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## Enhanced summertime PM<sub>2.5</sub>-suppression of O<sub>3</sub> formation over the Eastern U.S. following the O<sub>3</sub>-sensitivity variations†

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The suppression of ozone (O<sub>3</sub>) formation due to the presence of fine particulate matter (PM<sub>2.5</sub>) has recently been highlighted for further O<sub>3</sub> pollution controls in regions that suffer high ozone concentrations. Here we derive multiple PM<sub>2.5</sub>-suppression factors for the Eastern United States (U.S.) major cities based on a non-linear fitting of the PM<sub>2.5</sub> and O<sub>3</sub> relationship from the multiyear surface observations. Our results show that these PM<sub>2.5</sub>-suppression factors are increasing with time and generally follow the transition of the O<sub>3</sub>-sensitive regime towards NO<sub>x</sub>-limited chemistry. A spatial discrepancy of this suppression factor is seen currently with a higher value in the Southeastern U.S. than in the Northeastern U.S. A spatial similarity between urban regions and their downwind locations was observed for the New York City metro area. This more extensive formulation of the PM<sub>2.5</sub>-suppression factor will further improve the ability of models to help guide O<sub>3</sub> and PM<sub>2.5</sub> concentration pollution controls.

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### Environmental significance

Ozone and fine particulate matter (PM<sub>2.5</sub>) remain troublesome air pollution problems for a large number of areas, including metropolitan areas in the Northeastern U.S. like New York City. The paper's findings shed light on the interplay of these pollutants, namely the role that enhanced PM<sub>2.5</sub> can play in suppressing ozone formation. The magnitude of ozone suppression from PM<sub>2.5</sub> provides an additional indicator of the sensitivity of ozone formation from its VOC and NO<sub>x</sub> precursors. The PM<sub>2.5</sub> suppression of ozone formation per unit of PM<sub>2.5</sub> mass concentration has been increasing over the period 2004–2019 in the Northeast U.S., indicating a transition from VOC-limited to NO<sub>x</sub>-limited ozone formation sensitivity. It also provides guidance for further O<sub>3</sub>–PM<sub>2.5</sub> studies and pollution control regulations.

## 1. Introduction

The Eastern United States (U.S.) has been marked as a region persistently suffering from the co-occurrence of summertime ozone (O<sub>3</sub>) and particulate matter (with a diameter under 2.5 μm, PM<sub>2.5</sub>) pollution during the summertime.<sup>1</sup> However, these summertime concentrations of O<sub>3</sub> and PM<sub>2.5</sub> in the region's major cities have shown decreasing trends since the 1970s as a result of the implementation of emission control policies.<sup>2–6</sup> While the region has seen reductions in both pollutants, extreme concentrations of O<sub>3</sub> and PM<sub>2.5</sub> (defined as the top 5%

of measured values in a given year) in New York City (NYC) have shown different overall reductions with a more significant reduction for PM<sub>2.5</sub> than O<sub>3</sub>. This can be attributed to the different reduction rates of their precursors, with the control policies targeting sulfur dioxide (SO<sub>2</sub>) and primary PM<sub>2.5</sub>, than volatile organic compounds (VOCs) and nitrogen oxides (NO<sub>x</sub>).<sup>7</sup>

Co-occurrence of summertime maximum daily 8 h average O<sub>3</sub> (hereafter: MDA8 O<sub>3</sub>) and the daily 24 h average PM<sub>2.5</sub> (hereafter: DA24 PM<sub>2.5</sub> for simplification) based on ground measurements in NYC has shown a direct relationship between the pollutants,<sup>7</sup> with a monotonically increasing near-linear relationship for low PM concentrations. A leveling-off or even decreasing relationship for high PM concentrations was observed in megacity clusters in China.<sup>7–10</sup> This flat or declining relationship has been partly attributed to the scavenging of hydroperoxyl (HO<sub>2</sub>)/nitrate radicals (NO<sub>3</sub>) by high concentrations of PM<sub>2.5</sub> that inhibits the photochemical production of O<sub>3</sub>,<sup>11–15</sup> or reduced photolysis rates with PM<sub>2.5</sub> increasing.<sup>16</sup> A number of model simulations have used a uniform reactive uptake coefficient for HO<sub>2</sub> on aerosols (γ<sub>HO<sub>2</sub></sub> = 0.2)<sup>9,17–21</sup> to focus

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on (1) studying emission control policies for O<sub>3</sub> pollution reduction with the understanding that reduced PM<sub>2.5</sub> concentration promotes more efficient O<sub>3</sub> formation<sup>9,17–20</sup> and (2) possible consideration of a third ‘aerosol inhibited’ regime for O<sub>3</sub> formation in addition to the regular VOC-limited and NO<sub>x</sub>-limited regimes.<sup>21</sup>

According to Zhang *et al.* (2022),<sup>7</sup> a non-linear polynomial function can be used to depict the O<sub>3</sub>–PM<sub>2.5</sub> co-relationships for NYC based on surface measurements, with a positive linear term reflecting the O<sub>3</sub>/PM<sub>2.5</sub> co-occurrence and a negative power function term reflecting the O<sub>3</sub> formation suppression by PM<sub>2.5</sub> (hereafter PM<sub>2.5</sub>-suppression factor). The PM<sub>2.5</sub>-suppression factors were also identified and likely to change along with the O<sub>3</sub>-sensitivity of the chemical regime in NYC.<sup>7</sup> To verify the connection between the PM<sub>2.5</sub>-suppression factors and the O<sub>3</sub>-sensitive regime existing over a larger region, major cities of the Eastern U.S. and their downwind regions are selected in this study, with a focus on the Long Island Sound and surrounding area located just downwind of NYC.<sup>22–24</sup> This study will focus on the spatial variation of the PM<sub>2.5</sub>-suppression factors over several major Eastern U.S. cities and also from urban to downwind regions (NYC as an example) and the temporal variation from 2004 to 2019 to explore the relationship between the PM<sub>2.5</sub>-suppression factors and the corresponding O<sub>3</sub>-sensitivity regimes over this regional scale.

