Contents lists available at ScienceDirect





Atmospheric Environment

journal homepage: http://www.elsevier.com/locate/atmosenv

# The impact of volatile organic compounds on ozone formation in the suburban area of Shanghai

Kun Zhang <sup>a,b</sup>, Li Li <sup>a,b,\*</sup>, Ling Huang <sup>a,b</sup>, Yangjun Wang <sup>a,b</sup>, Juntao Huo <sup>c</sup>, Yusen Duan <sup>c</sup>, Yuhang Wang <sup>d</sup>, Qingyan Fu <sup>c,\*\*</sup>

<sup>a</sup> School of Environmental and Chemical Engineering, Shanghai University, Shanghai, 200444, China

<sup>b</sup> Key Laboratory of Organic Compound Pollution Control Engineering, Shanghai University, Shanghai, 200444, China

<sup>c</sup> Shanghai Environmental Monitoring Center, Shanghai, 200235, China

<sup>d</sup> School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA, 30332, USA

# HIGHLIGHTS

• Characteristics of ambient VOCs and their influences on O<sub>3</sub> formation in a rural area downwind Shanghai were investigated.

• Strong photochemical losses of VOCs, especially alkenes, were found under high O<sub>x</sub> concentrations situations.

• Abatement ratio of VOCs/NOx should be no less than 0.72 to effectively control O3.

## ARTICLE INFO

Keywords: Ozone formation Volatile organic compounds (VOCs) Observation-based model (OBM) Yangtze River Delta

# ABSTRACT

Volatile organic compounds (VOCs) are important precursors of photochemical smog and secondary organic aerosol (SOA). Quantitatively assessing the impact of VOCs on ozone (O<sub>3</sub>) formation could provide valuable information for the management of emission reduction and photochemical pollution control. In this study, we first figured out the ozone pollution episodes during 2018 at Dianshan Lake (DSL), which is located in the suburban area of Shanghai and is adjacent to three provinces of the YRD region. Then we analyzed continuous variation of O<sub>3</sub> precursors and meteorological parameters. The online measurements show that the average volume mixing ratio of total VOCs (TVOC) was  $15.41 \pm 11.39$  ppbv during the ozone pollution episodes, with the largest contribution from alkanes. To further identify the sources of VOCs, VOC concentration-weighted trajectories (CWT) were analyzed, and the results suggested that Zhejiang province could be the most important source region of VOCs at DSL. Analysis using an observation-base model showed that  $NO_x$  and alkenes exhibited the most significant negative and positive influences on O<sub>3</sub> formation, respectively. As for individual species, toluene and isoprene, whose S-weighted concentrations were  $6.67 \times 10^{-2}$  and  $5.94 \times 10^{-2}$  ppby, respectively, were the key factors promoting the formation of  $O_3$  at DSL. To control the increase of  $O_3$ , considering the policy feasibility, the abatement ratio of VOCs/NOx should be no less than 0.72. The findings advanced our knowledge of VOCs and their impact on O<sub>3</sub> formation and will be helpful in formulating emission control strategies for coping with O<sub>3</sub> pollution in YRD region.

## 1. Introduction

High levels of ozone  $(O_3)$  in urban and regional areas worldwide have long been a major air quality issue (Li et al., 2019; Paoletti et al., 2014; Wang et al., 2009a; Zhang et al., 2019a). In recently years, the O3 pollution has become more and more serious in China. For example, Li et al. (2019) reported severe summertime  $O_3$  pollution and regionally variable trends in about 1000 sites across China from 2013 to 2017. As the major  $O_3$  precursors, volatile organic compounds (VOCs) could contribute to the formation of  $O_3$  through a series of photochemical reactions, including the hydroxyl radical (OH) initiated oxidation of VOCs, nitrogen cycling driven by peroxyl (RO<sub>2</sub>) and hydroperoxyl (HO<sub>2</sub>) oxidation and photolysis, and the combination of oxygen atom (O) with molecular oxygen (O<sub>2</sub>) (Lyu et al., 2016). Therefore, understanding the

\*\* Corresponding author.

https://doi.org/10.1016/j.atmosenv.2020.117511

Received 3 January 2020; Received in revised form 8 April 2020; Accepted 13 April 2020 Available online 1 May 2020 1352-2310/© 2020 Elsevier Ltd. All rights reserved.

<sup>\*</sup> Corresponding author. School of Environmental and Chemical Engineering, Shanghai University, Shanghai, 200444, China.

