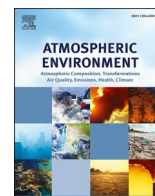




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## Observed dependence of surface ozone on increasing temperature in Shanghai, China

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### HIGHLIGHTS

- Surface O<sub>3</sub> in Shanghai increased during 2010–2017, with decreased NO<sub>x</sub> level in urban city.
- The high-temperature O<sub>3</sub> response is stronger in low NO<sub>x</sub> emission area.
- Biogenic VOCs dominate the high-temperature O<sub>3</sub> response in urban Shanghai.
- NO<sub>x</sub> reductions increase the sensitivity of O<sub>3</sub> to increases in temperature.

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### ABSTRACT

Eight-year measurements at urban (Xujiahui, XJH) and remote (Dongtan, DT) sites during time period 2010–2017 are employed to examine the surface ozone (O<sub>3</sub>)-temperature relationship in Shanghai, China. O<sub>3</sub> pollution was getting worse in Shanghai, with daily maximum O<sub>3</sub> concentrations increasing at a rate of 2.47 ppb yr<sup>-1</sup> in urban site. The climate penalty ( $m_{O_3-T}$ ), defined as the slope of O<sub>3</sub> change with increasing temperature, exhibited largest values in summer. Summertime O<sub>3</sub> increased faster as temperature increased, with mean rates of 6.65 and 13.68 ppb °C<sup>-1</sup>, respectively in XJH and DT above 30 °C. Sensitivity experiments indicate that the temperature dependence of biogenic volatile organic compounds (VOCs) emissions could be the main chemical driver of the high-temperature O<sub>3</sub> response in summer, since the simulated  $m_{O_3-T}$  are most sensitive to changes of biogenic isoprene emissions. NO<sub>x</sub> emission reductions strengthened the high-temperature O<sub>3</sub> response, with summer mean  $m_{O_3-T}$  values increasing from 1.52 ppb °C<sup>-1</sup> during 2010–2012 to 2.97 ppb °C<sup>-1</sup> during 2013–2017. As NO<sub>x</sub> emissions continue to decrease, the O<sub>3</sub> production in urban Shanghai tend to become transitional and the dependence of  $m_{O_3-T}$  on the biogenic VOC emissions might be weakened. Model results suggest that anthropogenic VOC emission reductions would effectively relieve O<sub>3</sub> pollution and reduce the sensitivity of O<sub>3</sub> to increasing temperatures in urban Shanghai. Tailored emission reductions as well as scientific city planning strategies should be formulated to balance VOC/NO<sub>x</sub> ratios, so as to wrestle with the challenges for future O<sub>3</sub> pollution under a warming climate.

### 1. Introduction

Ground-level ozone (O<sub>3</sub>) is a harmful photochemical pollutant threatening human health and land ecosystems (Sicard et al., 2013, 2016; Paoletti et al., 2014; Yue and Unger, 2014; Feng et al., 2019; Li et al., 2019a). Surface O<sub>3</sub> is produced through complex and nonlinear

photochemical oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides (NO<sub>x</sub>≡NO + NO<sub>2</sub>) (Sillman, 2003). Despite the strict emission reductions conducted in past years, many megacities (e.g. Shanghai) in China are suffering from severe O<sub>3</sub> pollution in warm seasons (Geng et al., 2008; Tie et al., 2013; Wang et al., 2017; Li et al., 2019b). Episodes with daily maximum 8-h average (MDA8) O<sub>3</sub> larger

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than 70 ppb occur frequently in eastern China. The 4th highest MDA8 ozone value averaged over China is 86 ppb during 2013–2017, approximately 20–25% higher than the value over Europe and the United States (US) (Lu et al., 2018). Identifying drivers of high O<sub>3</sub> levels is therefore critical to understand the O<sub>3</sub> pollution in China.

Temperature has been reported to be a good predictor of high ground-level O<sub>3</sub>, since it directly influences chemical kinetic rates and emission rates (e.g. biogenic VOCs) that are closely related to O<sub>3</sub> production (Jacob et al., 1993; Steiner et al., 2010). In addition, high temperature is usually associated with sunny, dry and stagnant atmospheric conditions which can further promote the accumulation of O<sub>3</sub> (Jacob et al., 1993; Jing et al., 2017; Li et al., 2019b). The climate change-driven warming is therefore expected to aggravate O<sub>3</sub> pollution and undermine the benefit of emission control measures (Liao et al., 2006; Jacob and Winner, 2009; Wang et al., 2013; Fu et al., 2015). To illustrate the potential effect of climate change on surface O<sub>3</sub>, the climate penalty factor is defined as the slope of the O<sub>3</sub> change with increasing temperature ( $m_{O_3-T}$ ,  $\Delta O_3/\Delta T$ ) (Bloomer et al., 2009). The values of  $m_{O_3-T}$  were reported in the range of 2–8 ppb °C<sup>-1</sup> during ozone pollution seasons based on observational and numerical studies (e.g. Bloomer et al., 2009; Steiner et al., 2010; Rasmussen et al., 2012). Understanding how O<sub>3</sub> responds to temperature changes is considered to be helpful to evaluate the climate impact on air quality and develop effective emission-cutting policies to reduce O<sub>3</sub> pollution.

Several studies have attempted to examine drivers of the observed O<sub>3</sub>-temperature relationship, suggesting that  $m_{O_3-T}$  is a function of multiple processes including peroxyacetyl nitrate (PAN) chemistry, biogenic VOC (BVOC) emissions, photochemical reactions, and temperature-related meteorological characteristics (Sillman and Samson, 1995; Steiner et al., 2010; Pusede et al., 2015; Shen et al., 2016). Based on observations and numerical experiments, Steiner et al. (2010) found that the decreases in PAN thermal decomposition and biogenic isoprene emissions at extremely high temperatures led to reductions in  $m_{O_3-T}$  at temperatures above approximately 39 °C in California. By analyzing long-term ground-level measurements in the Midwestern US during 1990–2015, Jing et al. (2017) indicated that dry tropical weather could aggravate the ozone-climate penalty despite the NO<sub>x</sub> emission reductions. Local VOC/NO<sub>x</sub> ratios could greatly influence the response of  $m_{O_3-T}$  to emission reductions. For NO<sub>x</sub>-limited areas, NO<sub>x</sub> reductions could efficiently weaken  $m_{O_3-T}$  (Bloomer et al., 2009; Rasmussen et al., 2012; Pusede et al., 2014), while for VOC-limited regions, O<sub>3</sub> concentrations and  $m_{O_3-T}$  could be more sensitive to changes in VOC emissions (Steiner et al., 2010). Thus, the high-temperature O<sub>3</sub> response and corresponding drivers should be carefully resolved under different emission circumstances.

Although studies have examined the impact of climate change on O<sub>3</sub> (Jacob and Winner, 2009; Steiner et al., 2010; Rasmussen et al., 2012; Jing et al., 2017), the high-temperature O<sub>3</sub> response was seldom evaluated observationally in Chinese megacities since O<sub>3</sub> has not been regularly monitored by environment agencies until 2013. Shanghai provides a typical locale to study the O<sub>3</sub>-temperature relationship due to the early conducted O<sub>3</sub> measurements since 2005. What's more, as one of the largest megacities in China, Shanghai is home to a population of more than 20 million and is frequently engulfed by severe O<sub>3</sub> pollution episodes recently (Geng et al., 2008; Tie et al., 2009; Wang et al., 2017; Li et al., 2019b). The observed summer MDA8 O<sub>3</sub> increased by about 2 ppb yr<sup>-1</sup> over Yangtze River Delta during 2013–2017 (Li et al., 2019b). The maximum 1-h O<sub>3</sub> concentrations could reach over 380 µg m<sup>-3</sup> during polluted days in Shanghai (Shi et al., 2015). O<sub>3</sub> formation in urban Shanghai has been proved to be under VOC-limited regime that prevails in urban China (Geng et al., 2007; Ran et al., 2009; Tie et al., 2009). Long-term measurements suggested that O<sub>3</sub> concentrations increased by 67% in urban Shanghai from 2006 to 2015, which were mainly attributed to the reduction of the local NO<sub>x</sub> emissions (Gao et al., 2017). Therefore, NO<sub>x</sub> reduction measures together with the warmer climate might result in further increases in O<sub>3</sub>

concentrations, leading to greater challenges for local O<sub>3</sub> pollution controls.

