. and Burch, M. and Burney, P. G. J. and Campos-Nonato, I. R. and Campuzano, J. C. and Cantoral, A. J. and Caravanas, J. and Cárdenas, R. and Cardis, E. and Carpenter, D. O. and Caso, V. and Castañeda-Orjuela, C. A. and Castro, R. E. and Catalá-López, F. and Cavalleri, F. and Çavlin, A. and Chadha, V. K. and Chang, J.-c. and Charlson, F. J. and Chen, H. and Chen, W. and Chen, Z. and Chiang, P. P. and Chimed-Ochir, O. and Chowdhury, R. and Christophi, C. A. and Chuang, T.-W. and Chugh, S. S. and Cirillo, M. and Claßen, T. K. D. and Colistro, V. and Colomar, M. and Colquhoun, S. M. and Contreras, A. G. and Cooper, C. and Cooperrider, K. and Cooper, L. T. and Coresh, J. and Courville, K. J. and Criqui, M. H. and Cuevas-Nasu, L. and Damsere-Derry, J. and Danawi, H. and Dandona, L. and Dandona, R. and Dargan, P. I. and Davis, A. and Davitoliu, D. V. and Dayama, A. and de Castro, E. F. and De la Cruz-Góngora, V. and De Leo, D. and de Lima, G. and Degenhardt, L. and del Pozo-Cruz, B. and Dellavalle, R. P. and Deribe, K. and Derrett, S. and Jarlais, D. C. D. and Dessalegn, M. and deVeber, G. A. and Devries, K. M. and Dharmaratne, S. D. and Dherani, M. K. and Dicker, D. and Ding, E. L. and Dokova, K. and Dorsey, E. R. and Driscoll, T. R. and Duan, L. and Durrani, A. M. and Ebel, B. E. and Ellenbogen, R. G. and Elshrek, Y. M. and Endres, M. and Ermakov, S. P. and Erskine, H. E. and Eshrati, B. and Esteghamati, A. and Fahimi, S. and Faraon, E. J. A. and Farzadfar, F. and Fay, D. F. J. and Feigin, V. L. and Feigl, A. B. and Fereshtehnejad, S.-M. and Ferrari, A. J. and Ferri, C. P. and Flaxman, A. D. and Fleming, T. D. and Foigt, N. and Foreman, K. J. and Paleo, U. F. and Franklin, R. C. and Gabbe, B. and Gaffikin, L. and Gakidou, E. and Gamkrelidze, A. and Gankpé, F. G. and Gansevoort, R. T. and García-Guerra, F. A. and Gasana, E. and Geleijnse, J. M. and Gessner, B. D. and Gething, P. and Gibney, K. B. and Gillum, R. F. and Ginawi, I. A. M. and Giroud, M. and Giussani, G. and Goenka, S. and Goginashvili, K. and Dantes, H. G. and Gona, P. and de Cosío, T. G. and González-Castell, D. and Gotay, C. C. and Goto, A. and Gouda, H. N. and Guerrant, R. L. and Gughani, H. C. and Guillemin, F. and Gunnell, D. and Gupta, R. and Gupta, R. and Gutiérrez, R. A. and Hafezi-Nejad, N. and Hagan, H. and Hagstromer, M. and Halasa, Y. A. and Hamadeh, R. R. and Hammami, M. and Hankey, G. J. and Hao, Y. and Harb, H. L. and Haregu, T. N. and Haro, J. M. and Havmoeller, R. and Hay, S. I. and Hedayati, M. T. and Heredia-Pi, I. B. and Hernandez, L. and Heuton, K. R. and Heydarpour, P. and Hajar, M. and Hoek, H. W. and Hoffman, H. J. and Hornberger, J. C. and Hosgood, H. D. and Hoy, D. G. and Hsaio, M. and Hu, G. and Hu, H. and Huang, C. and Huang, J. J. and Hubbell, B. J. and Huiart, L. and Hussein, A. and Iannarone, M. L. and Iburg, K. M. and Idrisov, B. T. and Ikeda, N. and Innos, K. and Inoue, M. and Islami, F. and Ismayilova, S. and Jacobsen, K. H. and Jansen, H. A. and Jarvis, D. L. and Jassal, S. K. and Jauregui, A. and Jayaraman, S. and Jeemon, P. and Jensen, P. N. and Jha, V. and Jiang, F. and Jiang, G. and Jiang, Y. and Jonas, J. B. and Juel, K. and Kan,