E-mail addresses: Lily@shu.edu.cn (L. Li), qingyanf@sheemc.cn (Q. Fu).

characteristics of VOCs is a fundamental process to investigate the influences of VOCs on the formation pathway of O<sub>3</sub>. Previous studies suggested that the chemical species and sources of VOCs vary significantly with different areas (He et al., 2019; Lyu et al., 2016; Zheng et al., 2009). For instance, He et al. (2019) suggested that the mean mixing ratio of total VOCs (TVOC) was  $34 \pm 3$  ppbv with largest contribution from alkanes in the Pearl River Delta (PRD) region, while Lyu et al. (2016) found that the TVOC level in Wuhan was relatively low (24.3  $\pm$  0.5 ppbv).

Due to the complicated photochemical reactions in the atmosphere, the relationship between  $O_3$  and its precursors (VOCs and  $NO_x$ ) is highly nonlinear. A huge number of researches have been carried out to investigate the VOCs-NO<sub>x</sub>-O<sub>3</sub> relationship based on observations and/or simulations (He et al., 2019; Lyu et al., 2019; Zhang et al., 2018, 2019a). For a given region, the entire range of VOCs-NO<sub>x</sub>-O<sub>3</sub> formation sensitivity could be divided into VOC-limited, NOx-limited or transition (Wang et al., 2018). Recently, many studies had investigated the mechanism of O<sub>3</sub> formation using observed-based model (OBM) coupled with Master Chemical Mechanism (MCM) (Ling et al., 2017; Lyu et al., 2019; Xue et al., 2014). For instance, Lyu et al. (2019) found the dominant factors influencing O<sub>3</sub> formation could differ sharply at different periods. In addition, the propene-equivalized concentration, maximum incremental reactivity (MIR), O<sub>3</sub> formation potential (OFP) have also been widely used to describe the contribution of VOCs to O3 formation.

Yangtze River Delta (YRD) region, as a prosperous economic city cluster, has been suffering from severe O<sub>3</sub> pollution in the past few years, as a result of fast economic development and the accompanied intense emissions of O<sub>3</sub> precursors. Given this situation, many studies have been carried out to investigate the formation mechanism of high O3 levels in the urban areas of YRD region (Gu et al., 2020; Li et al., 2016; Xu et al., 2019). For instance, Li et al. (2016) found  $O_3$  formation at urban Shanghai was VOC-limited by applying ozone source apportionment technology (OSAT) within the Comprehensive Air Quality Model with Extensions (CAMx). In addition, severe O3 pollution was also observed at the rural areas. However, only limited studies had investigated the cause of high O<sub>3</sub> over rural areas of YRD region (Xing et al., 2017; Zhang et al., 2019a). In those studies, the pattern of  $O_3$  and  $O_3$  precursors were analyzed while relevant photochemical processes were not well studied. Hence, further studies regarding the characteristics of VOCs and the impact of VOCs on O<sub>3</sub> in rural YRD regions are needed.

In this study, the characteristics of ambient VOCs, and their influences on  $O_3$  formation were investigated, based on the data at a rural site in the YRD region from April to September 2018. Combining the concentration-weighted trajectories (CWT) and calculation of initial VOCs concentrations, the potential sources of VOCs emissions were identified. The dominant VOC species affecting photochemical

formation of  $O_3$  were quantified using an observation-based box model. The outcomes of this study will be helpful to set up more effective control strategies for dealing with  $O_3$  pollution in the YRD region.

## 2. Methodology

# 2.1. Sampling site

The sampling site, namely Dianshan Lake (DSL) air quality monitoring supersite (120.98°E, 31.09°N), is located at the rural area of Shanghai, several hundred meters from Dianshan Lake, with Jiangsu and Zhejiang province lying to the northwest and southwest of it. Fig. 1 shows the location of DSL site. Since the prevailing wind across the YRD region in summer is southeast, this site is usually regarded as the downwind site of Shanghai. Continuous measurements were performed from April 7 to September 25 2018, when the high O<sub>3</sub> episodes occur frequently.

#### 2.2. Measurement of meteorological parameters and criteria air pollutants

The meteorological parameters including temperature (T), relative humidity (RH), atmospheric pressure (P), wind direction (WD) and wind speed (WS) were collected at the DSL supersite (Table 1). All the instruments used for the measurement of gaseous species, i.e., ozone (O<sub>3</sub>), nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), sulfur dioxide (SO<sub>2</sub>), carbon monoxide (CO) were housed on top of a 5-floor-high building, about 15 m above ground level. An ultraviolet photometric ozone analyzer (Thermo Scientific, Model 49i), with a method detection limit of 1 ppb

#### Table 1

Summary of the instruments used in this study.