## 2. Methods

### 2.1 Study locations and periods

Five air quality sites in NYC and downwind locations over Long Island Sound (Fig. S1† for the locations) were chosen as examples of the PM<sub>2.5</sub>-suppression factor variation from urban to downwind regions. These five sites include (a) two urban sites: the IS52 site in Bronx County of NYC and the Queens College (QC) site in Queens County of NYC in New York State, and (b) three downwind sites: the Eisenhower Park (EP) site in western Long Island in New York State, the Holtsville (HOL) site in central Long Island, and the Crisco Park (CP) site in New Haven in Connecticut state, which was chosen because it is frequently influenced by sea breezes that transport NYC urban outflow plumes.<sup>22–24</sup> The IS52, QC, EP, and HOL sites belong to the New York State Department of Environmental Conservation (NYSDEC), and the CP site belongs to the Connecticut Department of Energy and Environmental Protection. In addition to these five sites for NYC and downwind locations, another 11 major Eastern U.S. cities with the U.S. Environmental Protection Agency measurement sites for O<sub>3</sub> and PM<sub>2.5</sub> in the urban regions were chosen to investigate the spatial/temporal variation of the PM<sub>2.5</sub>-suppression factor. To better cover the study period (2004–2019) with a daily report for O<sub>3</sub> and PM<sub>2.5</sub> of each city, we generally select the data from 2–3 sites in or near (within 10 km) the downtown regions, with the location of the representative site of each city shown in Table S1.† The study period is from 2004 to 2019 during summertime (June, July, and August), which was separated into three subperiods based on the PM<sub>2.5</sub> variation (Fig. S2,† SP1: 2004–2008; SP2: 2009–2013, SP3: 2014–2019). These MDA8 O<sub>3</sub> and the PM<sub>2.5</sub> from the above

sites can be found at <https://www.epa.gov/outdoor-air-quality-data/download-daily-data>.

### 2.2 Non-linear fitting of the O<sub>3</sub>–PM<sub>2.5</sub> relationship

Eqn (1) includes (1) a positive linear term to reflect the O<sub>3</sub>/PM<sub>2.5</sub> co-occurrence with its slope influenced by the aerosol chemical composition (this slope varies as a function of the atmospheric chemical composition, which in turn varies with emission controls), (2) a negative power function term with an exponent of 5/3 reflecting the suppression of O<sub>3</sub> formation by PM<sub>2.5</sub>, (*i.e.*, the uptake of HO<sub>2</sub>/NO<sub>3</sub> by PM<sub>2.5</sub>, *etc.*), and (3) a constant with the possibility of implying the background O<sub>3</sub> without PM<sub>2.5</sub>.<sup>7</sup> The power function exponent was set to 5/3, based on the consideration that (a) the uptake coefficients of the radicals related to the aerosol surface concentration which is expected to be proportional to the 2/3 power of PM<sub>2.5</sub> mass concentration, and (b) the radical concentrations were simply assumed to relate with the O<sub>3</sub> concentration, which is proportional to the PM<sub>2.5</sub> mass concentration as mentioned in the above positive linear term.

$$O_3 = aPM_{2.5} - b(PM_{2.5})^{5/3} + c \quad (1)$$

The coefficient *a* is the slope of the linear term, *b* is the power function coefficient, and *c* is the constant. These three factors will be obtained through non-linear fitting. It should be noted that eqn (1) only represents a very idealized solution for the non-linear O<sub>3</sub>–PM<sub>2.5</sub> relationship, with oversimplified terms and factors, and will cause some uncertainty for the results. More specifically, the impact of aerosol on the O<sub>3</sub> formation could be much more complicated with additional or different processes, including other heterogeneous reactions besides the uptake of HO<sub>2</sub>/NO<sub>3</sub> by PM<sub>2.5</sub>, changes to photolysis rates and direct radiative forcing, changes to meteorological conditions, *i.e.*, boundary layer height and ventilation, temperature and wind speed, *etc.*<sup>25,26</sup> All of these would complicate the equation and introduce new terms to better describe the relationship between PM<sub>2.5</sub> and O<sub>3</sub>. Further studies related to the mechanism are warranted to explore a more accurate function.

The power function coefficient is defined as the “PM<sub>2.5</sub>-suppression factor”, which indicates the magnitude of suppression of O<sub>3</sub> formation by PM<sub>2.5</sub> at the same PM<sub>2.5</sub> level when doing spatial/temporal comparisons, and will be the focus of this study. In this study, the MDA8 O<sub>3</sub> and the DA24 PM<sub>2.5</sub> concentrations were used for the O<sub>3</sub> and PM<sub>2.5</sub> values. The PM<sub>2.5</sub> data were initially binned following the approach in Li *et al.*<sup>8</sup> and Buysse *et al.*<sup>27</sup> with increments of 5 μg m<sup>−3</sup>, which was used to ensure enough statistical points in each bin. However, any site with only four bins when using the increment of 5 μg m<sup>−3</sup> was binned in increments of 4 μg m<sup>−3</sup> to ensure sufficient points for fitting. In addition, discrete bins having only one or two highest PM<sub>2.5</sub> mass concentrations were left out, as they are considered quite probably to be due to the influence of other factors, such as the extreme wildfire smoke plumes. It should be noted that the binned dataset used in this study would constitute a simplified but empirically valid mechanism for the MDA8 O<sub>3</sub> and DA24 PM<sub>2.5</sub> relationship.