1085 H. and Roseline, S. S. K. and Karam, N. E. and Karch, A. and Karema, C. K. and Karthikeyan, G. and Kaul, A. and Kawakami, N. and Kazi, D. S. and Kemp, A. H. and Kengne, A. P. and Keren, A. and Khader, Y. S. and Khalifa, S. E. A. H. and Khan, E. A. and Khang, Y.-H. and Khatibzadeh, S. and Khonelidze, I. and Kieling, C. and Kim, D. and Kim, S. and Kim, Y. and Kimokoti, R. W. and Kinfu, Y. and Kinge, J. M. and Kissela, B. M. and Kivipelto, M. and Knibbs, L. D. and Knudsen, A. K. and Kokubo, Y. and Kose, M. R. and Kosen, S. and Kraemer, A. and Kravchenko, M. and Krishnaswami, S. and Kromhout,

1090 H. and Ku, T. and Defo, B. K. and Bicer, B. K. and Kuipers, E. J. and Kulkarni, C. and Kulkarni, V. S. and Kumar, G. A. and Kwan, G. F. and Lai, T. and Balaji, A. L. and Lalloo, R. and Lallukka, T. and Lam, H. and Lan, Q. and Lansingh, V. C. and Larson, H. J. and Larsson, A. and Laryea, D. O. and Lavados, P. M. and Lawrynnowicz, A. E. and Leasher, J. L. and Lee, J.-T. and Leigh, J. and Leung, R. and Levi, M. and Li, Y. and Li, Y. and Liang, J. and Liang, X. and Lim, S. S. and Lindsay, M. P. and Lipshultz, S. E. and Liu, S. and Liu, Y. and Lloyd, B. K. and Logroscino, G. and London, S. J. and Lopez, N. and Lortet-

1095 Tieulent, J. and Lotufo, P. A. and Lozano, R. and Lunevicius, R. and Ma, J. and Ma, S. and Machado, V. M. P. and MacIntyre, M. F. and Magis-Rodriguez, C. and Mahdi, A. A. and Majdan, M. and Malekzadeh, R. and Mangalam, S. and Mapoma, C. C. and Marape, M. and Marcenes, W. and Margolis, D. J. and Margono, C. and Marks, G. B. and Martin, R. V. and Marzan, M. B. and Mashal, M. T. and Masiye, F. and Mason-Jones, A. J. and Matsushita, K. and Matzopoulos, R. and Mayosi, B. M. and Mazorodze, T. T. and McKay, A. C. and McKee, M. and McLain, A. and Meaney, P. A. and Medina, C. and Mehndiratta, M.

1100 M. and Mejia-Rodriguez, F. and Mekonnen, W. and Melaku, Y. A. and Meltzer, M. and Memish, Z. A. and Mendoza, W. and Mensah, G. A. and Meretoja, A. and Mhimbira, F. A. and Micha, R. and Miller, T. R. and Mills, E. J. and Misganaw, A. and Mishra, S. and Ibrahim, N. M. and Mohammad, K. A. and Mokdad, A. H. and Mola, G. L. and Monasta, L. and Hernandez, J. C. M. and Montico, M. and Moore, A. R. and Morawska, L. and Mori, R. and Moschandreas, J. and Moturi, W. N. and Mozaffarian, D. and Mueller, U. O. and Mukaigawara, M. and Mullany, E. C. and Murthy, K. S. and Naghavi, M. and Nahas,

1105 Z. and Naheed, A. and Naidoo, K. S. and Naldi, L. and Nand, D. and Nangia, V. and Narayan, K. M. V. and Nash, D. and Neal, B. and Nejari, C. and Neupane, S. P. and Newton, C. R. and Ngalesoni, F. N. and de Dieu Ngirabega, J. and Nguyen, G. and Nguyen, N. T. and Nieuwenhuijsen, M. J. and Nisar, M. I. and Nogueira, J. R. and Nolla, J. M. and Nolte, S. and Norheim, O. F. and Norman, R. E. and Norrving, B. and Nyakarahuka, L. and Oh, I.-H. and Ohkubo, T. and Olusanya, B. O. and Omer, S. B. and Opio, J. N. and Orozco, R. and Pagcatipunan, R. S., Jr. and Pain, A. W. and Pandian, J. D. and Panelo, C.