Parameters	Instrument	Method	Detection limit/ Range/Precision
WS, WD, T,	Visala	Meteorological Station	$\pm 0.3$ m/s, $\pm 3^{\circ}$ , $\pm 0.1$
0.	Thermo	Ultraviolet	1 nnh (10 s average)
03	Scientific, Model 49i	Photometric	
NO, NO2	Thermo	Chemiluminescence	0.40 ppb
	Scientific, Model 43i		(60 s average)
SO2	Thermo	Pulsed Fluorescence	0.50 ppb
	Scientific, Model 42i		(300 s average)
CO	Thermo	Gas Filter	0.04 ppm
	Scientific, Model 48i	Correlation	(10 s average)
VOCs	Agilent, GC•866	GC-FID	-



Fig. 1. Location of the Yangtze River Delta region and the DSL supersite (red star). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

(10 s average) was used to measure the concentration of O<sub>3</sub>. NO<sub>x</sub> (NO and NO<sub>2</sub>) was measured by a NO<sub>x</sub> analyzer (Thermo Scientific, Model 43i), with the detection limit of up to 0.40 ppb (60 s average). Concentration of SO<sub>2</sub> was measured by a pulsed fluorescence analyzer (Thermo Scientific, Model 42i), with a detection limit of 0.5 ppb (300 s average). A gas filter correlation analyzer (Thermo Scientific, Model 48i) was used for the measurement of CO. Hourly averaged data of meteorological factors and criteria air pollutants was used in this study.

# 2.3. Measurement of VOCs

In order to capture the hourly variation of individual VOCs and to obtain abundant data for the subsequent calculation in the observationbased model, a total of 55 VOCs species, including 27 species within  $C_2 \sim C_6$ , and 28 species within  $C_7 \sim C_{12}$ , were measured by two on-line gas chromatograph (GC) with flame ionization detector (FID) systems. The atmospheric samples were inhaled directly into the system and was preconcentrated by a low carbon ( $C_2 \sim C_6$ ) analyzer and high carbon ( $C_6 \sim C_{12}$ ) analyzer, respectively. A built-in auto-calibration system, consisted of three permeation tube (loaded with butane, hexane, and benzene, respectively), was used for daily calibration. The VOC standards gas for photochemical assessment monitoring stations (PAMS) was used to perform monthly calibration for this system. Hourly VOCs data were obtained from this system.

#### 2.4. Estimate of initial concentration of VOCs

VOCs are usually composed of species with high chemical reactivities, especially with OH radicals, and their lifetime range from several hours to several days, depending on their reactivities and the mixing ratio of OH radicals. Hence, the VOCs, which were emitted from various sources, were detected after chemical consumption in the atmosphere. To get a better sense of the original sources of VOCs, the initial mixing ratio of VOCs is required. Several approaches have been developed previously to calculate the initial mixing ratio of VOCs (McKeen et al., 1996; Wiedinmyer et al., 2001). In this study, the approach used in (Kramp and Volz-Thomas, 1997) was adopted, and the description of this approach is given bellow:

$$[AH_i]_t = [AH_i]_0 \times exp(-k_i[OH]\Delta t)$$
<sup>(1)</sup>

where  $[AH_i]_t$  and  $[AH_i]_0$  is the observed and initial mixing ratio of anthropogenic hydrocarbon i, respectively.  $k_i$  is the reaction rate constant of AH<sub>i</sub> with OH radicals. [OH] is the mixing ratio of OH radicals.  $\Delta t$ is the reaction time of AH<sub>i</sub>. Since the [OH] and  $\Delta t$  are difficult to measure, an estimate of [OH] $\Delta t$  was used in this study, and the approach is given below:

$$[OH]\Delta t = \frac{1}{k_A - k_B} \times \left( ln \left\{ \frac{[A]}{[B]} \Big|_{t=t_0} \right\} - ln \left\{ \frac{[A]}{[B]} \Big|_{t=t} \right\} \right)$$
(2)