### 2.3 O<sub>3</sub>-sensitivity regime

The ratio of the HCHO column concentration and NO<sub>2</sub> column concentration from the Ozone Monitoring Instrument (OMI)<sup>28,29</sup> was used as the indicator for the early afternoon O<sub>3</sub>-sensitivity regime (considering the OMI overpass time around 01 : 30 pm at local time) for each site as described by Jin *et al.* (2020),<sup>27</sup> and the data can be found from <https://giovanni.gsfc.nasa.gov/giovanni>. Jin *et al.* (2020)<sup>30</sup> determined that the high ozone probability (over 70 ppb 8 hour average) peaks at an HCHO/NO<sub>2</sub> ratio near 3.6 with a range of [3.2–4.1] for the average of the 7 cities they studied (Los Angeles, New York, Chicago, Washington, Pittsburgh, Atlanta, Houston). The ratios below this are roughly considered as VOC-limited chemistry, and above as NO<sub>x</sub>-limited chemistry. In this study, a spatial range of 0.5° × 0.5° was used for each city to get the area-averaged column concentration of HCHO and NO<sub>2</sub>, which were used further to obtain the seasonal averaged HCHO/NO<sub>2</sub> ratio.

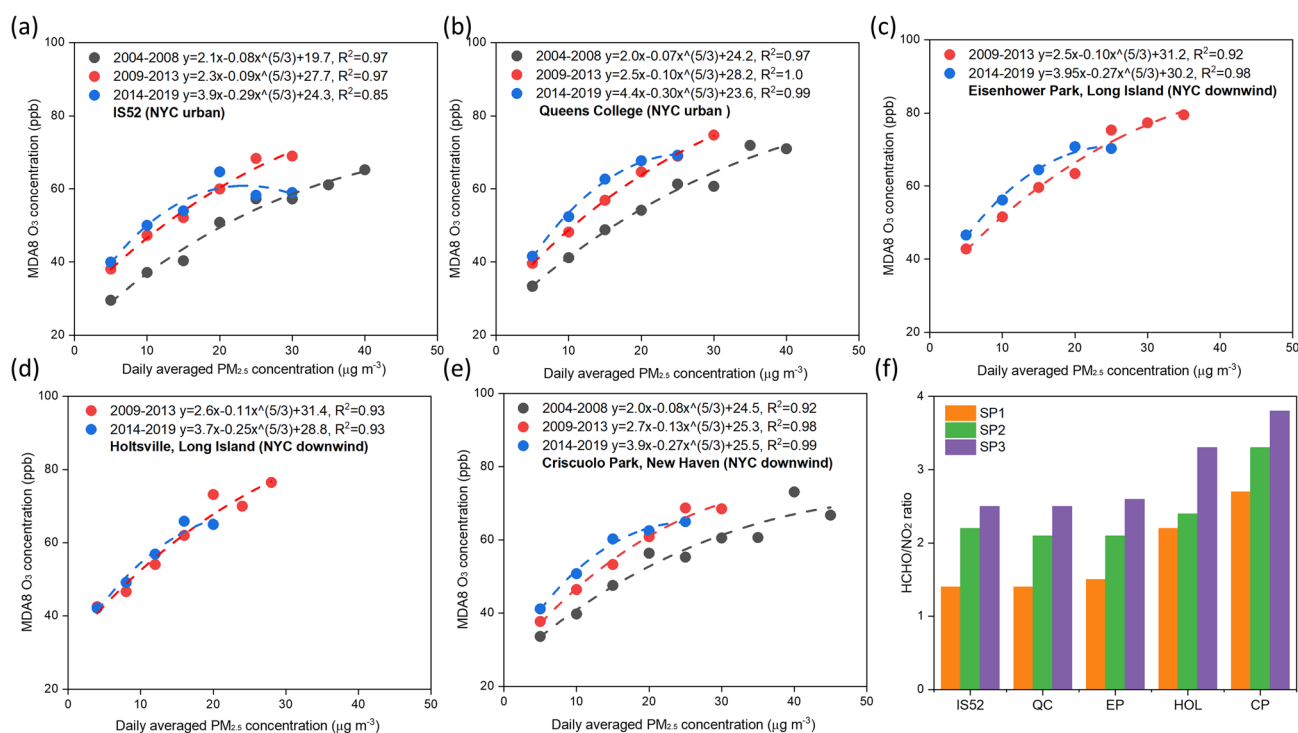
## 3. Results and discussion

### 3.1 Enhanced summertime PM<sub>2.5</sub>-suppression on O<sub>3</sub> formation over the NYC metro area from urban to downwind

The MDA8 O<sub>3</sub> and the DA24 PM<sub>2.5</sub> concentrations were used to derive their relationships for these subperiods (SP1: 2004–2008; SP2: 2009–2013, SP3: 2014–2019) of the study period (2004–2019), and these relationships were further fitted using eqn (1) as mentioned in Section 2.2. The subperiods were divided based on the variation of the DA24 PM<sub>2.5</sub> mass concentration, and the

standard deviation of the annual summertime average DA24 PM<sub>2.5</sub> in each period was below 1 μg m<sup>-3</sup>.<sup>7</sup> A detailed description of the polynomial equation for fitting the non-linear relationship between O<sub>3</sub> and PM<sub>2.5</sub> can be found in Zhang *et al.* (2022).<sup>7</sup> Over the past 16 years, the linear slope of the O<sub>3</sub>–PM<sub>2.5</sub> relationship increased with time for both NYC urban sites and its downwind ones (Fig. 1a–e), which was verified to be related to the increased mass fraction of the secondary organic aerosol (SOA) and ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), caused by the more significant reductions in the emissions of SO<sub>2</sub> and PM<sub>2.5</sub> than those of VOCs and NO<sub>x</sub>.<sup>7</sup>