This work aims to identify the response of O<sub>3</sub> to the increasing temperatures and tease apart the corresponding temperature-driven chemical and meteorological reasons. We focus on Shanghai, since the city is still going through increasing high-O<sub>3</sub> episodes though strict emission reductions are conducted (Gao et al., 2017; Wang et al., 2017). Analysis is based on 8-year surface observations as well as simulations using the National Center for Atmospheric Research (NCAR) Master Mechanism model in Xujiahui (XJH, urban) and Dongtan (DT, rural) sites in Shanghai. The research results will provide important implications for how O<sub>3</sub> pollution responds to warmer temperatures and help to guide scientific emission control strategies for megacities in China.

## 2. Material and methods

### 2.1. Observational data

The measurements of O<sub>3</sub>, NO<sub>x</sub>, VOCs, as well as meteorological parameters (temperature, precipitation and wind speed) in this study are obtained from routine observations conducted by the Yangtze River Delta Center for Environmental Meteorology Prediction and Warning in Shanghai. Measurements from two sites are analyzed to represent the urban and rural conditions, including an urban-center site (XJH) greatly influenced by anthropogenic emissions and a background site (DT) located at the east edge of the city along the coast of the East Sea. The DT site locates near the nature reserve of the Chongming Island, with large sources of BVOCs generated from the forest. Hourly data collected from January 2010 to December 2017, a period with available O<sub>3</sub> measurements in both sites, are used in this study. O<sub>3</sub> concentrations were measured with an analyzer from Ecotech, Australia (Model EC9810), which combined microprocessor control with ultraviolet photometry. NO and NO<sub>2</sub> concentrations were measured with a chemiluminescent trace level analyzer (TEI; Model 42iTL), with a detection limit of 0.025 ppb. The XJH site was equipped with additional instruments (a silonite canister with silonite coated valve, model 29–10622) for inconsecutive VOCs measurements in the morning (6–8 a.m.) during 2010–2015. The collected VOC samples include major atmospheric hydrocarbon compounds (e.g. alkane, alkene, and aromatic species) in Shanghai. More detailed information of VOC species, observation instruments, and methods can be found in Geng et al. (2009) and Gao et al. (2017).

### 2.2. Assessing trends of gases and temperature

The means of daily extremum concentrations of O<sub>3</sub>, NO, and NO<sub>2</sub> of each year are used to analyze their year-to-year changes during time period 2010–2017. O<sub>3</sub> exceedance is yearly calculated to analyze changes in O<sub>3</sub> air quality during 2010–2017, which is the number of days with O<sub>3</sub> concentration exceeding the Chinese Grade II national air quality standard, namely MDA8 O<sub>3</sub> larger than 160 µg m<sup>-3</sup>. The means of daily maximum and minimum temperature of each year are used to analyze the temperature changes from 2010 to 2017. Two non-parametric methods were used to assess the trends of variables. The Mann-Kendall (MK) trend test (Mann, 1945; Kendall, 1975; Gilbert, 1987) is used to examine the trend significance and the Sen trend estimate method (Sen, 1968) is used to estimate the slope of trend, which could also be considered as the changing rate, during the studied period. Compared to the parametric methods which require data to be independent and normally distributed, the non-parametric trend test methods only need the data be independent and been widely used in the detection of trends of meteorological variables (Gocic and Trajkovic, 2013).

### 2.3. Determining the O<sub>3</sub>-temperature relationship

The ozone-climate penalty factor ( $m_{O_3-T}$ ) is assessed to examine the dependence of surface O<sub>3</sub> on the increasing temperatures. The  $m_{O_3-T}$  is analyzed by fitting the relationship between daily maximum O<sub>3</sub> concentrations (O<sub>3-max</sub>) and daily maximum temperature (T<sub>max</sub>) by a second-order regression according to Bloomfield et al. (1996) and Jing et al. (2017). The regression equation can be expressed as  $[O_{3-max}] = b_0 + b_1[T_{max}] + b_2[T_{max}]^2$ , where the value of  $b_1/(-2b_2)$  reflects the temperature above which O<sub>3</sub> begins to increase as temperature goes up, and the value of  $2b_2$  (ppb °C<sup>-2</sup>) refers to the change rate of  $m_{O_3-T}$  with increasing temperature. Using this method, the slope of the O<sub>3</sub>-temperature relationship ( $m_{O_3-T}$ ) becomes a temperature-dependent variable rather than a constant, which helps to identify its response on the increasing temperatures. To make comparisons with the  $m_{O_3-T}$  in summer (June–August), the regression is also performed for other seasons.

### 2.4. Chemical box model description

To examine the sensitivity of  $m_{O_3-T}$  to changes in precursors and emissions, numerical experiments are conducted using the NCAR Master Mechanism model (v2.5, <https://www2.acom.ucar.edu/modeling/ncar-master-mechanism>). The model is a chemistry box model including approximately 5000 reactions among 2000 chemical species (Madronich and Calvert, 1990). The time-dependent chemical evolution of an air parcel can be calculated with known initial compositions, emissions and meteorological conditions, offering an opportunity to examine detailed chemical transformations for a single grid cell at a level that would be hard to achieve for 3-D models. The model used in this study is specified to consider major species involved in the urban O<sub>3</sub> chemistry, including NO<sub>x</sub>, carbon monoxide (CO) and more than 32 VOC species. The photolysis rate is calculated on-line using radiative transfer code (TUV) as described in Madronich and Flocke (1999).

The initial concentrations of species are assigned according to the mean concentrations from measurements in this study and from Geng et al. (2007) and Zhang, 2012. The assigned diurnal variations of the planetary boundary layer height (PBLH) obtained from daily calculation of the Regional Atmospheric Environmental Modeling System for eastern China (RAEMS, Zhou et al., 2017). Anthropogenic emissions (Fig. S1) are based on the multi-resolution emission inventory for China (MEIC inventory, <http://www.meicmodel.org/>; Li et al., 2014) for year

2010. Biogenic isoprene emission rates are based on the isoprene-temperature parameterization of Guenther et al. (2006) (Fig. S2).

## 3. Results

### 3.1. Changes of ozone air quality in Shanghai during time period 2010–2017

Fig. 1 shows the year-to-year changes of O<sub>3</sub> exceedance, means of daily extremum O<sub>3</sub> concentrations and temperature in urban (XJH) and rural (DT) sites, respectively. In general, all the variables exhibited increasing trends during time period 2010–2017, and the majority of the trends were significant at the 5% significance level. The number of O<sub>3</sub> exceedance days increased by 8.3 and 1.3 times from 2010 to 2017 in XJH and DT, respectively, indicating a worsening O<sub>3</sub> pollution environment in Shanghai. For urban site (XJH), the daily maximum and minimum 1-h O<sub>3</sub> concentrations (O<sub>3-max</sub> and O<sub>3-min</sub>) increased at rates of 2.47 ppb yr<sup>-1</sup>, and 1.18 ppb yr<sup>-1</sup>, respectively, much faster than those in DT (1.19 ppb yr<sup>-1</sup> for O<sub>3-max</sub>, and 0.42 ppb yr<sup>-1</sup> for O<sub>3-min</sub>).

Fig. 2 displays the year-to-year variations of NO<sub>x</sub>. In urban site (XJH), the observed means of daily maximum NO (NO<sub>max</sub>) and NO<sub>2</sub> (NO<sub>2-max</sub>) both exhibited significant decreases by -2.27 and -1.34 ppb yr<sup>-1</sup>, respectively, as a result of the NO<sub>x</sub> emission reductions since the release of the China's 'Twelfth Five-Year' Plan for environmental protection in 2011. At the same time, the observed means of daily minimum NO (NO<sub>min</sub>) and NO<sub>2</sub> (NO<sub>2-min</sub>) exhibited opposite changes in XJH, with changing rates of +0.19 and -0.39 ppb yr<sup>-1</sup>, respectively. For the background site (DT), the observed year-to-year variations of NO<sub>x</sub> were much smaller than those in the urban site for the lower anthropogenic emissions. The O<sub>3</sub> concentrations there are less sensitive to the changes of anthropogenic emissions, exhibiting slower increasing rates than those in XJH. Observational and modeling studies have proved that rural sites in Shanghai are influenced by air masses with more aged pollutants, leading to less ozone depression and higher O<sub>3</sub> level than in the urban city (Geng et al., 2007, 2008; Shan et al., 2010, 2016).