where [A], [B] indicate the mixing ration of VOC<sub>A</sub> and VOC<sub>B</sub>, respectively.  $k_A$  and  $k_B$  are the reaction rate constants of VOC<sub>A</sub> and VOC<sub>B</sub> with OH radicals, respectively. ([A]/[B])<sub>t=t0</sub> is the ratio between initial concentration of VOC<sub>A</sub> and VOC<sub>B</sub>. Similarly, ([A]/[B])<sub>t=t</sub> is the ratio between observed concentration of VOC<sub>A</sub> and VOC<sub>B</sub>. To use this method, VOC<sub>A</sub> and VOC<sub>B</sub> should have similar sources and different reaction rate constant with OH radicals (Wiedinmyer et al., 2001). Since the major loss of VOCs is assumed due to their reaction with OH radicals during daytime (Wang et al., 2013), the average [A]/[B] during nighttime was used for the substitution of ([A]/[B])<sub>t=t0</sub>. During the observation, the sunset time was mainly between 17:00 and 19:00, and the photochemical processes after 18:00 could be negligible because of the low solar radical intensity (El-Said and Abdelaziz, 2020; Parra et al., 2019). Hence, we chose a median time, which was 18:00, to roughly represent the average sunset time.

#### 2.5. Concentration weighted trajectory (CWT) model

The concentration weighted trajectory (CWT) model was used in the present study to identify the potential sources of VOCs. This model, based on the pollutant concentration and backward trajectories, had been widely used to identify the potential sources of atmospheric pollutants at a receptor (Bari and Kindzierski, 2018a, b; Liu et al., 2019). The backward trajectories utilized in CWT model were calculated by the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2003). The CWT is determined with the following equation:

$$CWT_{ij} = \frac{\sum_{l=1}^{M} C_{l}\tau_{ijl}}{\sum_{l=1}^{M} \tau_{ijl}}$$
(3)

where CWT<sub>ij</sub> means the average weighted concentration of the trajectory l in the ijth cell, C<sub>l</sub> is the observed concentration of a given pollutant in the trajectory l,  $\tau_{ijl}$  is the resident time of the lth trajectory in the ijth cell (Wang et al., 2009b). To reduce the uncertainty caused by the small values of the number of trajectories loading in ijth cell (n<sub>ij</sub>), a W<sub>ij</sub> function was used in this study. The W<sub>ij</sub> function can be defined as below:

$$W_{ij} = \begin{cases} 1.00 & 80 < n_{ij} \\ 0.70 & 20 < n_{ij} \le 80 \\ 0.42 & 10 < n_{ij} \le 20 \\ 0.05 & n_{ij} \le 10 \end{cases}$$

$$(4)$$

We use the weighted-CWT<sub>ij</sub> (WCWT<sub>ij</sub> =  $W_{ij} \times CWT_{ij}$ ) to describe the potential sources of a given pollutant (Wang et al., 2009b). The global meteorological data used for the calculation of backward trajectories was obtained from NOAA website (http://ftp://arlftp.arlhq.noaa.gov /pub/archives/gdas1).

## 2.6. Box model

The Framework for zero-Dimensional Atmospheric Modeling (F0AM) coupled with master chemical mechanism (MCM) (Wolfe et al., 2016) was applied to quantify the contribution of individual VOC to local  $O_3$  formation. This model was localized to be applicable in Shanghai, with the setting of latitude, longitude, altitude. The solar zenith angle (SZA) was calculated by this model. This model used the mixing ratio of VOCs, gaseous pollutants and meteorological parameters (such as T, RH, P) as the input for the calculation of photochemical  $O_3$  formation at a given site, based on the master chemical mechanism (version 3.2), which consists of more than 5900 chemical species and 16, 500 reactions. The dilution caused by wind or PBL was parameterized following the function form:

$$\frac{d[x]}{dt} = k_{dil}([x]_b - [x]) \tag{5}$$

where  $k_{dil}$  is a first order dilution ration constant and  $[x]_b$  is a fixed background concentration. More information about the  $k_{dil}$  can be found in the study of Wolfe et al. (2016). The photolysis frequencies (J value) were calculated based on the trigonometric parameterization provided by MCM (Wolfe et al., 2016):

$$J = Icos(SZA)^{m} \exp(-nsec(SZA))$$
(6)

where I, m, n are constants unique to each photolysis reaction, derived from least-square fits to J values computed with fixed solar spectra and literature cross-section and quantum yields. The selection of cross sections and quantum yields generally follow IUPAC recommendations (Wolfe et al., 2016). As a typical box model, horizonal and vertical transport were not considered.