For the highlighted PM<sub>2.5</sub>-suppression factor in this study, a clear trend was observed in the NYC urban sites (IS52 and Queens College, Fig. 1a and b) over the past 16 years, with a slight increase from SP1 to SP2 (both near 0.1) and a significantly enhanced step from SP2 to SP3 (near 0.3). The enhanced PM<sub>2.5</sub>-suppression factor is consistent with the increased HCHO/NO<sub>2</sub> ratio (Fig. 1f), which is used to indicate the O<sub>3</sub>-sensitivity regime through satellite observations.<sup>27</sup> An increase in the value of the HCHO/NO<sub>2</sub> ratio indicates a shift of the O<sub>3</sub>-sensitivity regime towards NO<sub>x</sub>-limited chemistry, and could be (1) a complete change in O<sub>3</sub> chemistry sensitivity from VOC-limited to NO<sub>x</sub>-limited, (2) a shift towards NO<sub>x</sub> sensitivity (VOC-limited to weakly VOC-limited/transitional), or (3) increasingly NO<sub>x</sub>-limited O<sub>3</sub> chemistry. Fig. 1f shows that the NYC urban region (IS52 and QC) shifted from a strong VOC-limited regime at SP1 (HCHO/NO<sub>2</sub> ~ 1.5) to a weak VOC-limited regime near the lower end of the transitional regime



**Fig. 1** (a–e) The O<sub>3</sub> vs. PM<sub>2.5</sub> relationships over the NYC (a): the IS52 site of NYC, (b): the Queens College site of NYC and its downwind regions (c): the Eisenhower Park site of Long Island, (d): the Holtsville site of Long Island, and (e): the Criscuolo Park site of New Haven), and (f) the OMI HCHO/NO<sub>2</sub> ratios for the subperiods of each site (QC: Queens College; EP: Eisenhower Park; HOL: Holtsville; CP: Criscuolo Park). (SP1: 2004–2008; SP2: 2009–2013, SP3: 2014–2019).



at SP3 ( $\text{HCHO}/\text{NO}_2 \sim 2.7$ ). However, the variation of the  $\text{HCHO}/\text{NO}_2$  ratio comparing SP2 to SP1 (SP2 vs. SP1: 2.2 vs. 1.5, 46% increasing compared to SP1) was larger than the variation of the  $\text{PM}_{2.5}$ -suppression factor (both near 0.1, Fig. 1a and b), and this generally matches the current model simulation result about the  $\text{O}_x$ - $\text{NO}_x$  relationship considering the  $\text{PM}_{2.5}$  effect over Chinese urban regions from Li *et al.* (2022),<sup>31</sup> which indicated that the  $\text{PM}_{2.5}$ -suppression effect was weaker at higher  $\text{NO}_x$  concentrations in the VOC-limited regime, but strengthened as the  $\text{O}_3$ -sensitivity approached the transitional regime. The weak  $\text{PM}_{2.5}$ -suppression effect in the VOC-limited regime could be due to the competition for the consumption of  $\text{HO}_x$  by  $\text{NO}_x$  rather than  $\text{PM}_{2.5}$ , making the  $\text{NO}_x$  concentration the dominant factor for  $\text{O}_3$  concentration sensitivity under these conditions.<sup>31</sup>

For the NYC downwind sites (Eisenhower Park site, Fig. 1c; Holtsville site, Fig. 1d, and Criscuolo Park site, Fig. 1e), their  $\text{PM}_{2.5}$ -suppression factors for each subperiod were similar to the NYC urban sites (IS51 site, Fig. 1a and Queens College site,

Fig. 1b). This can be attributed to urban plume transport, which has been discussed in some detail from recent and current studies based on the 2018 Long Island Sound Tropospheric Ozone Study (LISTOS),<sup>22–24</sup> and the formed  $\text{O}_3$  and  $\text{PM}_{2.5}$  and some unreacted precursors can be carried to downwind regions. Meanwhile, based on the fact that the averaging time period for MDA8  $\text{O}_3$  (8 hours) and DA24  $\text{PM}_{2.5}$  (24 hours) is generally much longer than the time scale of the photochemical reactions, it is reasonable to believe that the urban plume transport could result in the similar  $\text{PM}_{2.5}$ -suppression factors for both urban and downwind sites. However, except for the Eisenhower Park site which had an  $\text{HCHO}/\text{NO}_2$  ratio for each subperiod similar to the Queens College site as their proximity to each other (<20 km), the  $\text{HCHO}/\text{NO}_2$  ratios of each subperiod for the Holtsville site (around 70 km from Queens College site) and the Criscuolo Park site (around 100 km from the Queens College site) were much higher than the values of the NYC urban sites (Fig. 1f). Based on satellite observations, this indicates that Holtsville

