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Enhanced summertime $PM_{2.5}$-suppression of O_3 formation over the Eastern U.S. following the O_3-sensitivity variations†

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The suppression of ozone (O_3) formation due to the presence of fine particulate matter ($PM_{2.5}$) has recently been highlighted for further O_3 pollution controls in regions that suffer high ozone concentrations. Here we derive multiple $PM_{2.5}$-suppression factors for the Eastern United States (U.S.) major cities based on a non-linear fitting of the $PM_{2.5}$ and O_3 relationship from the multiyear surface observations. Our results show that these $PM_{2.5}$-suppression factors are increasing with time and generally follow the transition of the O_3-sensitive regime towards NO_x-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 $PM_{2.5}$-suppression factor will further improve the ability of models to help guide O_3 and $PM_{2.5}$ concentration pollution controls.

Environmental significance

Ozone and fine particulate matter ($PM_{2.5}$) 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 $PM_{2.5}$ can play in suppressing ozone formation. The magnitude of ozone suppression from $PM_{2.5}$ provides an additional indicator of the sensitivity of ozone formation from its VOC and NO_x precursors. The $PM_{2.5}$ suppression of ozone formation per unit of $PM_{2.5}$ mass concentration has been increasing over the period 2004–2019 in the Northeast U.S., indicating a transition from VOC-limited to NO_x-limited ozone formation sensitivity. It also provides guidance for further O_3–$PM_{2.5}$ 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_3) and particulate matter (with a diameter under 2.5 μm, $PM_{2.5}$) pollution during the summertime.[1] However, these summertime concentrations of O_3 and $PM_{2.5}$ in the region's major cities have shown decreasing trends since the 1970s as a result of the implementation of emission control policies.[2–6] While the region has seen reductions in both pollutants, extreme concentrations of O_3 and $PM_{2.5}$ (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 $PM_{2.5}$ than O_3. This can be attributed to the different reduction rates of their precursors, with the control policies targeting sulfur dioxide (SO_2) and primary $PM_{2.5}$, than volatile organic compounds (VOCs) and nitrogen oxides (NO_x).[7]

Co-occurrence of summertime maximum daily 8 h average O_3 (hereafter: MDA8 O_3) and the daily 24 h average $PM_{2.5}$ (hereafter: DA24 $PM_{2.5}$ for simplification) based on ground measurements in NYC has shown a direct relationship between the pollutants,[7] 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.[7–10] This flat or declining relationship has been partly attributed to the scavenging of hydroperoxyl (HO_2)/nitrate radicals (NO_3) by high concentrations of $PM_{2.5}$ that inhibits the photochemical production of O_3,[11–15] or reduced photolysis rates with $PM_{2.5}$ increasing.[16] A number of model simulations have used a uniform reactive uptake coefficient for HO_2 on aerosols $(\gamma_{HO_2} = 0.2)$[9,17–21] to focus

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on (1) studying emission control policies for O_3 pollution reduction with the understanding that reduced $PM_{2.5}$ concentration promotes more efficient O_3 formation[9,17–20] and (2) possible consideration of a third 'aerosol inhibited' regime for O_3 formation in addition to the regular VOC-limited and NO_x-limited regimes.[21]

According to Zhang *et al.* (2022),[7] a non-linear polynomial function can be used to depict the O_3–$PM_{2.5}$ co-relationships for NYC based on surface measurements, with a positive linear term reflecting the $O_3/PM_{2.5}$ co-occurrence and a negative power function term reflecting the O_3 formation suppression by $PM_{2.5}$ (hereafter $PM_{2.5}$-suppression factor). The $PM_{2.5}$-suppression factors were also identified and likely to change along with the O_3-sensitivity of the chemical regime in NYC.[7] To verify the connection between the $PM_{2.5}$-suppression factors and the O_3-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.[22–24] This study will focus on the spatial variation of the $PM_{2.5}$-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 $PM_{2.5}$-suppression factors and the corresponding O_3-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 $PM_{2.5}$-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 Criscuolo 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.[22–24] 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_3 and $PM_{2.5}$ in the urban regions were chosen to investigate the spatial/temporal variation of the $PM_{2.5}$-suppression factor. To better cover the study period (2004–2019) with a daily report for O_3 and $PM_{2.5}$ 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 $PM_{2.5}$ variation (Fig. S2,† SP1: 2004–2008; SP2: 2009–2013, SP3: 2014–2019). These MDA8 O_3 and the $PM_{2.5}$ 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_3–$PM_{2.5}$ relationship

Eqn (1) includes (1) a positive linear term to reflect the $O_3/PM_{2.5}$ 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_3 formation by $PM_{2.5}$, (*i.e.*, the uptake of HO_2/NO_3 by $PM_{2.5}$, *etc.*), and (3) a constant with the possibility of implying the background O_3 without $PM_{2.5}$.[7] 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 $PM_{2.5}$ mass concentration, and (b) the radical concentrations were simply assumed to relate with the O_3 concentration, which is proportional to the $PM_{2.5}$ mass concentration as mentioned in the above positive linear term.