In this study, the FOAM model was used to assess the sensitivity (S) of

the photochemical production of  $O_3$  to the change of its precursors. The S of a specific precursor X is given by the following equation:

$$S(X) = \frac{[MaxO_3(X) - MaxO_3(X - \Delta X)]/MaxO_3(X)}{\Delta X/X}$$
(7)

where X is the concentration of precursor X in the base scenario;  $\Delta X$  is the hypothetical change of the concentration of X (10% X in this study). MaxO<sub>3</sub>(X) and MaxO<sub>3</sub> (X- $\Delta X$ ) is maximum value of O<sub>3</sub> in base scenario and the hypothetical scenario. A positive S value of an individual precursor means the O<sub>3</sub> production could be increased if the emission of this precursor increased.

#### 3. Results and discussions

#### 3.1. General statistics

Fig. 2 (A) shows the wind rose during the observation period, suggesting that the wind speed concentrated within 4 m/s and the prevailing wind was southeast. The rainfall flux data during April  $\sim$ September was obtained from National Aeronautics and Space Administration (https://www.nasa.gov/) and was exhibited in Fig. 2 (B). Influenced by the summer monsoon, the spatial distribution of rainfall showed an obvious decreasing pattern from south to north (Fig. 2 (B)). During the observation, the rainfall at this site was on average level when compared to other areas in China. Without too much rainfall or drought, this period was suitable for analyzing O<sub>3</sub> formation. Fig. 3 shows the time series of maximum daily 8-h average (MDA8) O<sub>3</sub> concentration, daily average mixing ratio of total VOCs, temperature and relative humidity observed at DSL site from 7 April to 25 September 2018. As is shown in Fig. 3, high O<sub>3</sub> levels (grey shaded period) were always observed when the site was influenced by air masses from southeast. However, strong south wind (yellow shaded period) could also dilute the concentration of air pollutants, leading to relatively lower level of O<sub>3</sub> and other pollutants. During the observation period, the air mass near DSL site was warm and moist (Fig. 3), with the average T and RH of 25.44  $\pm$  5.33 °C and 77.86  $\pm$  17.41%, respectively. High O<sub>3</sub> level (MAD8 > 160  $\mu$ g/m<sup>3</sup> (or 74.67 ppb, China II standard for O<sub>3</sub>) were frequently observed during this period, especially during April 25  $\sim$ April 30, June 11 ~ June 13, July 26 ~ July 30, August 23 ~ August 24, and September 4 ~ September 6. The average MDA8 during this period was  $63.67 \pm 26.53$  ppb, with the maximum value of 131.13 ppb (occurred on 28 April). The average mixing ratio of TVOC was 15.41  $\pm$ 11.39 ppbv, with the maximum and minimum value of 112.36 and 2.35 ppbv, respectively. The TVOC level was relatively lower than that observed in the PRD region (He et al., 2019) and Wuhan (Lyu et al., 2016). Consistent with higher  $O_3$  levels, the mixing ratio of TVOCs during O<sub>3</sub> episode days were relatively higher. According to the previous study, if the average measured ratio of VOC (in ppbC) to NO<sub>x</sub> (in ppb) during 6:00 am and 9:00 am is more than 8, the local O<sub>3</sub> formation should be in VOC-control regime, otherwise the O<sub>3</sub> formation is in NO<sub>x</sub>-control regime (National Research Council, 1991). In this study, the average ratio of VOC/NO<sub>x</sub> was  $3.96 \pm 2.00$  (ppbC/ppb). Hence, the local O<sub>3</sub> formation should be in VOC-control regime.

The measured 55 VOCs species included 28 alkanes, 16 aromatics, 10 alkenes and acetylene. During the observation period, the mean mixing ratios of alkanes, alkenes, and aromatics were 9.16  $\pm$  7.39, 2.76  $\pm$  2.98,  $3.51 \pm 3.46$  ppbv, respectively. Table 2 summarizes the top 10 VOC species. Among those VOCs, propane was the most abundant specie (6.67  $\pm$  4.37 ppbv), followed by toluene (1.87  $\pm$  1.26 ppbv), ethylene (1.56  $\pm$  1.03 ppbv), n-butane (1.45  $\pm$  1.06 ppbv), and ethane (1.26  $\pm$ 1.14 ppbv). Abundant C3~C5 alkanes, such as propane, n-butane, ibutane and i-pentane, were observed in this site. Propane and n-butane are typical tracers of emissions from liquefied petroleum gas (LPG) or natural gas (NG) combustion, while acetylene and ethylene are key tracers for combustion (Song et al., 2019; Zhu et al., 2018). Therefore, the emission from combustion could be an important source at this site. For the last few years, increasing use of NG was pronounced in YRD, but few control strategies have been applied, which could lead to the emissions from LPG/NG. In addition, toluene and m, p-xylene were listed as the second and eighth abundant VOC species during the observation. The high loading in these aromatics suggested this site could also be influenced by emissions from solvent use or printing processes (Song et al., 2019; Zhang et al., 2019b).