After eliminating the effect of long-range transport, solar radiation, and VOC species, Gao et al. (2017) suggested that the rapid O<sub>3</sub> increase in Shanghai was mainly due to the changes of NO<sub>x</sub> concentration. The calculated correlation coefficient (R) values are provided in Table S1. The R values was -0.80 between O<sub>3-max</sub> and NO<sub>max</sub>, and -0.82 between

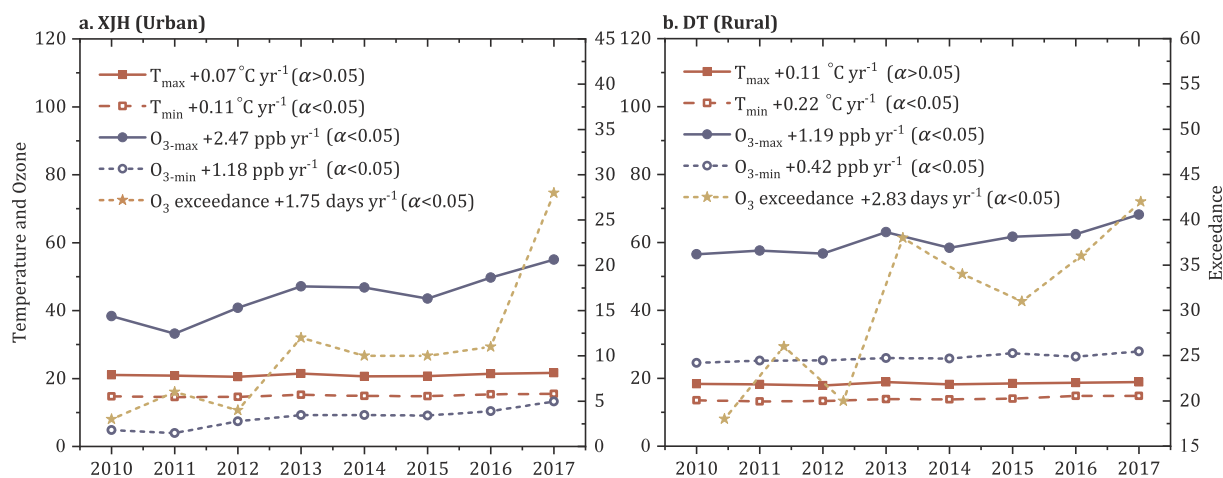


Fig. 1. Changes of O<sub>3</sub> exceedance (number of days with O<sub>3</sub> concentration exceeding the Chinese Grade II national air quality standard, defined as MDA8 > 160 µg m<sup>-3</sup>, unit: days yr<sup>-1</sup>), O<sub>3-max</sub> (mean of daily maximum 1-h O<sub>3</sub>, unit: ppb), O<sub>3-min</sub> (mean of daily minimum 1-h O<sub>3</sub>, unit: ppb), mean of daily maximum temperature (T<sub>max</sub>, unit: °C), and mean of daily minimum temperature (T<sub>min</sub>, unit: °C) in a. Xujiashui (XJH) and b. Dongtan (DT) from 2010 to 2017. The Mann-Kendall trend significance and the Sen trend estimate methods were used to assess the trends of variables. The slopes of the trends and the significance level as represented by the  $\alpha$  value are provided in the plots.

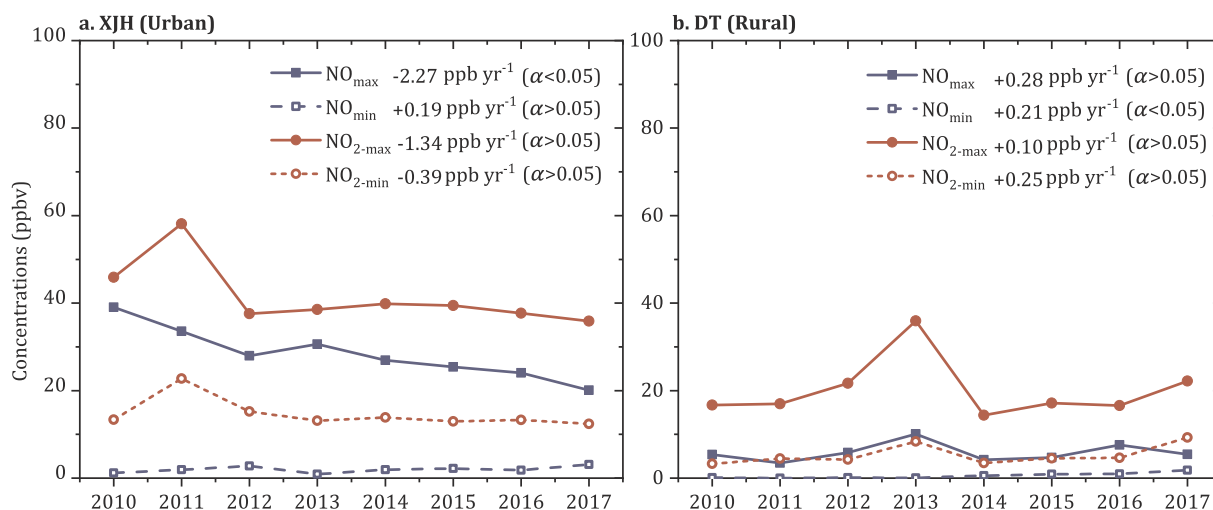


Fig. 2. Same as Fig. 1, but for NO<sub>max</sub> (mean of daily maximum 1-h NO), NO<sub>2-max</sub> (mean of daily maximum 1-h NO<sub>2</sub>), NO<sub>min</sub> (mean of daily minimum 1-h NO), and NO<sub>2-min</sub> (mean of daily minimum 1-h NO<sub>2</sub>) in a. Xujiahui (XJH) and b. Dongtan (DT), respectively. The slopes of the trends and the significance level as represented by the α value are provided in the plots.