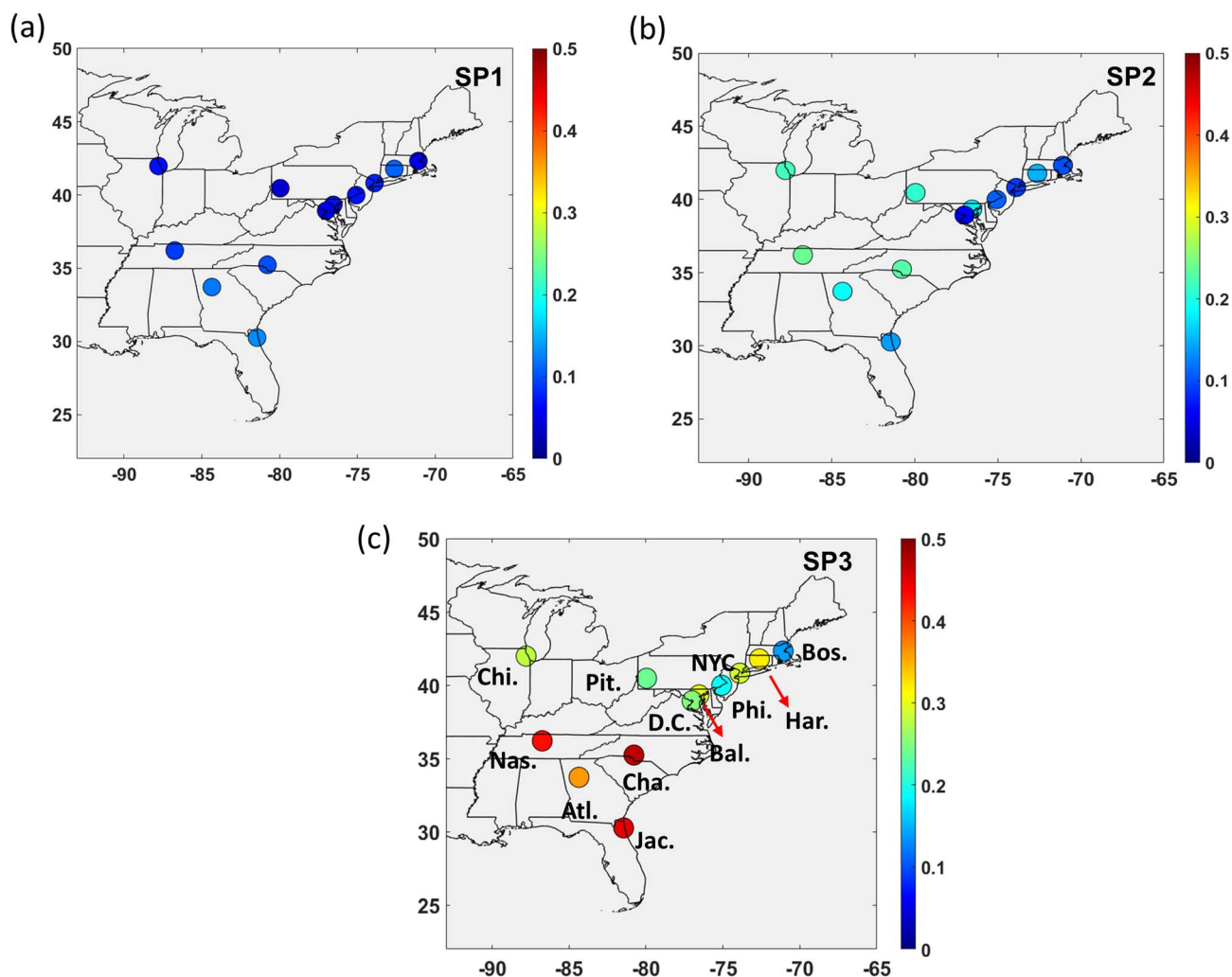


Fig. 2 The  $\text{PM}_{2.5}$ -suppression factor distribution map for the twelve major cities in the Eastern U.S. for (a) Subperiod 1 (SP1: 2004–2008), (b) Subperiod 2 (SP2: 2009–2013), and (c) Subperiod 3 (SP3: 2014–2019). These twelve major cities include Chicago (Chi., Illinois), Pittsburgh (Pit., Pennsylvania), Boston (Bos., Massachusetts), Hartford (Har., Connecticut), NYC (New York), Philadelphia (Phi., Pennsylvania), Baltimore (Bal., Maryland), Washington, D.C. (District of Columbia), Charlotte (Cha., North Carolina), Atlanta (Atl., Georgia), Jacksonville (Jac., Florida), and Nashville (Nas., Tennessee).



and Criscoolo Park were closer to the  $\text{NO}_x$ -limited regime than NYC urban sites. These differences between the  $\text{PM}_{2.5}$ -suppression factors and the  $\text{HCHO}/\text{NO}_2$  ratios could come from the discrepancy between the hourly/daily averaged ground measurements and the early afternoon much shorter time period of satellite data capture.

### 3.2 Enhanced summertime $\text{PM}_{2.5}$ -suppression on $\text{O}_3$ formation over major cities in the Eastern U.S.

The analysis of the increased  $\text{PM}_{2.5}$ -suppression effect was also expanded to other major cities of the Eastern U.S., as shown in Fig. 2. More detailed information about the  $\text{O}_3$  vs.  $\text{PM}_{2.5}$  relationships of each city and their fitting results are shown in Fig. S3.† The  $\text{PM}_{2.5}$ -suppression factors of these major cities were below/near 0.1 in SP1 (Fig. 2a and 3) and over 0.2 in SP3 (Fig. 2c and 3), and generally increased following the  $\text{O}_3$ -sensitivity regime moving toward a stronger  $\text{NO}_x$ -limited chemistry, being indicated by their increased  $\text{HCHO}/\text{NO}_2$  ratios from SP1 to SP3 (Fig. 3). Meanwhile, the  $\text{PM}_{2.5}$ -suppression factors showed a clear spatial discrepancy throughout the Eastern U.S. comparing north and south, especially in SP3 (2014–2019). The  $\text{PM}_{2.5}$ -suppression factors of the southern cities (*i.e.*, Nashville, Atlanta, Charlotte, and Jacksonville) in SP3 were near or over 0.4, which were clearly higher than the ones of the northern cities (Chicago, Pittsburgh, Boston, NYC, Philadelphia, Baltimore, and Washington, D.C.) with a major range of [0.2–0.3]. The  $\text{PM}_{2.5}$ -suppression factors of these southern cities, to some extent, matched their stronger  $\text{NO}_x$ -limited chemistry, as shown by their relatively higher  $\text{HCHO}/\text{NO}_2$  ratios. Under a stronger  $\text{NO}_x$ -limited chemistry, the  $\text{O}_3$  concentration is more sensitive to the  $\text{NO}_x$  variation, which will enhance the effect of the  $\text{NO}_3$  uptake by  $\text{PM}_{2.5}$  on  $\text{O}_3$  formation and match a higher  $\text{PM}_{2.5}$ -suppression factor.