1110 I. A. and Papachristou, C. and Park, E.-K. and Parry, C. D. and Caicedo, A. J. P. and Patten, S. B. and Paul, V. K. and Pavlin, B. I. and Pearce, N. and Pedraza, L. S. and Pedroza, A. and Stokic, L. P. and Pekerikli, A. and Pereira, D. M. and Perez-Padilla, R. and Perez-Ruiz, F. and Perico, N. and Perry, S. A. L. and Pervaiz, A. and Pesudovs, K. and Peterson, C. B. and Petzold, M. and Phillips, M. R. and Phua, H. P. and Plass, D. and Poenaru, D. and Polanczyk, G. V. and Polinder, S. and Pond, C. D. and Pope, C. A. and Pope, D. and Popova, S. and Pourmalek, F. and Powles, J. and Prabhakaran, D. and Prasad, N. M. and Qato,

1115 D. M. and Quezada, A. D. and Quistberg, D. A. A. and Racapé, L. and Rafay, A. and Rahimi, K. and Rahimi-Movaghgar, V. and Rahman, S. U. and Raju, M. and Rakovac, I. and Rana, S. M. and Rao, M. and Razavi, H. and Reddy, K. S. and Refaat, A. H. and Rehm, J. and Remuzzi, G. and Ribeiro, A. L. and Riccio, P. M. and Richardson, L. and Riederer, A. and Robinson, M. and Roca, A. and Rodriguez, A. and Rojas-Rueda, D. and Romieu, I. and Ronfani, L. and Room, R. and Roy, N. and