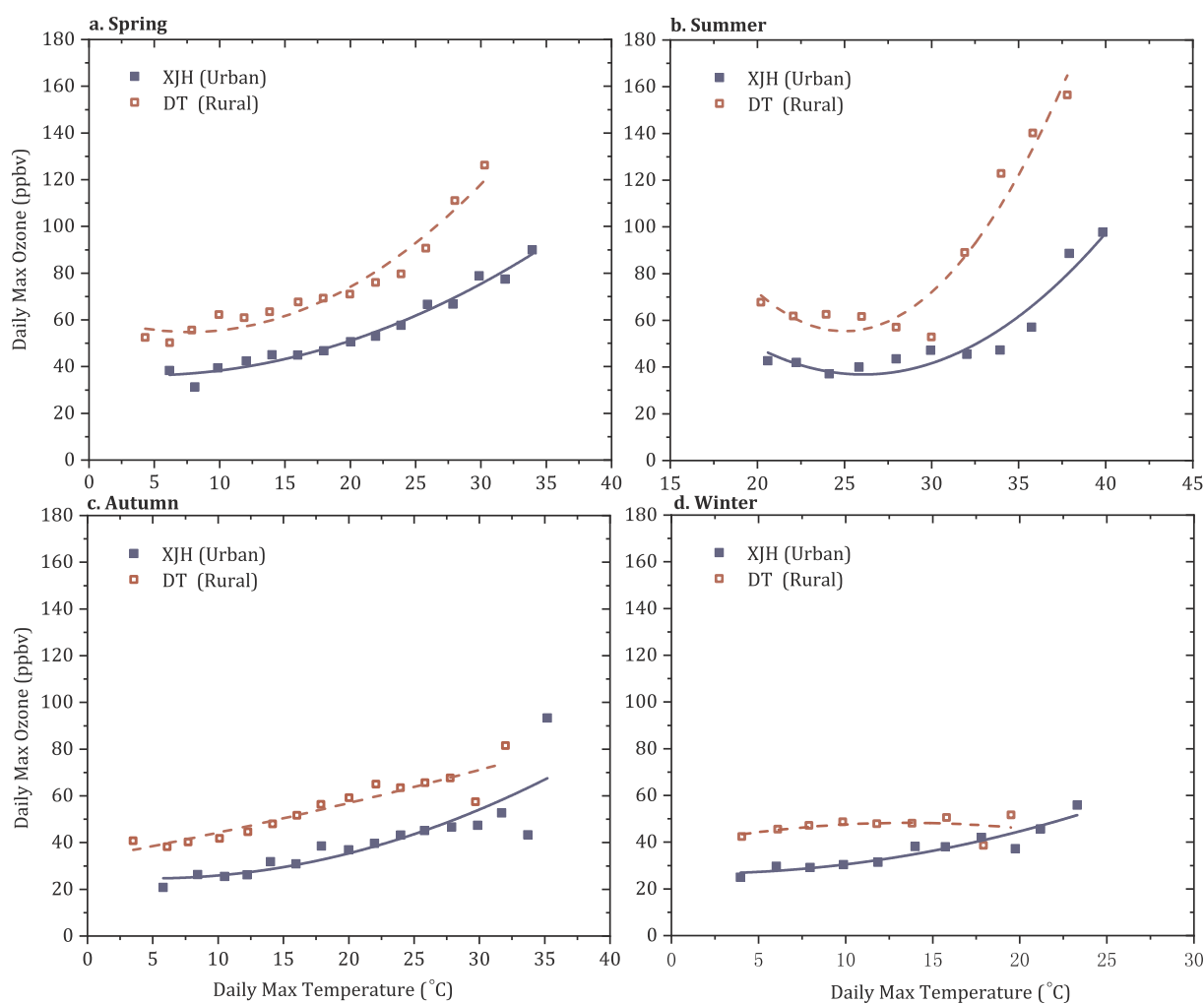


Fig. 3. Observed ozone-temperature relationships in Shanghai for the period 2010–2017. Points represent the mean of the daily maximum O<sub>3</sub> versus local daily maximum surface temperature for each temperature bin in Xujiahui (XJH) and Dongtan (DT), respectively. Data are binned to 2 °C intervals, and results are shown for a. spring, b. summer, c. autumn, and d. winter.

$O_{3\text{-max}}$  and  $NO_{2\text{-max}}$  XJH, indicating a strong depression of  $NO_x$  on  $O_3$  at urban site. In addition, The increases in  $O_3$  will very likely be further aggravated by warmer temperature, since the measured  $O_{3\text{-max}}$  showed strong positive correlations with  $T_{\text{max}}$  in both XJH and DT, with R values of 0.62 and 0.87, respectively, during time period 2010–2017. Clarifying  $O_3$  response to the increasing temperature and examining its drivers would be crucial to guild future emission-control policy making for megacities in China.

### 3.2. Observed relationship between ozone and temperature in Shanghai

Fig. 3 displays the observed  $O_3$ -temperature relationship in Shanghai during 2010–2017, separated by seasons and sites. The statistical results of the second-order regression, as described in Sec. 2.3, are displayed in Table 1. Most of the time,  $O_{3\text{-max}}$  increased as temperature went up. The  $2b_2$  values were close to zero in spring, autumn and winter, suggesting that  $O_{3\text{-max}}$  changes approximately linearly as  $T_{\text{max}}$  increases. In summer,  $m_{O_3\text{-T}}$  increased as temperature increased, with increasing rates ( $2b_2$ ) of 0.62 ppb  $^{\circ}C^{-2}$  in XJH and 1.34 ppb  $^{\circ}C^{-2}$  in DT. Observed  $m_{O_3\text{-T}}$  exhibited most significant increases at temperature above 30  $^{\circ}C$  in summer, with mean values of 6.65 and 13.68 ppb  $^{\circ}C^{-1}$  in XJH and DT, respectively. The observed summertime temperature dependence of  $m_{O_3\text{-T}}$  exhibited larger values in rural site than in urban site in Shanghai, which are quite different from those reported in Jing et al. (2017) with increasing rates ranging from 0.12 to 0.27 ppb  $^{\circ}C^{-2}$  in urban sites and 0.09–0.14 ppb  $^{\circ}C^{-2}$  in rural sites during 2008–2015 in US. The differences between the two regions could be largely attributed the different  $O_3$  production regime. Since surface  $O_3$  production were  $NO_x$ -limited in most sites reported in Jing et al. (2017),  $O_3$  production was more sensitive to  $NO_x$  instead of VOCs.

Compared to those reported in studies from the US and Europe (e.g. Bloomer et al., 2009; Steiner et al., 2006, 2010), the observed  $O_3$  changes and the  $O_3$ -temperature relationship in Shanghai exhibited distinct regional characteristics (Fig. 1–3). First, although strict  $NO_x$  emission control measures have been conducted, the observed  $NO_{2\text{-max}}$  concentrations of approximately 40 ppb in urban Shanghai were still 2 times higher than those in US. (Jing et al., 2017). Secondly, the strong VOC-sensitive  $O_3$  production regime in Shanghai resulted in different high-temperature  $O_3$  response in urban and rural areas. Observed values of  $m_{O_3\text{-T}}$  in rural site are much larger than those in urban site, which is different from the findings in Sillman and Samson (1995) and Jing et al. (2017) who reported that rural sites with low  $NO_x$  emissions had smaller  $m_{O_3\text{-T}}$  than urban sites in the  $NO_x$ -limited regions. Therefore, it is very essential to identify the local drivers of the high-temperature  $O_3$  response in Shanghai, especially in summer when  $O_3$  concentrations exhibit the fastest increase with the increasing temperatures.

**Table 1**

Statistical results for the observed  $O_3$ -temperature relationships,  $y = b_0 + b_1x + b_2x^2$ , in Xujiahui (XJH, urban site) and Dongtan (DT, rural site), where  $x$  is daily maximum temperature ( $^{\circ}C$ ) and  $y$  is daily maximum  $O_3$  (ppb), in Spring (March–May), Summer (June–August), autumn (September–November), and winter (December–February).

Site	Seasons	$b_0$	$b_1$	$b_2$	$b_1/(-2b_2)$	$2b_2$
XJH	Spring	37.13*	-0.46*	0.06*	3.83*	0.12*
	Summer	249.18*	-16.29*	0.31*	26.27*	0.62*
	Autumn	25.73*	-0.44*	0.05*	4.40*	0.10*
	Winter	26.65*	-0.13*	0.05*	1.30*	0.10*
DT	Spring	62.29*	-1.94*	0.13*	7.46*	0.26*
	Summer	473.50*	-33.45*	0.67*	24.96*	1.34*
	Autumn	33.10*	1.04*	0.01*	-52.00*	0.02*
	Winter	38.26	1.48	-0.05	14.80	-0.10

\*Statistically significant values at the 5% significance level.

### 3.3. Factors driving $m_{O_3\text{-T}}$ in Shanghai

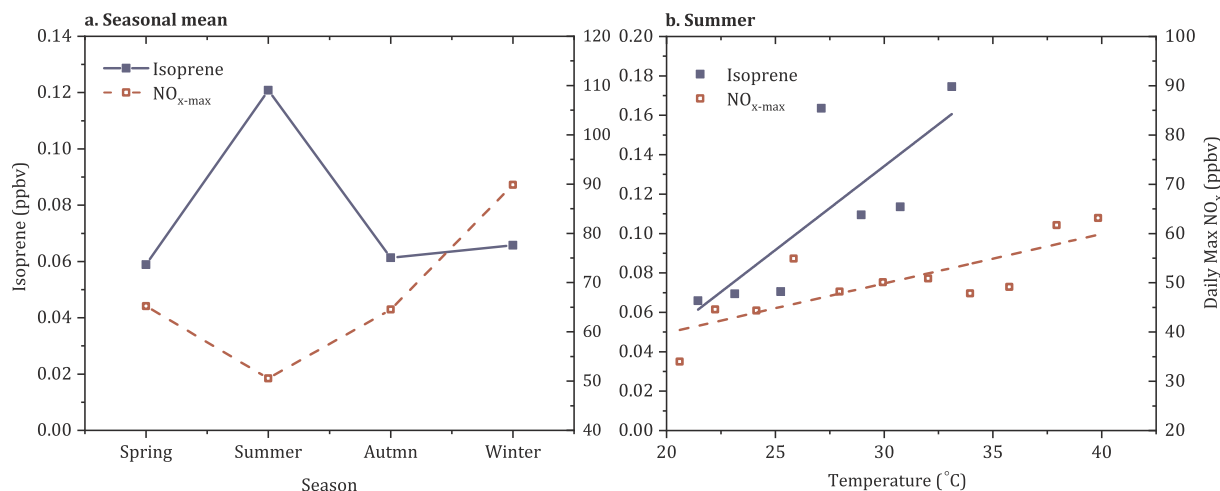
#### 3.3.1. Observed precursors and their relationships with temperature in summer

The responses of  $O_3$  precursors to increasing temperature were usually considered to be extremely important in determining the  $O_3$  climate penalty (e.g. Bloomer et al., 2009; Steiner et al., 2010). To evaluate the changes in  $O_3$  precursors and their impacts on  $m_{O_3\text{-T}}$ , observed seasonal variations of isoprene and  $NO_x$ , as well as their relationships with temperature in summer are examined in Fig. 4. Since isoprene measurements are unavailable in DT, we only analyze observations in XJH here. It should be noted that the values of isoprene concentrations during summertime could be larger than those displayed in Fig. 4, since the isoprene measurements were only available in the morning hours (6–8 a.m.).