#### 3.2. Photochemical loss of VOCs

As mentioned above, photochemical loss of VOCs can directly affect the observed mixing ratio of individual VOCs. To further evaluate the influence of photochemical processes on VOCs, the photochemical-agebased approach mentioned in section 2.4 was used to estimate the initial concentration of individual VOCs. Different  $VOC_A$  and  $VOC_B$  were chosen in previous studies. For instance, Parrish et al. (2007) chose n-butane and ethane for the calculation of photochemical age. Wang et al. (2013) and He et al. (2019) used the ratio of ethylbenzene and m. p-xylene ([E]/[X]) to calculate the initial mixing ration of VOCs. In this study, we chose [E]/[X] to calculate the initial concentration of VOCs. The scatter plot of ethylbenzene and m, p-xylene and the result of linear regression in Fig. 4 reveals that there is a strong relationship between ethylbenzene and m, p-xylene, with R value of 0.93 (p < 0.01), suggesting the sources of ethylbenzene and m, p-xylene were quite similar. Therefore, [E]/[X] is suitable for the calculation of OH exposure ( $[OH]\Delta$ t). The reaction rate constants of ethylbenzene and m, p-xylene with OH radicals were obtained from the study of (Atkinson and Arey, 2003). Previous studies suggested the value of  $([E]/[X])_{t=t0}$  for vehicle



Fig. 2. (A) Wind rose during the observation at DSL site; (B) rainfall flux, in kg m<sup>-2</sup> s<sup>-1</sup>, averaged over April ~ September 2018.



Fig. 3. Time series of VOCs, MDA8, T, and RH observed at DSL site.

 Table 2

 Summary of top 10 VOCs species during the observation at DSL site.

VOCs	Mean (ppbv)	Median (ppbv)	SD (ppbv)	Max (ppbv)	Min (ppbv)
Propane	2.93	2.33	2.83	38.87	0.25
Toluene	1.87	1.26	1.88	15.64	0.02
Ethylene	1.56	1.03	1.42	10.16	0.00
N-butane	1.45	1.06	1.58	23.40	0.11
Ethane	1.26	1.14	0.86	7.40	0.00
I-butane	0.95	0.72	0.81	7.57	0.09
Acetylene	0.73	0.62	0.50	4.46	0.11
M, p- xylene	0.71	0.54	0.59	3.76	0.04
I-pentane	0.69	0.50	0.61	6.35	0.07
Propene	0.62	0.26	0.99	11.21	0.04

emission and coal combustion to be 0.3-0.4, and about 0.65 for biomass burning (Wang et al., 2013). In the present study, the initial ([E]/[X]) was 0.47, suggesting that the air masses at DSL site were less influenced by biomass burning in the summer season.

The photochemical loss of VOCs was defined as the difference between initial mixing ratio and observed mixing ratio for a given VOCs. Fig. 5 (A) shows the diurnal mean mixing ratio of observed and photochemical loss of alkanes, alkenes, and aromatics from 7 April to 25 September, respectively. During daytime, the highest contribution of



Fig. 4. Scatter plot of ethylbenzene and m, p-xylene at DSL site.

TVOC was from alkanes (8.34  $\pm$  5.36 ppbv, 57.35%), followed by



Fig. 5. Daytime variation of observed and consumed VOCs concentrations at DSL site.

aromatics (3.41  $\pm$  2.79 ppbv, 23.53%), and alkenes (2.78  $\pm$  1.77 ppbv, 19.12%). Although the observed mixing ratio of alkenes was the lowest among the three VOC groups, the chemical loss of alkenes was highest (5.44  $\pm$  12.18 ppbv), followed by alkanes (3.86  $\pm$  2.37 ppbv), and aromatic (2.44  $\pm$  2.63 ppbv). The relatively higher consumed values of alkenes were attributed to fast reactions between OH radical and active alkenes.