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

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_3–$PM_{2.5}$ relationship, with oversimplified terms and factors, and will cause some uncertainty for the results. More specifically, the impact of aerosol on the O_3 formation could be much more complicated with additional or different processes, including other heterogeneous reactions besides the uptake of HO_2/NO_3 by $PM_{2.5}$, changes to photolysis rates and direct radiative forcing, changes to meteorological conditions, *i.e.*, boundary layer height and ventilation, temperature and wind speed, *etc.*[25,26] All of these would complicate the equation and introduce new terms to better describe the relationship between $PM_{2.5}$ and O_3. Further studies related to the mechanism are warranted to explore a more accurate function.

The power function coefficient is defined as the "$PM_{2.5}$-suppression factor", which indicates the magnitude of suppression of O_3 formation by $PM_{2.5}$ at the same $PM_{2.5}$ level when doing spatial/temporal comparisons, and will be the focus of this study. In this study, the MDA8 O_3 and the DA24 $PM_{2.5}$ concentrations were used for the O_3 and $PM_{2.5}$ values. The $PM_{2.5}$ data were initially binned following the approach in Li *et al.*[8] and Buysse *et al.*[27] with increments of 5 $\mu g\ m^{-3}$, which was used to ensure enough statistical points in each bin. However, any site with only four bins when using the increment of 5 $\mu g\ m^{-3}$ was binned in increments of 4 $\mu g\ m^{-3}$ to ensure sufficient points for fitting. In addition, discrete bins having only one or two highest $PM_{2.5}$ 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_3 and DA24 $PM_{2.5}$ relationship.

2.3 O_3-sensitivity regime

The ratio of the HCHO column concentration and NO_2 column concentration from the Ozone Monitoring Instrument (OMI)[28,29] was used as the indicator for the early afternoon O_3-sensitivity regime (considering the OMI overpass time around 01 : 30 pm at local time) for each site as described by Jin *et al.* (2020),[27] and the data can be found from **https://giovanni.gsfc.nasa.gov/giovanni**. Jin *et al.* (2020)[30] determined that the high ozone probability (over 70 ppb 8 hour average) peaks at an HCHO/NO_2 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_x-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_2, which were used further to obtain the seasonal averaged HCHO/NO_2 ratio.

3. Results and discussion

3.1 Enhanced summertime $PM_{2.5}$-suppression on O_3 formation over the NYC metro area from urban to downwind

The MDA8 O_3 and the DA24 $PM_{2.5}$ 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 $PM_{2.5}$ mass concentration, and the standard deviation of the annual summertime average DA24 $PM_{2.5}$ in each period was below 1 μg m^{-3}.[7] A detailed description of the polynomial equation for fitting the non-linear relationship between O_3 and $PM_{2.5}$ can be found in Zhang *et al.* (2022).[7] Over the past 16 years, the linear slope of the O_3–$PM_{2.5}$ 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_4NO_3), caused by the more significant reductions in the emissions of SO_2 and $PM_{2.5}$ than those of VOCs and NO_x.[7]

For the highlighted $PM_{2.5}$-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 $PM_{2.5}$-suppression factor is consistent with the increased HCHO/NO_2 ratio (Fig. 1f), which is used to indicate the O_3-sensitivity regime through satellite observations.[27] An increase in the value of the HCHO/NO_2 ratio indicates a shift of the O_3-sensitivity regime towards NO_x-limited chemistry, and could be (1) a complete change in O_3 chemistry sensitivity from VOC-limited to NO_x-limited, (2) a shift towards NO_x sensitivity (VOC-limited to weakly VOC-limited/transitional), or (3) increasingly NO_x-limited O_3 chemistry. Fig. 1f shows that the NYC urban region (IS52 and QC) shifted from a strong VOC-limited regime at SP1 (HCHO/NO_2 ~ 1.5) to a weak VOC-limited regime near the lower end of the transitional regime