Based on the fact that (1) the  $\text{PM}_{2.5}$ -suppression factor increases as the  $\text{O}_3$ -sensitivity regime shifts toward stronger

$\text{NO}_x$ -limited chemistry and (2) the relatively small variation range of the  $\text{PM}_{2.5}$ -suppression factors for the cities with similar urban conditions (*i.e.*, those northeast urban cities with a range of [0.2–0.3] in SP3), it is reasonable to suppose the summertime  $\text{PM}_{2.5}$ -suppression factor derived from the polynomial fits can be used provide information for identifying the  $\text{O}_3$ -sensitivity regimes based on the ground measurement, in addition to the satellite measurements using the  $\text{HCHO}/\text{NO}_2$  ratios. However, it is hard to build a highly correlated relationship between the  $\text{PM}_{2.5}$ -suppression factor and the  $\text{HCHO}/\text{NO}_2$  ratios (as shown in Fig. S4†), considering the facts that (1)  $\text{PM}_{2.5}$ -suppression factor changed little in the VOC-limited regime, (2) local atmospheric chemistry varied, (3) the  $\text{HCHO}/\text{NO}_2$  ratios are for early afternoon photochemistry while the  $\text{PM}_{2.5}$ -suppression factor for a daily average, *etc.* More studies are warranted for exploring the usage of the  $\text{PM}_{2.5}$ -suppression factor for  $\text{O}_3$ -sensitivity regimes and its relationship with the satellite-measured  $\text{HCHO}/\text{NO}_2$  ratios in a world range. More especially, the future datasets from the TEMPO satellite (<https://tempo.si.edu>) with hourly fluctuations in  $\text{HCHO}/\text{NO}_2$  values will largely promote the understanding the hourly variation of the  $\text{O}_3$ -sensitivity regimes and the daily averaged  $\text{O}_3$ -sensitivity regimes, which could build a better relationship to the ground measurements/derived suppression factors from this study.

### 3.3 Atmospheric implications of the increased summertime $\text{PM}_{2.5}$ -suppression factor

The relationship of the  $\text{PM}_{2.5}$ -suppression factor with the  $\text{O}_3$ -sensitivity regime also indicates the necessity of considering the effect of the  $\text{HO}_2$  uptake coefficient ( $\gamma_{\text{HO}_2}$ ) on aerosol surfaces, which is most commonly implemented as a constant value, *i.e.*,  $\gamma_{\text{HO}_2} = 0.2$  for a number of previous studies.<sup>15–21</sup> The increased  $\text{PM}_{2.5}$ -suppression factor following the  $\text{O}_3$ -sensitivity regime from VOC-limited to  $\text{NO}_x$ -limited can also partly explain the

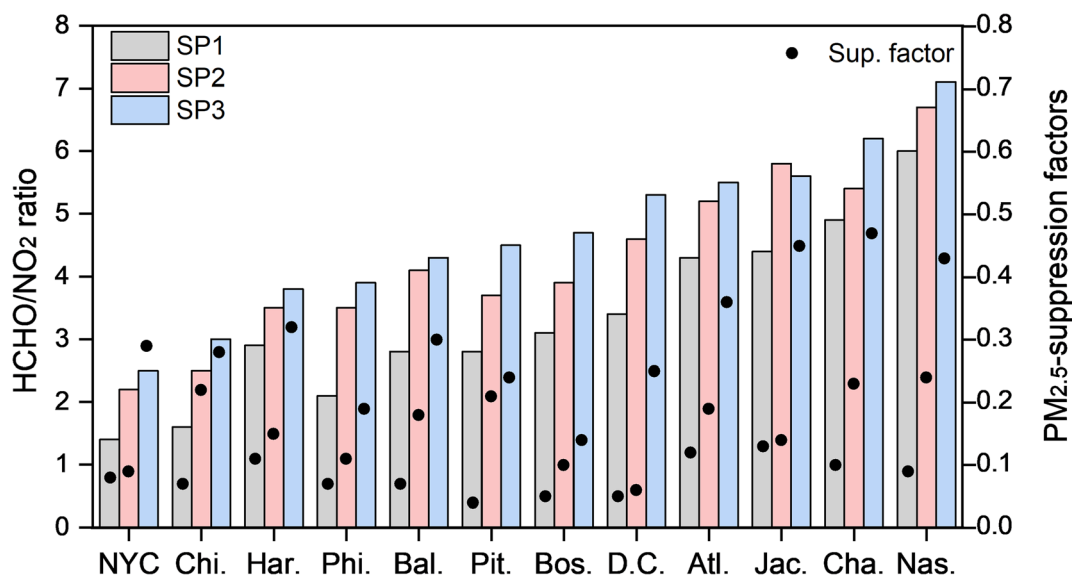


Fig. 3 The OMI  $\text{HCHO}/\text{NO}_2$  ratios and  $\text{PM}_{2.5}$ -suppression factors for the subperiods of each city mentioned in Fig. 2.



discrepancy between the ambient measurement of HO<sub>2</sub> uptake from a rural site in North China Plain (Wangdu County, Hebei province, China) by Tan *et al.* (2020)<sup>32</sup> and the model result for Chinese urban areas from Li *et al.* (2019).<sup>8</sup> Given that Wangdu County was located at a VOC-limited regime in 2014,<sup>32,33</sup> it is reasonable to infer that its PM<sub>2.5</sub>-suppression factor was relatively low, considering (1) the rural Wangdu measurement site in 2014 was highly influenced by polluted regions upwind (Baoding City with a distance of about 35 km and Shijiazhuang City with a distance of about 85 km), making it similar to the conditions of the NYC downwind sites, and (2) a derived PM<sub>2.5</sub>-suppression factor of approximately 0.02 was determined for North China Plain major cities (including Shijiazhuang City and Baoding City, Zhang *et al.*, 2022).<sup>7</sup> This quite low PM<sub>2.5</sub>-suppression factor implies little influence of HO<sub>x</sub> uptake by aerosol and matches the derived low HO<sub>2</sub> uptake coefficient during daytime (~0.08) from Tan *et al.* (2020)<sup>32</sup> and Song *et al.* (2022).<sup>33</sup> Following the increase in PM<sub>2.5</sub>-suppression factor from 0.02 to 0.06 from 2014–2016 to 2017–2019 for North China Plain major cities,<sup>7</sup> the  $\gamma_{\text{HO}_2}$  would be expected to increase to be nearer to the value ( $\gamma_{\text{HO}_2} = 0.2$ ) used in the model.<sup>15–21</sup> However, the uptake coefficients  $\gamma_{\text{HO}_2}$  vary significantly depending on both aerosol size and composition, and ambient conditions such as the humidity. Its variation related to the change in PM<sub>2.5</sub>-suppression factor under different O<sub>3</sub>-sensitivity regimes, as well as the underlying mechanism needed to be verified and explored through more field measurements, especially in the highly air polluted regions.