To obtain the detailed variation of VOCs, we summarized the daytime observed value and photochemical loss value of each VOCs group with a resolution of 1 h (Fig. 5 (B)). Since the atmospheric oxidants (Ox  $= O_3 + NO_2$ ) also exhibit distinct diurnal variations (He et al., 2019), caused by the complicated production and sink process of O3 and NO2 in the atmosphere, the diurnal variation of  $O_x$  was also given in Fig. 5 to provide insights into the effect of atmospheric oxidizing capacity on the consumption of VOCs. The lowest  $O_r$  mixing ratio (37.92  $\pm$  15.20 ppb) occurred at 07:00 a.m., which implied weak atmospheric oxidizing capability, followed by an increasing pattern. Thereafter, O<sub>x</sub> reached the maximum value during 14:00 to 15:00, suggesting fast consumption of VOCs. Similar pattern of O<sub>r</sub> was also found in the study of (Ismail et al., 2016; Wang et al., 2013; Xu et al., 2011). The maximum observed mixing ratio of VOCs occurred at 07:00 a.m., which could be the joint effects of intensive emissions of VOCs, relatively shallow atmospheric boundary layer (ABL), and the relatively low atmospheric oxidizing ability during morning. Thereafter, a decreasing pattern of observed mixing ratio of VOCs appeared and reached the lowest value at around 14:00, which was usually caused by the development of ABL and the active oxidation processes of VOCs. After 14:00, the observed mixing ratio of VOCs increased gradually as a result of shrink of ABL, decreasing of O<sub>x</sub>, and the emission from evening peak. As for the consumption of VOCs, the minimum value (8.02  $\pm$  7.87 ppbv) occurred at 18:00. However relatively higher value of consumed VOCs was found during 12:00 to 15:00, when the O<sub>x</sub> was abundant. Among the three VOCs groups, alkenes exhibited the most obvious variation of chemical consumption during daytime, with the maximum and the minimum value of 12.81  $\pm$  23.66 ppbv and 2.05  $\pm$  3.11 ppbv, respectively. As for the consumption of alkenes, trans-2-butene is the highest contributor (3.36  $\pm$  15.41 ppbv, 48.14%), followed by trans-2-pentene, and ethylene.

#### 3.3. Potential sources of ambient VOCs

To identify the sources of air masses influencing DSL during the observation period, the 48-h backward trajectories during daytime were plotted (Fig. 6). The backward trajectories were classified into 3 clusters. Cluster-1 (in red), originating from coastal areas of Zhejiang province and transported slowly to DSL, was the dominant one (62.72%), in which the initial mixing ratios of alkanes, alkenes, and aromatics were  $13.65\pm8.17,\,9.93\pm12.84$  and 7.14  $\pm\,5.16$  ppbv, respectively. The high loading of VOCs in this cluster suggests the VOCs observed at DSL might mainly originate from Zhejiang province. In addition, the proportion of alkenes in Cluster-1 was the highest (32.32%), indicating the Cluster-1 could be more active than other clusters. More detailed information about the top 10 VOCs species in each cluster is given in Table S2. High levels of reactive alkenes such as trans-2-butene, trans-2-pentene, ethylene, and cis-2-butene were found in Cluster-1. As suggested by Liu et al. (2008), these VOCs were typical tracers of gasoline usage. This is consistent with the huge car ownership in Zhejiang province. The O<sub>3</sub> concentrations in Cluster-1 was the highest, with an average level of  $63.07 \pm 36.79$  ppbv. The abundant reactive O<sub>3</sub> precursors in Cluster-1



Fig. 6. The 48-h backward trajectories from DSL site and component of initial TVOC in three clusters.

could cause the high O<sub>3</sub> concentration. Custer-2 (in black), accounting for 20.78% of total trajectories, was the cleanest cluster, in which the initial mixing ratios of alkanes, alkenes, and aromatics were only 7.15  $\pm$ 2.76, 3.98  $\pm$  7.39, and 2.90  $\pm$  1.19 ppbv, respectively. This suggested that the air mass from East China Sea only contributes a small proportion of TVOC. The mean  $O_3$  concentration in Cluster-2 was only 44.50  $\pm$ 19.85 ppbv. Cluster-3 (in Blue), travelling through the Yellow Sea and Jiangsu province, only accounted for 16.50% of the total trajectories. The initial mixing ratios of the three VOC groups were 44.50  $\pm$  19.85 and 56.56  $\pm$  30.09 ppbv, respectively. Relatively high level of i-butane, cis-2-butene, and ethane were found in this cluster. As reported by Liu et al. (2008) and Zhang et al. (2015), use of LPG and vehicle exhaust could be the major sources of these VOCs. The average O<sub>3</sub> concentration in Cluster-3 was 56.26  $\pm$  30.09 ppbv, which was between that in Cluster-1 and Cluster-2. This result suggested that the more the trajectories passing through land, the more active VOCs they may contain, which could further cause higher O<sub>3</sub> concentration in these trajectories.