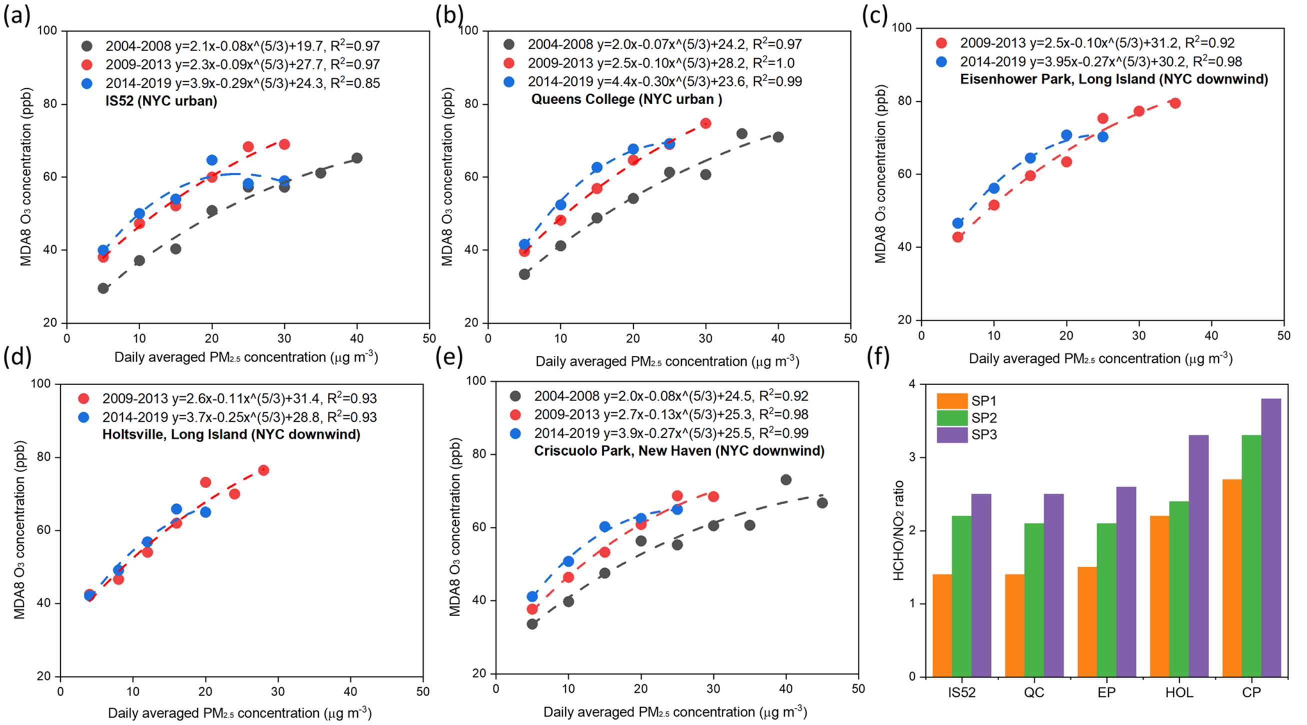

Fig. 1 (a–e) The O_3 *vs.* $PM_{2.5}$ relationships over the NYC (a): the IS52 site of NYC, (b): the Queens College site of NYC and its downwind regions (c): the Eisenhower Park site of Long Island, (d): the Holtsville site of Long Island, and €: the Criscuolo Park site of New Haven), and (f) the OMI HCHO/NO_2 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 ($HCHO/NO_2 \sim 2.7$). However, the variation of the $HCHO/NO_2$ 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 $PM_{2.5}$-suppression factor (both near 0.1, Fig. 1a and b), and this generally matches the current model simulation result about the O_x–NO_x relationship considering the $PM_{2.5}$ effect over Chinese urban regions from Li *et al.* (2022),[31] which indicated that the $PM_{2.5}$-suppression effect was weaker at higher NO_x concentrations in the VOC-limited regime, but strengthened as the O_3-sensitivity approached the transitional regime. The weak $PM_{2.5}$-suppression effect in the VOC-limited regime could be due to the competition for the consumption of HO_x by NO_x rather than $PM_{2.5}$, making the NO_x concentration the dominant factor for O_3 concentration sensitivity under these conditions.[31]