## 4. Conclusion

The PM<sub>2.5</sub>-suppression factors on the surface ozone production of Eastern US major cities were derived based on non-linear fitting of the PM<sub>2.5</sub> and O<sub>3</sub> relationship. These factors derived from urban regions showed increasing trends over 16 years of continuous ground measurements and increased from a value below 0.1 during 2004–2008 to over 0.2 during 2014–2019, and generally followed the transition of the O<sub>3</sub>-sensitivity regime from VOC-limited toward NO<sub>x</sub>-limited chemistry.

A spatial similarity for the PM<sub>2.5</sub>-suppression factors between urban regions and their downwind locations was shown for the New York City metro area. However, the spatial distribution of the PM<sub>2.5</sub>-suppression factors of different urban regions showed generally larger values over cities with higher HCHO/NO<sub>2</sub> values – which implies a more NO<sub>x</sub>-limited regime. The temporal and spatial variation of these PM<sub>2.5</sub>-suppression factors was consistent with the variation in the O<sub>3</sub>-sensitivity regime and provides a feasible way of identifying the O<sub>3</sub>-sensitivity regimes through this factor with the possibility of better representing the near ground O<sub>3</sub>-sensitivity chemistry than the current satellite-measured HCHO/NO<sub>2</sub> column concentration ratios. The variation of PM<sub>2.5</sub>-suppression factors raises the possibility of a changeable HO<sub>2</sub>/NO<sub>3</sub> uptake coefficient on aerosol surfaces for the model simulation of O<sub>3</sub> pollution, and more studies/measurements are required to verify this possibility. The results from this study will provide useful guidance for further O<sub>3</sub>-PM<sub>2.5</sub> studies considering a range of PM<sub>2.5</sub>-

suppression factors, which in turn will constrain/evaluate model simulations for O<sub>3</sub> and PM<sub>2.5</sub> concentrations after considering the varied PM<sub>2.5</sub>-suppression factors and/or the varied HO<sub>2</sub>/NO<sub>3</sub> uptake coefficients. These also benefit the ability of models to develop accurate O<sub>3</sub> and PM<sub>2.5</sub> concentration pollution control policies.

## Conflicts of interest

There are no conflicts of interest to declare.

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## References

- 1 J. L. Schnell and M. J. Prather, Co-occurrence of extremes in surface ozone, particulate matter, and temperature over eastern North America, *Proc. Natl. Acad. Sci. U.S.A.*, 2017, **114**(11), 2854–2859.
- 2 S. A. Strode, J. M. Rodriguez, J. A. Logan, O. R. Cooper, J. C. Witte, L. N. Lamsal, *et al.*, Trends and variability in surface ozone over the United States, *J. Geophys. Res. Atmos.*, 2015, **120**(17), 9020–9042.
- 3 T. J. Sullivan, C. T. Driscoll, C. M. Beier, D. Burtraw, I. J. Fernandez, J. N. Galloway, *et al.*, Air pollution success stories in the United States: The value of long-term observations, *Environ. Sci. Policy*, 2018, **84**, 69–73.
- 4 EPA, *Our Nation's Air: Status and Trends through 2021*, 2021. <https://gispub.epa.gov/air/trendsreport/2021/>.
- 5 C. L. Blanchard, S. L. Shaw, E. S. Edgerton and J. J. Schwab, Emission influences on air pollutant concentrations in New York State: I. ozone, *Atmos. Environ. X*, 2019, **3**, 100033.
- 6 C. L. Blanchard, S. L. Shaw, E. S. Edgerton and J. J. Schwab, Emission influences on air pollutant concentrations in New York state: II. PM<sub>2.5</sub> organic and elemental carbon constituents, *Atmos. Environ. X*, 2019, **3**, 100039.
- 7 J. Zhang, J. Wang, Y. Sun, J. Li, M. Ninneman, J. Ye, *et al.*, Insights from ozone and particulate matter pollution control in New York City applied to Beijing, *NPJ Clim. Atmos. Sci.*, 2022, **5**(85), 1–7.
- 8 K. Li, D. J. Jacob, H. Liao, J. Zhu, V. Shah, L. Shen, *et al.*, A two-pollutant strategy for improving ozone and particulate air quality in China, *Nat. Geosci.*, 2019, **12**(11), 906–910.
- 9 X. Chen, Z. Jiang, Y. Shen, R. Li, Y. Fu, J. Liu, *et al.*, Chinese regulations are working—why is surface ozone over industrialized areas still high? Applying lessons from Northeast US air quality evolution, *Geophys. Res. Lett.*, 2021, **48**(14), e2021GL092816.