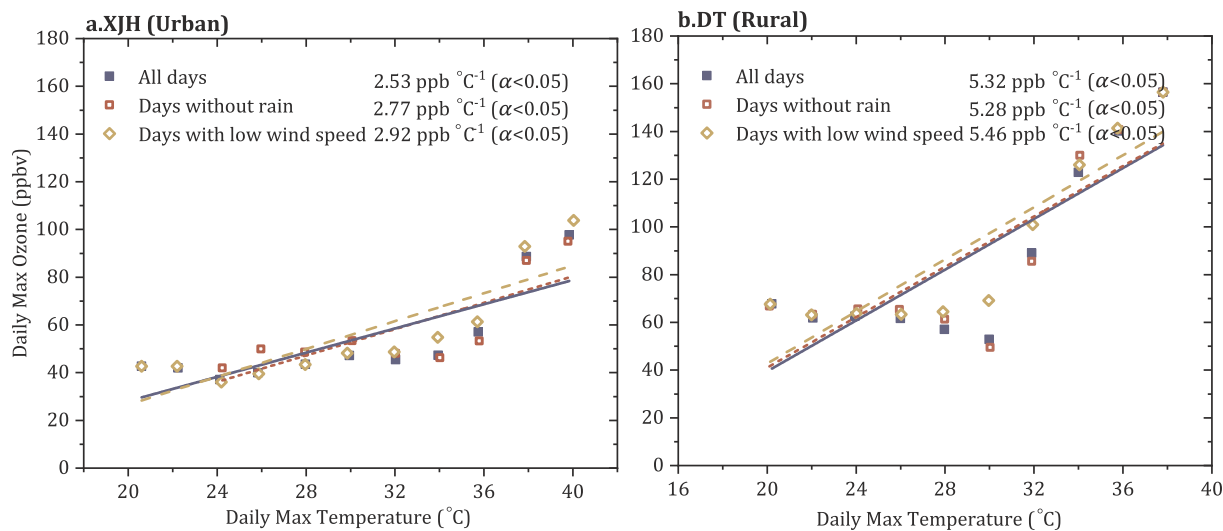
In Fig. 4a, the observed isoprene concentrations exhibited distinct seasonal variations in XJH, with maximum of 0.12 ppb in summer. Zhang (2012) reported that observed isoprene concentrations also showed remarkable diurnal variations in Shanghai, suggesting that the observed isoprene in Shanghai mainly came from biogenic sources. According to the government report (<http://www.shanghai.gov.cn/nw2/nw2314/nw3766/nw3826/nw20410/u1aw463.html>), the vegetation coverage in Shanghai greatly increased in past years, which could be major sources of the BVOCs. Isoprene emissions are expected to change largely follows the case of biogenic emissions which increase exponentially with temperature until approximately 40  $^{\circ}C$  and then decrease due to the biophysical high-temperature constrains (Guenther et al., 1993; Di Carlo et al., 2004). In Fig. 4b, observed isoprene concentrations in XJH showed significant increases as temperature went up in summer, with an average increasing rate of 0.01 ppb  $^{\circ}C^{-1}$ . Since urban Shanghai is VOC-sensitive, the temperature-dependent increases in isoprene emissions could contribute to the increases in  $O_3$  at warmer temperature.

Fig. 4a also shows the observed seasonal variations of  $NO_{x\text{-max}}$  in XJH. Observed seasonal mean  $NO_{x\text{-max}}$  concentrations exhibited lowest values in summer as a result of the higher photo-activity, relatively deep PBLH and dilution effects of the prevailing winds (Geng et al., 2008). In Fig. 4b, summertime  $NO_{x\text{-max}}$  concentrations slightly increased as temperature became warmer, with an average increasing rate of 1.01 ppb  $^{\circ}C^{-1}$ . Early studies suggested that the increase in summertime  $NO_x$  could be attributed to the enhancement of PAN decomposition (Sillman and Samson, 1995; Steiner et al., 2010). As temperature increases, more  $NO_x$  are released which tends to remove more OH radicals from the active VOC oxidation cycle, and then retard the production of  $O_3$  (Seinfeld and Pandis, 2006). Emissions of  $NO_x$  and VOCs from anthropogenic sources might also increase at warmer temperatures due to rises in energy demand and evaporative emission in summer (Steiner et al., 2010). However, there are large uncertainties in the relationships between anthropogenic emissions and warmer temperatures (Rubin et al., 2006; Steiner et al., 2010). Observed  $NO_{x\text{-max}}$  concentrations still exhibit lowest values in summer, suggesting that the temperature-related changes in anthropogenic emissions could not be dominant in influencing  $NO_x$  concentrations.

Meteorological conditions (Chang et al., 2019; Li et al., 2019b) may also affect the  $m_{O_3\text{-T}}$ . In summer, high temperature is usually related to changes in convective precipitation, winds and even the subtropical high control type weather in Shanghai, which influence  $O_3$  production. We shown the observed summertime  $O_3$ -temperature relationships during rainless days and days with lower wind speeds in the two sites of Shanghai in Fig. 5. However, the differences between  $m_{O_3\text{-T}}$  values in different days were quite small, suggesting small influence of precipitation and wind on the climate penalty in Shanghai. The observed mean values of  $T_{\text{max}}$  in XJH and DT are 33.0  $^{\circ}C$  and 29.3  $^{\circ}C$ , respectively in summer during time period 2010–2017. However, The rural site (DT) with low  $T_{\text{max}}$  and high isoprene emissions has much larger  $m_{O_3\text{-T}}$  values than the urban site with high  $T_{\text{max}}$  and low isoprene emissions (Fig. 3).



**Fig. 4.** a. Observed seasonal mean variations of NO<sub>x-max</sub> and isoprene concentrations, and b. observed corresponding summertime relationships with temperature in Xujiahui (XJH). Since isoprene measurements are only conducted during 6–8 am in inconsecutive days during 2010–2015, solid points in blue color represent the diurnal 3-h averaged isoprene concentrations versus corresponding temperature. Hollow points in red color represent the means of daily maximum NO<sub>x</sub> concentrations versus corresponding daily maximum temperatures during 2010–2017. Data are binned same as Fig. 3.



**Fig. 5.** Observed summertime ozone-temperature relationships for all days, days without rain, and days with daily mean wind speeds lower than the seasonal mean wind speeds in a. Xujiahui (XJH) and b. Dongtan (DT), respectively during 2010–2017. The seasonal mean wind speeds are 1.0 and 4.8 ms<sup>-1</sup> in XJH and DT, respectively in summer. The significance level is represented by the  $\alpha$  value in the plots.

As such, the result indicates that  $m_{O_3-T}$  should be mainly driven by temperature-dependent emissions through atmospheric chemistry and ecosystem-climate interactions rather than the temperature-induced meteorological conditions.