For the NYC downwind sites (Eisenhower Park site, Fig. 1c; Holtsville site, Fig. 1d, and Criscuolo Park site, Fig. 1e), their $PM_{2.5}$-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),[22–24] and the formed O_3 and $PM_{2.5}$ and some unreacted precursors can be carried to downwind regions. Meanwhile, based on the fact that the averaging time period for MDA8 O_3 (8 hours) and DA24 $PM_{2.5}$ (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 $PM_{2.5}$-suppression factors for both urban and downwind sites. However, except for the Eisenhower Park site which had an $HCHO/NO_2$ ratio for each subperiod similar to the Queens College site as their proximity to each other (<20 km), the $HCHO/NO_2$ 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

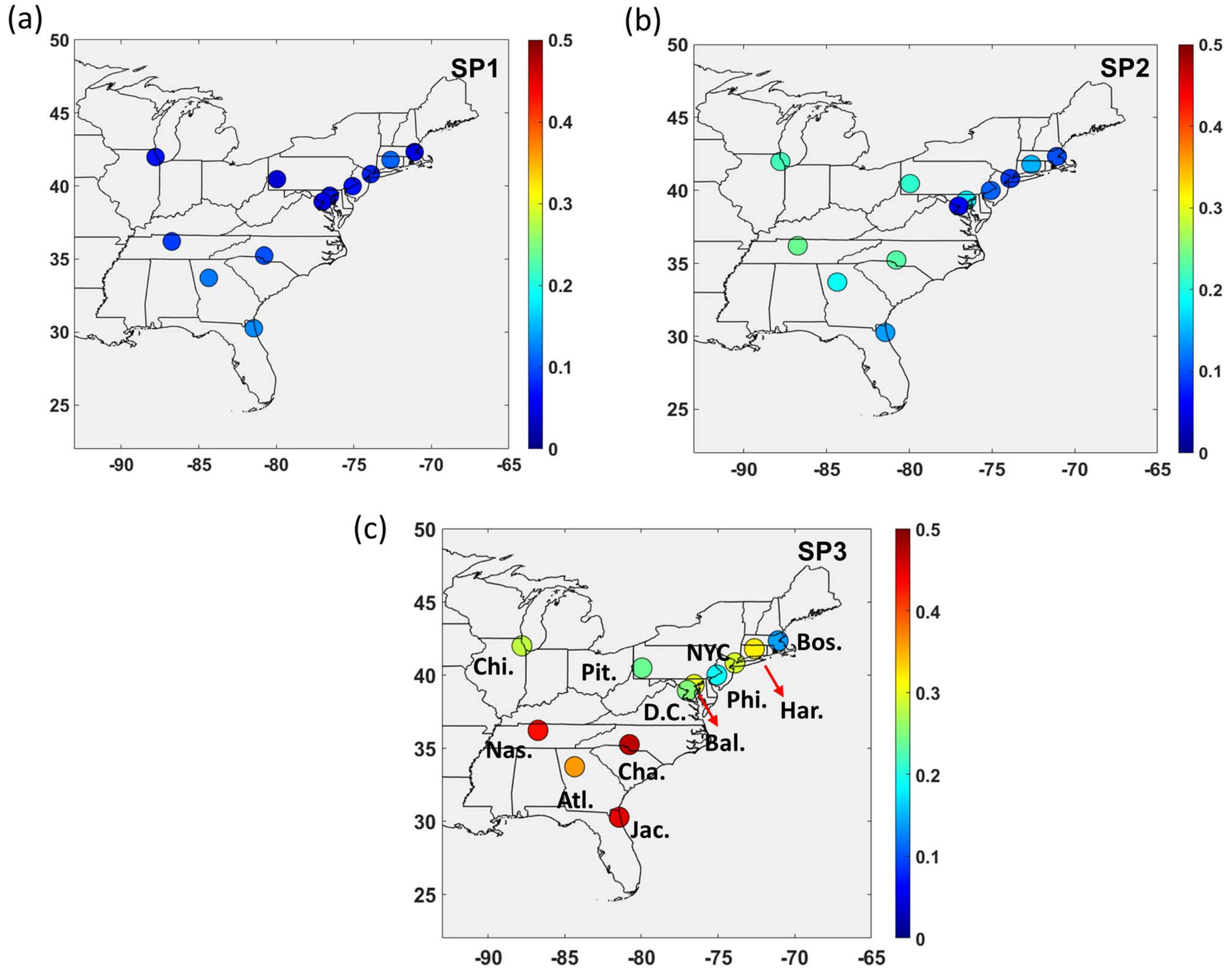

Fig. 2 The $PM_{2.5}$-suppression factor distribution map for the twelve major cities in the Eastern U.S. for (a) Subperiod 1 (SP1:2004–2008), (b) Subperiod 2 (SP2: 2009–2013), and (c) Subperiod 3 (SP3: 2014–2019). These twelve major cities include Chicago (Chi., Illinois), Pittsburgh (Pit., Pennsylvania), 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 Criscuolo Park were closer to the NO_x-limited regime than NYC urban sites. These differences between the $PM_{2.5}$-suppression factors and the $HCHO/NO_2$ 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 $PM_{2.5}$-suppression on O_3 formation over major cities in the Eastern U.S.

The analysis of the increased $PM_{2.5}$-suppression effect was also expanded to other major cities of the Eastern U.S., as shown in Fig. 2. More detailed information about the O_3 *vs.* $PM_{2.5}$ relationships of each city and their fitting results are shown in Fig. S3.† The $PM_{2.5}$-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 O_3-sensitivity regime moving toward a stronger NO_X-limited chemistry, being indicated by their increased $HCHO/NO_2$ ratios from SP1 to SP3 (Fig. 3). Meanwhile, the $PM_{2.5}$-suppression factors showed a clear spatial discrepancy throughout the Eastern U.S. comparing north and south, especially in SP3 (2014–2019). The $PM_{2.5}$-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 $PM_{2.5}$-suppression factors of these southern cities, to some extent, matched their stronger NO_x-limited chemistry, as shown by their relatively higher $HCHO/NO_2$ ratios. Under a stronger NO_x-limited chemistry, the O_3 concentration is more sensitive to the NO_x variation, which will enhance the effect of the NO_3 uptake by $PM_{2.5}$ on O_3 formation and match a higher $PM_{2.5}$-suppression factor.