Ruhago, G. M. and Rushton, L. and Sabin, N. and Sacco, R. L. and Saha, S. and Sahathevan, R. and Sahraian, M. A. and Salomon, J. A. and Salvo, D. and Sampson, U. K. and Sanabria, J. R. and Sanchez, L. M. and Sánchez-Pimienta, T. G. and Sanchez-Riera, L. and Sandar, L. and Santos, I. S. and Sapkota, A. and Satpathy, M. and Saunders, J. E. and Sawhney, M. and Saylan, M. I. and Scarborough, P. and Schmidt, J. C. and Schneider, I. J. C. and Schöttker, B. and Schwebel, D. C. and Scott, J. G. and Seedat, S. and Sepanlou, S. G. and Serdar, B. and Servan-Mori, E. E. and Shaddick, G. and Shahraz, S. and Levy, T. S. and Shangquan, S. and She, J. and Sheikhbahaei, S. and Shibuya, K. and Shin, H. H. and Shinohara, Y. and Shiri, R. and Shishani, K. and Shiue, I. and Sigfusdottir, I. D. and Silberberg, D. H. and Simard, E. P. and Sindi, S. and Singh, A. and Singh, G. M. and Singh, J. A. and Skirbekk, V. and Sliwa, K. and Soljak, M. and Soneji, S. and Søreide, K. and Soshnikov, S. and Sposato, L. A. and Sreeramareddy, C. T. and Stapelberg, N. J. C. and Stathopoulou, V. and Steckling, N. and Stein, D. J. and Stein, M. B. and Stephens, N. and Stöckl, H. and Straif, K. and Stroumpoulis, K. and Sturua, L. and Sunguya, B. F. and Swaminathan, S. and Swaroop, M. and Sykes, B. L. and Tabb, K. M. and Takahashi, K. and Talongwa, R. T. and Tandon, N. and Tanne, D. and Tanner, M. and Tavakkoli, M. and Te Ao, B. J. and Teixeira, C. M. and Téllez Rojo, M. M. and Terkawi, A. S. and Texcalac-Sangrador, J. L. and Thackway, S. V. and Thomson, B. and Thorne-Lyman, A. L. and Thrift, A. G. and Thurston, G. D. and Tillmann, T. and Tobollik, M. and Tonelli, M. and Topouzis, F. and Towbin, J. A. and Toyoshima, H. and Traebert, J. and Tran, B. X. and Trasande, L. and Trillini, M. and Trujillo, U. and Dimbuene, Z. T. and Tsilimbaris, M. and Tuzcu, E. M. and Uchendu, U. S. and Ukwaja, K. N. and Uzun, S. B. and van de Vijver, S. and Van Dingenen, R. and van Gool, C. H. and van Os, J. and Varakin, Y. Y. and Vasankari, T. J. and Vasconcelos, A. M. N. and Vavilala, M. S. and Veerman, L. J. and Velasquez-Melendez, G. and Venketasubramanian, N. and Vijayakumar, L. and Villalpando, S. and Violante, F. S. and Vlassov, V. V. and Vollset, S. E. and Wagner, G. R. and Waller, S. G. and Wallin, M. T. and Wan, X. and Wang, H. and Wang, J. and Wang, L. and Wang, W. and Wang, Y. and Warouw, T. S. and Watts, C. H. and Weichenthal, S. and Weiderpass, E. and Weintraub, R. G. and Werdecker, A. and Wessells, K. R. and Westerman, R. and Whiteford, H. A. and Wilkinson, J. D. and Williams, H. C. and Williams, T. N. and Woldeyohannes, S. M. and Wolfe, C. D. A. and Wong, J. Q. and Woolf, A. D. and Wright, J. L. and Wurtz, B. and Xu, G. and Yan, L. L. and Yang, G. and Yano, Y. and Ye, P. and Yenesew, M. and Yentür, G. K. and Yip, P. and Yonemoto, N. and Yoon, S.-J. and Younis, M. Z. and Younoussi, Z. and Yu, C. and Zaki, M. E. and Zhao, Y. and Zheng, Y. and Zhou, M. and Zhu, J. and Zhu, S. and Zou, X. and Zunt, J. R. and Lopez, A. D. and 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&#x2013;2013: a systematic analysis for the Global Burden of Disease Study 2013, *The Lancet*, 386, 2287-2323, 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, *Environmental Research Letters*, 16, 094039, 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, 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, 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, *Atmospheric Environment*, 270, 118870, <https://doi.org/10.1016/j.atmosenv.2021.118870>, 2022.
- 1155 Gu, Y., Li, K., Xu, J., Liao, H., and Zhou, G.: Observed dependence of surface ozone on increasing temperature in Shanghai, China, *Atmospheric Environment*, 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, 10.5194/gmd-5-1471-2012, 2012.
- 1160 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, *Geophysical Research Letters*, 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.
- 1165 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, 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, *Atmospheric Environment*, 167, 323-334, <https://doi.org/10.1016/j.atmosenv.2017.08.036>, 2017.
- 1170 Jin, X. and Holloway, T.: Spatial and temporal variability of ozone sensitivity over China observed from the Ozone Monitoring Instrument, *Journal of Geophysical Research: Atmospheres*, 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 heatwaves in Birmingham, UK, *Sustainable Cities and Society*, 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
- 1175 Kondo, Y.: Urban photochemistry in central Tokyo: 1. Observed and modeled OH and HO<sub>2</sub> radical concentrations during the winter and summer of 2004, *Journal of Geophysical Research: Atmospheres*, 112, <https://doi.org/10.1029/2007JD008670>, 2007.
- Kavassalis, S. C. and Murphy, J. G.: Understanding ozone-meteorology correlations: A role for dry deposition, *Geophysical Research Letters*, 44, 2922-2931, <https://doi.org/10.1002/2016GL071791>, 2017.
- 1180 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, *Environmental Chemistry Letters*, 19, 3981-3989, 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, *Environmental Research Letters*, 15, 094044, 10.1088/1748-9326/ab9be3,
- 1185 2020.