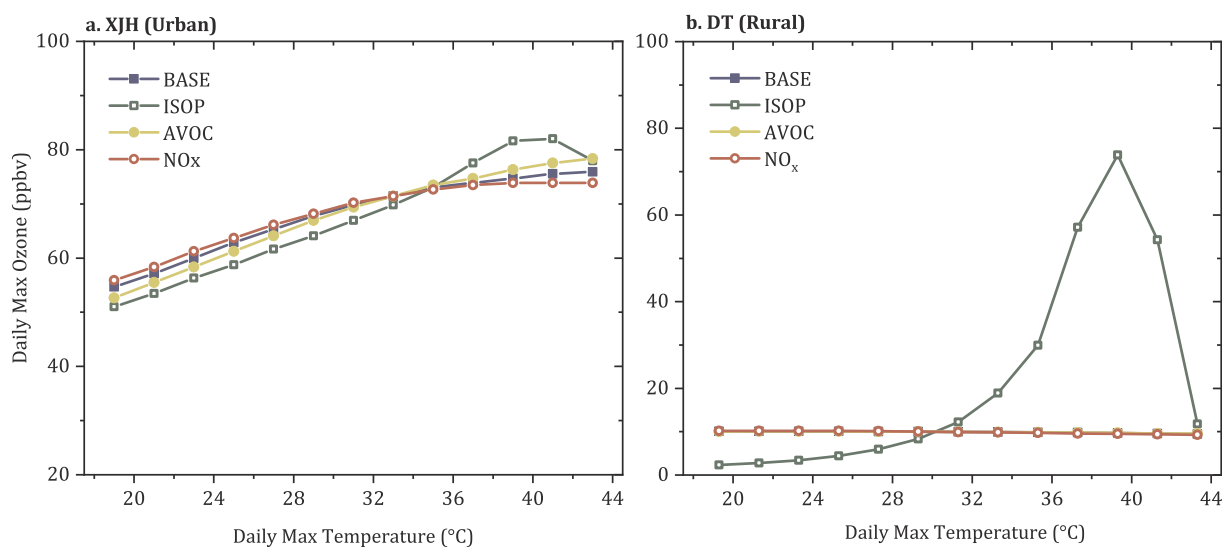
### 3.3.2. Modeled sensitivity of $m_{O_3-T}$ to emissions

To further examine the role of precursors in determining  $m_{O_3-T}$  during summertime, sensitivity experiments are performed using the NCAR Master Mechanism model in Shanghai. Separate simulations are conducted under different emission scenarios in XJH and DT, respectively. The basic diurnal variations of temperature in XJH and DT are assigned according to the observed mean values in summer during time period 2010–2017 (Fig. S3). The diurnal variations for each temperature bin are assigned by increasing/decreasing multiples of 2 °C based on the basic diurnal variations, with daily maximum temperature ranging from 19 to 43 °C. To obtain a stable state in the simulations, the photochemistry for O<sub>3</sub> is calculated for a 2-day period for each station, and model results of the last day are used to explore the roles of precursor emissions in O<sub>3</sub> formation of Shanghai. The detailed descriptions of the

experiments are in the following:

- (1) BASE case: Simulation with basic anthropogenic emissions and fixed biogenic isoprene emissions scaled to the basic temperature.
- (2) ISOP case: Same as BASE but with a temperature-dependent change in biogenic isoprene emissions for each temperature bin. The emission rates are derived based on the isoprene-temperature parameterization of Guenther et al. (2006) (Fig. S2).
- (3) AVOC case: Same as BASE but with a temperature-dependent change in anthropogenic VOC (AVOC) emissions for each temperature bin. The emission rates increase 1% per 3 °C according to Steiner et al. (2010).
- (4) NO<sub>x</sub> case: Same as BASE but with a temperature-dependent change in NO<sub>x</sub> emissions for each temperature bin. The emission rates increase 1% per 3 °C, similar as AVOC emissions.

Fig. 6 exhibits the calculated relationships between O<sub>3-max</sub> and T<sub>max</sub> in different cases for XJH and DT. In the BASE case, the modeled changes in O<sub>3-max</sub> with T<sub>max</sub> are only attributed to the impact of temperature on



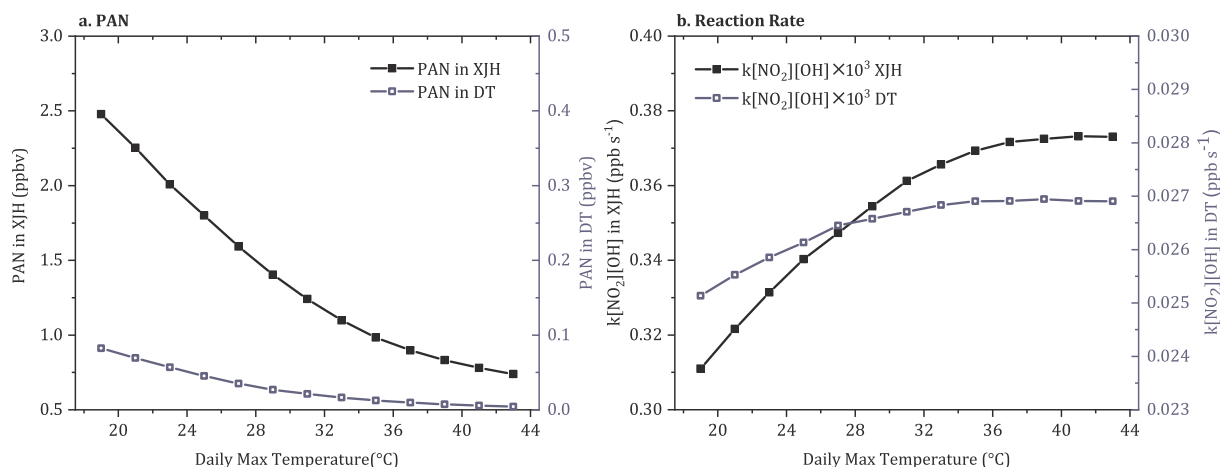
**Fig. 6.** Modeled ozone–temperature relationships in a. Xujiahui (XJH) and b. Dongtan (DT) from BASE (solid square in blue), ISOP (hollow square in green), AVOC (solid circle in yellow), and NO<sub>x</sub> (hollow circle in red) cases, respectively. Data are binned same as Fig. 3. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

chemical reactions since emissions remain unchanged in simulations conducted for each temperature bin. The simulated BASE case O<sub>3</sub> increases slower as temperature goes up in XJH, and the result can be well explained by the temperature-induced acceleration of PAN decomposition. Fig. 7a displays the relationship of daily maximum PAN with the increasing temperature in the BASE case simulations. Simulated PAN concentration exhibits an apparent decline as temperature becomes warmer in both urban and rural sites. Reaction rate for (NO<sub>2</sub>+OH→HNO<sub>3</sub>) could be expressed as  $k[\text{NO}_2][\text{OH}]$ , where  $k$  is the rate constant calculated according to the temperature. As displayed in Fig. 7b, the values of  $k[\text{NO}_2][\text{OH}]$  increase as temperature goes up in both sites, indicating that more OH radicals could be removed by NO<sub>x</sub> with current VOCs/NO<sub>x</sub> ratios, hindering the production of O<sub>3</sub>. The magnitudes of the simulated PAN and  $k[\text{NO}_2][\text{OH}]$  are comparable to those reported in previous studies (Sillman and Samson, 1995; Lin et al., 2009).

Fig. 6 also displays the model results from the ISOP, AVOC and NO<sub>x</sub> cases, which reflect the changes in  $m_{\text{O}_3-T}$  depending on the degree of VOC or NO<sub>x</sub> emissions. In the ISOP case,  $m_{\text{O}_3-T}$  in both sites exhibit most significant changes as the temperature increases. The simulated O<sub>3</sub> concentrations grow faster as temperature goes up, and show decreasing

changes at approximately 40 °C when the isoprene emissions begin to decrease. The pattern is similar to the observed summertime O<sub>3</sub>-temperature relationships (Fig. 3), though decreases in O<sub>3</sub> at extremely high temperature don't appear in the observational results due to the limited measurements. In spite of low anthropogenic emissions, both the observational and model results suggest that O<sub>3</sub> concentrations in DT increase faster than those in XJH since the isoprene emissions in DT are much higher and more sensitive to the increasing temperature (Fig. 6b). From this point of view, the temperature dependence of biogenic isoprene emissions could be very important in determining the observed responses of O<sub>3</sub> to the increasing temperature.