Based on the fact that (1) the $PM_{2.5}$-suppression factor increases as the O_3-sensitivity regime shifts toward stronger NO_X-limited chemistry and (2) the relatively small variation range of the $PM_{2.5}$-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 $PM_{2.5}$-suppression factor derived from the polynomial fits can be used provide information for identifying the O_3-sensitivity regimes based on the ground measurement, in addition to the satellite measurements using the $HCHO/NO_2$ ratios. However, it is hard to build a highly correlated relationship between the $PM_{2.5}$-suppression factor and the $HCHO/NO_2$ ratios (as shown in Fig. S4†), considering the facts that (1) $PM_{2.5}$-suppression factor changed little in the VOC-limited regime, (2) local atmospheric chemistry varied, (3) the $HCHO/NO_2$ ratios are for early afternoon photochemistry while the $PM_{2.5}$-suppression factor for a daily average, *etc.* More studies are warranted for exploring the usage of the $PM_{2.5}$-suppression factor for O_3-sensitivity regimes and its relationship with the satellite-measured $HCHO/NO_2$ ratios in a world range. More especially, the future datasets from the TEMPO satellite (**https://tempo.si.edu**) with hourly fluctuations in $HCHO/NO_2$ values will largely promote the understanding the hourly variation of the O_3-sensitivity regimes and the daily averaged 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 $PM_{2.5}$-suppression factor

The relationship of the $PM_{2.5}$-suppression factor with the O_3-sensitivity regime also indicates the necessity of considering the effect of the HO_2 uptake coefficient (γ_{HO_2}) on aerosol surfaces, which is most commonly implemented as a constant value, *i.e.*, $\gamma_{HO_2} = 0.2$ for a number of previous studies.[15–21] The increased $PM_{2.5}$-suppression factor following the O_3-sensitivity regime from VOC-limited to NO_x-limited can also partly explain the