- 10 J. Zhu, L. Chen, H. Liao and R. Dang, Correlations between PM<sub>2.5</sub> and ozone over China and associated underlying reasons, *Atmosphere*, 2019, **10**(7), 352.
- 11 D. J. Jacob, Heterogeneous chemistry and tropospheric ozone, *Atmos. Environ.*, 2000, **34**(12–14), 2131–2159.
- 12 Y. Kanaya, P. Pochanart, Y. Liu, J. Li, H. Tanimoto, S. Kato, *et al.*, Rates and regimes of photochemical ozone production over Central East China in June 2006: a box model analysis using comprehensive measurements of ozone precursors, *Atmos. Chem. Phys.*, 2009, **9**(20), 7711–7723.
- 13 L. K. Whalley, K. L. Furneaux, A. Goddard, J. D. Lee, A. Mahajan, H. Oetjen, *et al.*, The chemistry of OH and HO<sub>2</sub> radicals in the boundary layer over the tropical Atlantic Ocean, *Atmos. Chem. Phys.*, 2010, **10**(4), 1555–1576.
- 14 Y. Sakamoto, Y. Sadanaga, J. Li, K. Matsuoka, M. Takemura, T. Fujii, *et al.*, Relative and absolute sensitivity analysis on ozone production in Tsukuba, a city in Japan, *Environ. Sci. Technol.*, 2019, **53**(23), 13629–13635.
- 15 S. Stadtler, D. Simpson, S. Schröder, D. Taraborrelli, A. Bott and M. Schultz, Ozone impacts of gas–aerosol uptake in global chemistry transport models, *Atmos. Chem. Phys.*, 2018, **18**(5), 3147–3171.
- 16 R. R. Dickerson, S. Kondragunta, G. Stenchikov, K. L. Civerolo, B. G. Doddridge and B. N. Holben, The impact of aerosols on solar ultraviolet radiation and photochemical smog, *Science*, 1997, **278**(5339), 827–830.
- 17 K. Li, D. J. Jacob, H. Liao, L. Shen, Q. Zhang and K. H. Bates, Anthropogenic drivers of 2013–2017 trends in summer surface ozone in China, *Proc. Natl. Acad. Sci. U.S.A.*, 2019, **116**(2), 422–427.
- 18 F. Taketani, Y. Kanaya, P. Pochanart, Y. Liu, J. Li, K. Okuzawa, *et al.*, Measurement of overall uptake coefficients for HO<sub>2</sub> radicals by aerosol particles sampled from ambient air at Mts. Tai and Mang (China), *Atmos. Chem. Phys.*, 2012, **12**(24), 11907–11916.
- 19 L. K. Xue, T. Wang, J. Gao, A. J. Ding, X. H. Zhou, D. R. Blake, *et al.*, Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes, *Atmos. Chem. Phys.*, 2014, **14**(23), 13175–13188.
- 20 W. Wang, D. D. Parrish, X. Li, M. Shao, Y. Liu, Z. Mo, *et al.*, Exploring the drivers of the increased ozone production in Beijing in summertime during 2005–2016, *Atmos. Chem. Phys.*, 2020, **20**, 15617–15633.
- 21 P. D. Ivatt, M. J. Evans and A. C. Lewis, Suppression of surface ozone by an aerosol-inhibited photochemical ozone regime, *Nat. Geosci.*, 2022, **15**(7), 536–540.
- 22 J. Zhang, M. Ninneman, E. Joseph, M. J. Schwab, B. Shrestha and J. J. Schwab, Mobile laboratory measurements of high surface ozone levels and spatial heterogeneity during LISTOS 2018: Evidence for sea breeze influence, *J. Geophys. Res. Atmos.*, 2020, **125**(11), e2019JD031961.
- 23 M. H. Couillard, M. J. Schwab, J. J. Schwab, C. H. Lu, E. Joseph, B. Stutsrim, *et al.*, Vertical Profiles of Ozone Concentrations in the Lower Troposphere Downwind of New York City During LISTOS 2018–2019, *J. Geophys. Res. Atmos.*, 2021, **126**(23), e2021JD035108.
- 24 J. Zhang, A. Catena, B. Shrestha, J. Freedman, E. McCabe, M. J. Schwab, *et al.*, Unraveling the interaction of urban emission plumes and marine breezes involved in the formation of summertime coastal high ozone on Long Island, *Environ. Sci. Atmos.*, 2022, **2**(6), 1438–1449.
- 25 J. Xing, R. Mathur, J. Pleim, C. Hogrefe, C. M. Gan, D. C. Wong, *et al.*, Air pollution and climate response to aerosol direct radiative effects: a modeling study of decadal trends across the northern hemisphere, *J. Geophys. Res.*, 2015, **120**, 12221–12236.
- 26 J. Xing, J. Wang, R. Mathur, S. Wang, G. Sarwar and J. Pleim, *et al.*, Impacts of aerosol direct effects on tropospheric ozone through changes in atmospheric dynamics and photolysis rates, *Atmos. Chem. Phys.*, 2017, **17**, 9869–9883.
- 27 C. E. Buysse, A. Kaulfus, U. Nair and D. A. Jaffe, Relationships between particulate matter, ozone, and nitrogen oxides during Urban smoke events in the Western US, *Environ. Sci. Technol.*, 2019, **53**, 12519–12528.
- 28 K. F. Boersma, H. Eskes, A. Richter, I. D. Smedt, A. Lorente, S. Beirle, *et al.*, QA4ECV NO<sub>2</sub> Tropospheric and Stratospheric Column Data from OMI (2017), 2017, <https://doi.org/10.21944/qa4ecv-no2-omi-v1.1>.
- 29 I. De Smedt, N. Theys, H. Yu, T. Danckaert, C. Lerot, S. Compernelle, *et al.*, Algorithm theoretical baseline for formaldehyde retrievals from S5P TROPOMI and from the QA4ECV project, *Atmos. Meas. Tech.*, 2018, **11**, 2395–2426.
- 30 X. Jin, A. Fiore, K. F. Boersma, I. D. Smedt and L. Valin, Inferring changes in summertime surface Ozone–NO<sub>x</sub>–VOC chemistry over US urban areas from two decades of satellite and ground-based observations, *Environ. Sci. Technol.*, 2020, **54**(11), 6518–6529.
- 31 C. Li, Q. Zhu, X. Jin and R. C. Cohen, Elucidating Contributions of Anthropogenic Volatile Organic Compounds and Particulate Matter to Ozone Trends over China, *Environ. Sci. Technol.*, 2022, **56**(18), 12906–12916.
- 32 Z. Tan, A. Hofzumahaus, K. Lu, S. S. Brown, F. Holland, L. G. Huey, *et al.*, No evidence for a significant impact of heterogeneous chemistry on radical concentrations in the North China Plain in summer 2014, *Environ. Sci. Technol.*, 2020, **54**(10), 5973–5979.
- 33 H. Song, K. Lu, H. Dong, Z. Tan, S. Chen, L. Zeng, *et al.*, Reduced aerosol uptake of hydroperoxyl radical may increase the sensitivity of ozone production to volatile organic compounds, *Environ. Sci. Technol. Lett.*, 2021, **9**(1), 22–29.