- 丽水简介 [Introduction of Lishui; in Chinese]: <http://tjj.lishui.gov.cn/col/col1229215882/index.html>, last access: 17 Sep 2025.
- 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, *Atmospheric Environment*, 173, 223-230, <https://doi.org/10.1016/j.atmosenv.2017.11.014>, 2018.
- 1190 Liu, P. and Miao, Y.: Biogenic VOCs from Regional Forests Amplify Ozone Pollution in Shanghai Under Extreme Heat Stress Conditions, *Bulletin of Environmental Contamination and Toxicology*, 117, 23, 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, *Science of The Total Environment*, 778, 146265, <https://doi.org/10.1016/j.scitotenv.2021.146265>, 2021a.
- 1195 Liu, Z., Doherty, R. M., Wild, O., Holloway, 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://acp.copernicus.org/articles/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
- 1200 Urban Green Spaces in China, *Environmental Science & Technology*, 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 HO<sub>2</sub> radical chemistry at a suburban site during the EXPLORE-YRD campaign in 2018, *Atmos. Chem. Phys.*, 22, 7005-7028, 10.5194/acp-22-7005-2022, 2022b.
- 1205 McDuffie, E. E., Edwards, P. M., Gilman, J. B., Lerner, B. M., Dubé, W. P., Trainer, M., Wolfe, D. E., Angevine, W. M., deGouw, 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, *Journal of Geophysical Research: Atmospheres*, 121, 8712-8729, <https://doi.org/10.1002/2016JD025265>, 2016.
- 1210 Meehl, G. A., Tebaldi, C., Tilmes, S., Lamarque, J.-F., Bates, S., Pendergrass, A., and Lombardozzi, D.: Future heat waves and surface ozone, *Environmental Research Letters*, 13, 064004, <https://dx.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, *Science of The Total Environment*, 874, 162424, <https://doi.org/10.1016/j.scitotenv.2023.162424>, 2023.
- 1215 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 NO<sub>2</sub> over a ponderosa pine ecosystem: observational evidence for within-canopy chemical removal of NO<sub>x</sub>, *Atmos. Chem. Phys.*, 14, 5495-5512, 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.,
- 1220 Hardacre, C., Hill, R., Johnson, B., Jones, A., Kipling, Z., Mann, G., Mollard, J., O'Connor, F. M., Palmiéri, J., Reddington,

- C., Rumbold, S. T., Richardson, M., Schutzgens, 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, 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.-
- 1225 T.: Tropospheric ozone and NO<sub>x</sub>: A review of worldwide variation and meteorological influences, *Environmental Technology & 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, *Geophysical Research Letters*, 49, e2021GL097090, <https://doi.org/10.1029/2021GL097090>, 2022.
- 1230 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, *Journal of the Air & Waste Management Association*, 71, 1251-1264, 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.
- 1235 Otero, N., Rust, H. W., and Butler, T.: Temperature dependence of tropospheric ozone under NO<sub>x</sub> reductions over Germany, *Atmospheric Environment*, 253, 118334, <https://doi.org/10.1016/j.atmosenv.2021.118334>, 2021.
- Pacifico, F., Harrison, S. P., Jones, C. D., Ameth, A., Sitch, 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-
- 1240 4389, 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, *Journal of Geophysical Research: Atmospheres*, 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
- 1245 analysis of results in the boreal forest and implications for the measurement of PAN fluxes, *Atmos. Chem. Phys.*, 13, 1129-1139, 10.5194/acp-13-1129-2013, 2013.
- Pope, R. J., Kerridge, B. J., Chipperfield, M. P., Siddans, R., Latter, 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
- 1250 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, *Chemical Reviews*, 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, *Nature Geoscience*, 18, 50-56, 10.1038/s41561-024-01608-w, 2025.
- Ren, J., Guo, F., and Xie, S.: Diagnosing ozone-NO<sub>x</sub>-VOC sensitivity and revealing causes of ozone increases in China based on 2013-2021 satellite retrievals, *Atmos. Chem. Phys.*, 22, 15035-15047, 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 HO<sub>2</sub> in the winter atmosphere in New York City, *Atmospheric Environment*, 40, 252-263, <https://doi.org/10.1016/j.atmosenv.2005.11.073>, 2006.
- 2023 年上海市国民经济和社会发展统计公报 [Statistical Communiqué of Shanghai on the 2023 National Economic and Social Development; in Chinese]: <https://tjj.sh.gov.cn/tjgb/20240321/f66c5b25ce604a1f9af755941d5f454a.html>, last access: 17 Sep 2025.
- Shen, L., Mickley, L. J., and Gilleland, E.: Impact of increasing heat waves on U.S. ozone episodes in the 2050s: Results from a multimodel analysis using extreme value theory, *Geophysical Research Letters*, 43, 4017-4025, <https://doi.org/10.1002/2016GL068432>, 2016.
- Sillman, S.: The relation between ozone, NO<sub>x</sub> and hydrocarbons in urban and polluted rural environments, *Atmospheric Environment*, 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<sub>x</sub> and VOC Emissions, *Environmental Science & Technology*, 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, *Journal of Geophysical Research: Atmospheres*, 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, *Journal of Geophysical Research: Atmospheres*, 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, *Proceedings of the National Academy of Sciences*, 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, *Agricultural and Forest Meteorology*, 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, *Geophysical Research Letters*, 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, *Environmental Research Letters*, 15, 104099, 10.1088/1748-9326/abb8a3, 2020.
- 1290 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, 10.1017/9781009157896.008, 2021.
- 1295 Tang, Y., Tang, J., Yu, X., Qiu, L., Wang, J., Hou, X., and Chen, D.: Land ecological protection polices improve ecosystem services: A case study of Lishui, China, *Frontiers in Environmental Science*, Volume 10 - 2022, 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, 10.5194/gmd-6-161-2013, 2013.
- 1300 Box model (UKCA Wiki): [https://www.ukca.ac.uk/wiki/index.php/Box\\_model](https://www.ukca.ac.uk/wiki/index.php/Box_model), last access: 6 Oct 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, <https://doi.org/10.3390/atmos9120466>, 2018.
- 1305 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., Whitall, 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, 10.5194/gmd-12-1909-2019, 2019.
- 1310 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, 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.
- 1315 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, 10.5194/acp-22-8935-2022, 2022b.
- Wesely, M. L.: Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models, *Atmospheric Environment* (1967), 23, 1293-1304, [https://doi.org/10.1016/0004-6981\(89\)90153-4](https://doi.org/10.1016/0004-6981(89)90153-4), 1989.
- 1320