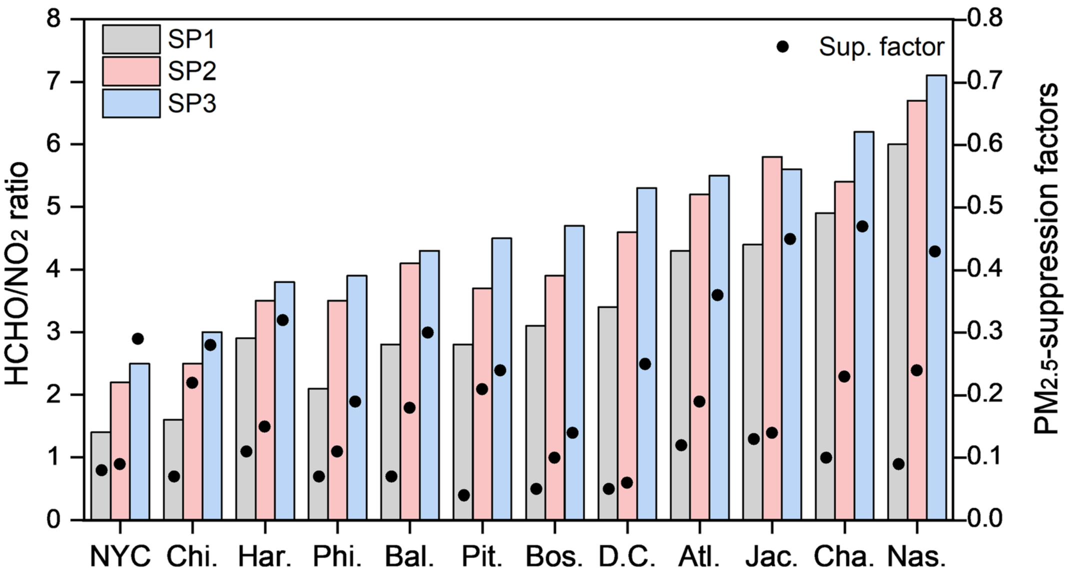

Fig. 3 The OMI $HCHO/NO_2$ ratios and $PM_{2.5}$-suppression factors for the subperiods of each city mentioned in Fig. 2.

discrepancy between the ambient measurement of HO_2 uptake from a rural site in North China Plain (Wangdu County, Hebei province, China) by Tan *et al.* (2020)[32] and the model result for Chinese urban areas from Li *et al.* (2019).[8] Given that Wangdu County was located at a VOC-limited regime in 2014,[32,33] it is reasonable to infer that its $PM_{2.5}$-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 $PM_{2.5}$-suppression factor of approximately 0.02 was determined for North China Plain major cities (including Shijiazhuang City and Baoding City, Zhang *et al.*, 2022).[7] This quite low $PM_{2.5}$-suppression factor implies little influence of HO_x uptake by aerosol and matches the derived low HO_2 uptake coefficient during daytime ($\sim$0.08) from Tan *et al.* (2020)[32] and Song *et al.* (2022).[33] Following the increase in $PM_{2.5}$-suppression factor from 0.02 to 0.06 from 2014–2016 to 2017–2019 for North China Plain major cities,[7] the γ_{HO_2} would be expected to increase to be nearer to the value ($\gamma_{HO_2} = 0.2$) used in the model.[15–21] However, the uptake coefficients γ_{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 $PM_{2.5}$-suppression factor under different O_3-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 $PM_{2.5}$-suppression factors on the surface ozone production of Eastern US major cities were derived based on non-linear fitting of the $PM_{2.5}$ and O_3 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_3-sensitivity regime from VOC-limited toward NO_x-limited chemistry.

A spatial similarity for the $PM_{2.5}$-suppression factors between urban regions and their downwind locations was shown for the New York City metro area. However, the spatial distribution of the $PM_{2.5}$-suppression factors of different urban regions showed generally larger values over cities with higher $HCHO/NO_2$ values – which implies a more NO_x-limited regime. The temporal and spatial variation of these $PM_{2.5}$-suppression factors was consistent with the variation in the O_3-sensitivity regime and provides a feasible way of identifying the O_3-sensitivity regimes through this factor with the possibility of better representing the near ground O_3-sensitivity chemistry than the current satellite-measured $HCHO/NO_2$ column concentration ratios. The variation of $PM_{2.5}$-suppression factors raises the possibility of a changeable HO_2/NO_3 uptake coefficient on aerosol surfaces for the model simulation of O_3 pollution, and more studies/measurements are required to verify this possibility. The results from this study will provide useful guidance for further O_3–$PM_{2.5}$ studies considering a range of $PM_{2.5}$-suppression factors, which in turn will constrain/evaluate model simulations for O_3 and $PM_{2.5}$ concentrations after considering the varied $PM_{2.5}$-suppression factors and/or the varied HO_2/NO_3 uptake coefficients. These also benefit the ability of models to develop accurate O_3 and $PM_{2.5}$ concentration pollution control policies.

Conflicts of interest

There are no conflicts of interest to declare.

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