Model results from the AVOC and NO<sub>x</sub> case simulations indicate that only considering the temperature-related changes in AVOC and NO<sub>x</sub> emissions cannot bring out the observed increases in O<sub>3</sub> as temperature goes up (Fig. 6). In the AVOC case, increases in AVOC emissions promote the increases in O<sub>3</sub> as temperature goes up in XJH as well; however, the effects are much smaller than those of the isoprene emissions. Since XJH is strongly VOC-sensitive, model result from the NO<sub>x</sub> case exhibits a decrease in both O<sub>3</sub> concentrations and  $m_{\text{O}_3-T}$  at high temperature due to the increases in NO<sub>x</sub> emissions. DT is less VOC-sensitive and has fairly low anthropogenic emissions, thus the impacts of AVOC and NO<sub>x</sub>



**Fig. 7.** Modeled relationships of daily maximum a. PAN and b.  $k[\text{NO}_2][\text{OH}]$  with daily maximum temperatures in the BASE case simulations in Xujiahui (XJH) and Dongtan (DT), respectively.  $k[\text{NO}_2][\text{OH}]$  is the reaction rates of (NO<sub>2</sub>+OH→HNO<sub>3</sub>) calculated by the NCAR Master Mechanism.

emissions are both inconspicuous.

It should be noted that values of modeled  $O_{3-max}$  and  $m_{O_3-T}$  differs from observed values (Figs. 3 and 6). Similar mismatch has been noted in previous studies (e.g. Steiner et al., 2010) indicating the roles of meteorological characteristics (e.g. stagnation and transport) that are not considered in box model except for uncertainties in emissions and initial conditions. In real atmosphere, for example, long-distance transport of pollutants can be also important in  $O_3$  formation, especially in rural site with low anthropogenic emissions like DT. Transport of air mass and aged pollutants from the urban region might further influence changes in  $m_{O_3-T}$  in rural sites as temperature becomes warmer.

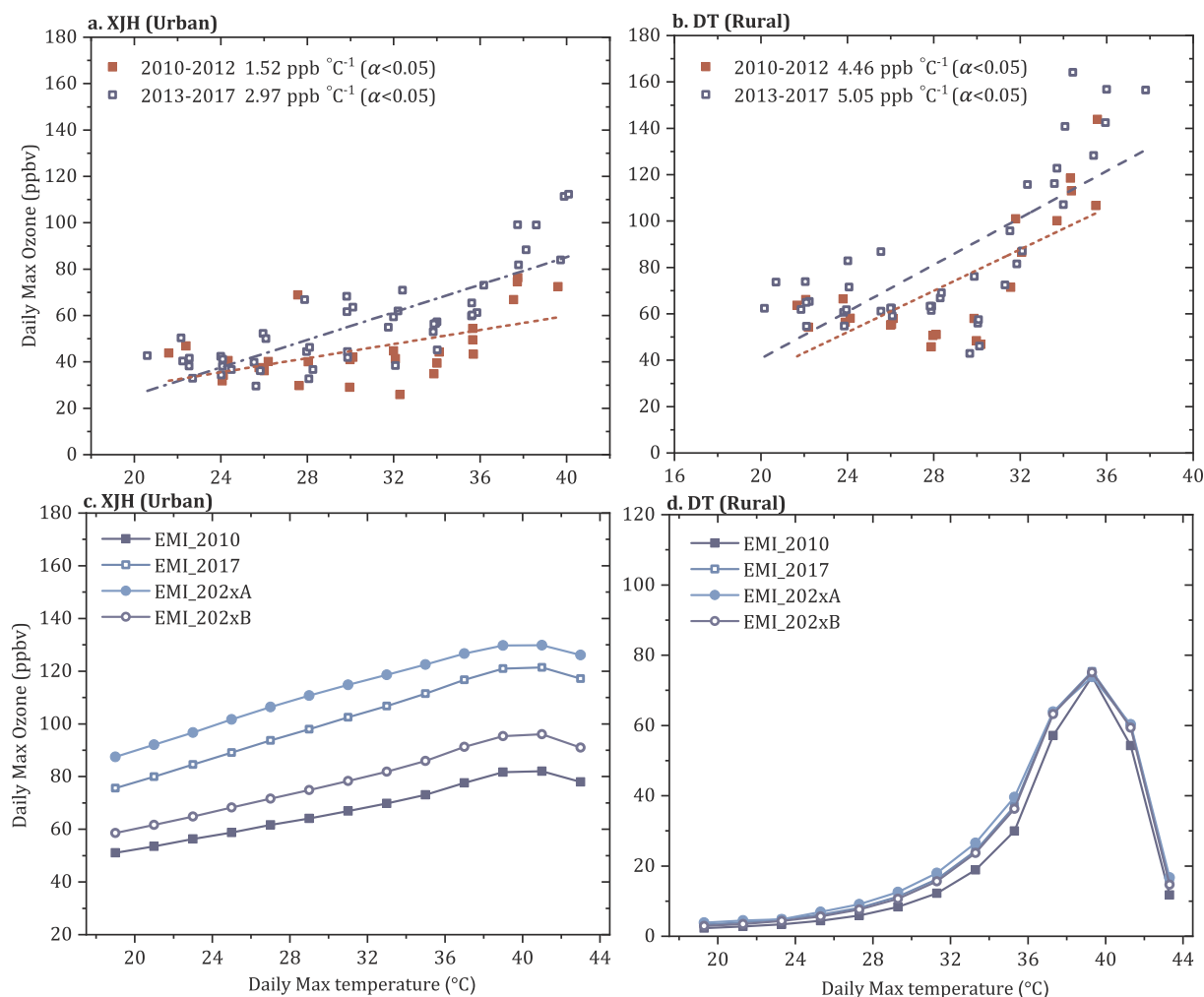
### 3.4. Effect of emission reductions on $m_{O_3-T}$

The increasing severity of  $O_3$  pollution in Chinese megacities raises a new challenge to current emission control policies. To evaluate the response of  $m_{O_3-T}$  to emission reductions, we examine the variations of  $m_{O_3-T}$  during time period 2010–2017 and discuss the possible changes under future emission control actions in this section based on observations as well as numerical experiments.

According to the observed  $O_3$  exceedance and  $NO_x$  concentrations in Fig. 1–2, we divide the period of 2010–2017 into two parts: Period 1 (2010–2012) with less  $O_3$  exceedance days and higher  $NO_x$  concentrations, and Period 2 (2013–2017) with more  $O_3$  exceedance days and

lower  $NO_x$  concentrations. Fig 8a–b display the observed summertime  $O_3$ -temperature relationships during Period 1 and Period 2 in XJH and DT, respectively. In urban site (XJH), the mean value of  $m_{O_3-T}$  increased from 1.52  $ppb\ ^\circ C^{-1}$  in Period 1 to 2.97  $ppb\ ^\circ C^{-1}$  in Period 2, suggesting that the reductions in  $NO_x$  emissions might strengthen the high-temperature  $O_3$  response in urban Shanghai. The observed mean  $m_{O_3-T}$  value in DT slightly increased from 4.46  $ppb\ ^\circ C^{-1}$  in Period 1 to 5.05  $ppb\ ^\circ C^{-1}$  in Period 2, the increase of which were smaller than that in XJH. Since DT exhibited a little  $NO_x$ -sensitive as discussed in Sec. 3.1, the changes might result from the slightly increases in  $NO_x$  concentrations during the two periods. According to the observational results, the  $m_{O_3-T}$  in urban Shanghai are more sensitive to the changes in anthropogenic emissions and could be aggravated by the current  $NO_x$  reduction actions.

Numerical experiments are performed to further examine the response of  $m_{O_3-T}$  to various emission reduction measures. As discussed in Sec. 3.3, the temperature dependence of biogenic isoprene emissions could be the key driver of the observed responses of  $O_3$  to the increasing temperature in Shanghai. Therefore, we conducted the following sensitivity experiments to evaluate the effect of different emission reductions on the  $O_3$ -temperature relationship. Similar to the experiments in Sec. 3.3.2, the second day calculations from the 2-day simulations are used for the analyses.