- 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, *Atmospheric Environment*, X, 16, 100195, <https://doi.org/10.1016/j.aeaoa.2022.100195>, 2022.
- Climate change and heatwaves: <https://wmo.int/content/climate-change-and-heatwaves>, last access: 2 June 2025.
- 1325 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, *Atmospheric Research*, 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, *Journal of Geophysical Research: Atmospheres*, 113, <https://doi.org/10.1029/2007JD008917>, 2008.
- 1330 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, *Environmental Science & Technology*, 58, 5430-5441, 10.1021/acs.est.3c09122, 2024.
- 1335 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, *Atmospheric Environment*, 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, *Atmospheric Environment*, 218, 117024, <https://doi.org/10.1016/j.atmosenv.2019.117024>, 2019.
- 1340 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, *Environmental Research Letters*, 17, 064001, 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, *Science of The Total Environment*, 752, 141928, <https://doi.org/10.1016/j.scitotenv.2020.141928>, 2021.
- 1345 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, *Science of The Total Environment*, 917, 170373, <https://doi.org/10.1016/j.scitotenv.2024.170373>, 2024.
- 1350 Yamada, H.: Contribution of evaporative emissions from gasoline vehicles toward total VOC emissions in Japan, *Science of The Total Environment*, 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<sub>x</sub> and SO<sub>2</sub> mixing ratios from 2006 to 2016 at a background site in the Yangtze River Delta region, China, *Atmos. Chem. Phys.*, 22, 1015-1033, 10.5194/acp-22-1015-2022, 2022.

- 1355 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, *Environmental Pollution*, 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 HOx radicals in an urban area in Shanghai, China, *Science of The Total Environment*, 810, 152275, <https://doi.org/10.1016/j.scitotenv.2021.152275>, 2022.
- 1360 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, 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, 10.5194/acp-3-2067-2003, 2003.
- 1365 Zhao, A., Bollasina, M. A., and Stevenson, D. S.: Strong Influence of Aerosol Reductions on Future Heatwaves, *Geophysical Research Letters*, 46, 4913-4923, <https://doi.org/10.1029/2019GL082269>, 2019.