**Fig. 8.** Observed summertime ozone-temperature relationships in a. Xujiahui (XJH) and b. Dongtan (DT) for separate years during Period 1 (2010–2012) and Period 2 (2013–2017). Also shown is the modeled ozone-temperature relationships in c. XJH and d. DT from EMI\_2010, EMI\_2017, EMI\_202xA, and EMI\_202xB case simulations, respectively. Data are binned same as Fig. 3. The significance level as represented by the  $\alpha$  value are also provided.



- (1) EMI\_2010: Same as ISOP case in Sec.3.3.2, with anthropogenic emissions based on MEIC inventory for year 2010.
- (2) EMI\_2017: Same as EMI\_2010 but with a 30% reduction in NO<sub>x</sub> emissions. The reductions are obtained from comparisons between MEIC inventories for the year 2010 and 2017 (Zheng et al., 2018).
- (3) EMI\_202xA: Same as EMI\_2017 but with a 15% reduction in NO<sub>x</sub> emissions.
- (4) EMI\_202xB: Same as EMI\_2017 but with a 15% reduction in anthropogenic VOC emissions.

Fig. 8c–d exhibit the calculated O<sub>3</sub>-temperature relationships from various sensitivity experiments. For the rural site (DT), the local emission reductions have little influence on O<sub>3</sub> concentrations and m<sub>O<sub>3</sub>-T</sub> since the anthropogenic emissions are quite low. For the urban site (XJH), decreases in NO<sub>x</sub> emissions result in increases in O<sub>3</sub> concentrations, while decreases in AVOC emissions lead to reductions in O<sub>3</sub> concentrations. The calculated mean values of m<sub>O<sub>3</sub>-T</sub> in XJH are 1.35 and 2.00 ppb °C<sup>-1</sup> in EMI\_2010 and EMI\_2017 simulations, respectively, suggesting that NO<sub>x</sub> emission reductions can greatly increase the response of O<sub>3</sub> to the increasing temperatures at present. If the NO<sub>x</sub> emissions continue to decrease following the EMI\_202xA case, O<sub>3</sub> concentrations would increase further. However, as NO<sub>x</sub> emissions decrease, the O<sub>3</sub> production in urban Shanghai would convert from the VOC-sensitive regime to the transitional regime. As such, the sensitivity of m<sub>O<sub>3</sub>-T</sub> to the BVOC emissions might be weakened, resulting in slight decrease in m<sub>O<sub>3</sub>-T</sub> in the EMI\_202xA (1.83 ppb °C<sup>-1</sup>) compared to that in EMI\_2017. For the substantial emissions and complex sources, VOC emission reduction actions have just started in China recently ([http://www.gov.cn/zhengce/content/2018-07/03/content\\_5303158.htm](http://www.gov.cn/zhengce/content/2018-07/03/content_5303158.htm)). As reported in Gao et al. (2017), the VOC concentrations in urban Shanghai were relatively unchanged during past years. However, in the next few years, the VOC emission reductions would influence the O<sub>3</sub> formation in China with the advancing of the emission control policies. In the EMI\_202xB case, the calculated mean value of m<sub>O<sub>3</sub>-T</sub> decreases to 1.63 ppb °C<sup>-1</sup> in XJH compared to that in EMI\_2017, indicating that reductions in AVOC emissions would not only relieve the O<sub>3</sub> pollution, but also decrease the high-temperature O<sub>3</sub> response in megacities like Shanghai.

#### 4. Conclusions and discussion

Surface O<sub>3</sub> pollution in Shanghai worsened during time period 2010–2017, with the numbers of O<sub>3</sub> exceedance days increased by 8.3 and 1.3 times in urban (XJH) and rural (DT) sites, respectively. The observed O<sub>3-max</sub> and NO<sub>max</sub> (NO<sub>2-max</sub>) were strongly anti-correlated in XJH from 2010 to 2017, indicating a strong depression of NO<sub>x</sub> on O<sub>3</sub> at urban site. Based on observational data, the ozone-climate penalty, defined as the slope of the O<sub>3</sub>-temperature relationship (m<sub>O<sub>3</sub>-T</sub>), was examined in Shanghai over the period 2010–2017. Statistical results show that the response of O<sub>3</sub> on the temperature increases was most significant in summer, with mean m<sub>O<sub>3</sub>-T</sub> values of 6.65 and 13.68 ppb °C<sup>-1</sup> above 30 °C in XJH and DT, respectively. Different with observational result in NO<sub>x</sub>-limited sites in previous studies (Sillman and Samson, 1995; Jing et al., 2017), the rural site (DT) with lower NO<sub>x</sub> emissions had steeper m<sub>O<sub>3</sub>-T</sub> than the urban site (XJH) during summertime in Shanghai, indicating that local VOC/NO<sub>x</sub> ratios greatly influence the ozone-climate penalty effect.

The dominant drivers in determining m<sub>O<sub>3</sub>-T</sub> of Shanghai are evaluated based on measurements and numerical experiments. The observed summertime isoprene concentrations in XJH exhibited remarkable diurnal and seasonal variations in urban Shanghai, and showed significant increase as temperature went up, with mean rate of 0.01 ppb °C<sup>-1</sup> in summer. The observational results suggest that the isoprene emissions are mainly biogenic. The simulated m<sub>O<sub>3</sub>-T</sub> values in Shanghai show strong sensitivities to the temperature-induced changes in the biogenic

isoprene emissions, while the impact of increasing temperature on chemical reactions cannot well explain the observed increases in O<sub>3</sub>. Higher isoprene emissions in DT result in larger m<sub>O<sub>3</sub>-T</sub> values in spite of low anthropogenic emissions. The VOCs and NO<sub>x</sub> from anthropogenic sources may increase at warmer temperatures, but their influence is minor. Though the high temperature-related meteorological features could amplify the O<sub>3</sub> increase in summer, the influence of which on m<sub>O<sub>3</sub>-T</sub> should be inferior to that of the biogenic factor in Shanghai. As a result, we conclude that the main driver of m<sub>O<sub>3</sub>-T</sub> in Shanghai is the temperature-related behaviors of BVOC emissions through ecosystem-climate interactions.

In this study, we just examine the roles of isoprene for the limited observations. It should be noted that although isoprene is the largest BVOC species accounting for ~40% of the total BVOC emissions in Shanghai (Liu et al., 2018), other BVOC species (e.g., monoterpene) can be greatly influenced by the temperatures. According to the Shanghai Master Plan (2017–2035) (<http://www.shanghai.gov.cn/nw2/nw2314/nw32419/nw42806/>), the vegetated area in Shanghai will continue to expand and will increase by a factor of 1.5 in 2035 compared to that in 2015. The urban afforestation measures will further promote the emissions of the biogenic sources and then affect the O<sub>3</sub> response to the increasing temperatures in Shanghai.

Climate change will increase the surface O<sub>3</sub> concentrations and the frequency of high O<sub>3</sub> episodes, implying a more significant ozone-climate penalty effect that can be mainly attributed to climate-induced increases in biogenic emissions of VOCs over East China (Lin et al., 2008; Wang et al., 2013). The calculated 2000–2050 changes in summertime temperature could be 0.8–1.5 °C in the Shanghai area. As a result of warmer temperature and stonger solar radiation, the 2000–2050 climate change would result in a 34% increase in isoprene emissions in China, and lead to a 8% increase in the sensitivity of surface O<sub>3</sub> to a given change in anthropogenic emissions in East China (Wang et al., 2013). The warming climate requires more aggressive emission controls to wrestle with the challenges for future O<sub>3</sub> pollution.

Emission reduction actions greatly influence the dependence of O<sub>3</sub> on increasing temperatures in Shanghai. NO<sub>x</sub> emission reductions could strengthen the high-temperature O<sub>3</sub> response in urban Shanghai at present. NO<sub>x</sub> emissions will continue to decrease as require by recent governmental Clear Air Action (Li et al., 2019a), the O<sub>3</sub> production in urban Shanghai tend to convert to the transitional regime and the sensitivity of m<sub>O<sub>3</sub>-T</sub> to the temperature-related BVOC changes might be weakened. AVOC emission control measures would effectively relieve O<sub>3</sub> pollution and reduce the high-temperature O<sub>3</sub> response in urban Shanghai. Therefore, to effectively control O<sub>3</sub> pollution towards a warmer climate, strict emission reductions as well as scientific city planning strategies are needed to balance the VOC/NO<sub>x</sub> ratios in Shanghai.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2019.117108>.

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