The potential sources of initial VOCs were identified by the CWT models in this part. A higher WCWT value suggests a region with a higher contribution to the target VOCs group. The WCWT map of initial alkane is shown in Fig. 7. Hot spots of WCWT (>14) were frequently found in Zhejiang, and Jiangsu province, especially near the junction of Zhejiang, Jiangsu, and Anhui province. That could be attributed to summer monsoon, which could transport the alkanes emitted in south China to the monitoring site. In addition, under certain conditions, the alkanes emitted from Jiangsu province could be transported to DSL site by Boreas. As for alkenes, high WCWT value appear along the coastal areas near Zhejiang and Fujian province (Fig. 8). That might be due to the emissions from petrochemical industrial parks located along the coastal areas of Zhejiang province and the Hangzhou bay area. With respect to aromatics, the distribution of WCWT value is similar to that of alkanes. The dominant contribution of initial aromatics is located in Zhejiang province (Fig. 9). Overall, Zhejiang province was the major contributor regarding the sources of initial VOCs at DSL site during the observation period. Hence, to reduce the VOCs concentrations in O3 episode days at DSL site, regional (especially in Zhejiang province) reduction of VOCs are necessary.

# 3.4. The impact of VOCs on ozone formation

To assess the roles of different  $O_3$  precursors (VOCs and  $NO_x$ ) for  $O_3$  formation, we applied FOAM model to the observed VOC concentrations. The observed and simulated  $O_3$  concentrations are shown in Fig. 10, in which the days with insufficient FOAM input data were not shown. Despite the discrepancies, the simulation well caught the pattern of  $O_3$ . In this study, we used the index of agreement (IOA) to quantitively evaluate the performance of this model. IOA had been widely used for



Fig. 7. The WCWT map of initial alkanes.



Fig. 8. The WCWT map of initial alkenes.



Fig. 9. The WCWT map of initial aromatics.

the evaluation of OBM models and can be calculated by equation (6). Detailed description of IOA can be found in previous studies (He et al., 2019; Lyu et al., 2016, 2019). In the present study, the IOA of  $O_3$  was 0.786, suggesting the model could reasonably reproduce the variation in  $O_3$  and could be used for further analysis. In this model, the dilution of air pollutants was mainly controlled by the  $k_{dil}$ , which might be underestimated in certain situations. Therefore, the simulated  $O_3$  concentration would be higher than the observed value.

$$IOA = 1 - \frac{\sum_{n=1}^{n} (O_i - S_i)^2}{\sum_{i=1}^{n} (|O_i - \overline{O}| + |S_i - \overline{O}|)^2}$$
(8)

Due to the complexity in atmosphere, O<sub>3</sub> formation could be VOClimited, NO<sub>x</sub>-limited or both-limited in different regions. Therefore, quite different control strategies could be applied in individual area. To preliminarily investigate the potential influence of VOCs and NO<sub>x</sub> on O<sub>3</sub> formation, we adopted ozone formation sensitivity (S value). Fig. 11 exhibits the S values of different VOC groups, NO, NO2 and CO. Clearly the S values of different VOC groups were positive, while that of NO and NO<sub>2</sub> were negative, suggesting that O<sub>3</sub> formation at DSL site was mainly VOC-limited. The implication is that reducing VOCs could lead to O<sub>3</sub> reduction, while cutting  $NO_x$  might result in the increase of  $O_3$  at DSL site. Similar VOCs-limited regime was also identified in previous studies (He et al., 2019; Xue et al., 2014; Zeng et al., 2018). Among the three VOC groups, relatively higher S value were found for alkenes, accounting for  $\sim$ 60% of the total S from all VOCs, followed by aromatics  $(\sim 33\%)$  and alkanes  $(\sim 7\%)$ . The high S value of alkenes indicates that local O3 formation was more sensitive to changes of alkenes, although



Fig. 11. The S value for different kinds of O<sub>3</sub> precursors.

alkenes only contributed ~19% of observed TVOC. As for NO<sub>2</sub>, the large negative S value (-0.26) could be attributed to the reaction between NO<sub>2</sub> and OH radicals (equation (7)), which was considered as an important pathway for O<sub>3</sub> destruction, by which the OH<sub>x</sub> radicals and NO<sub>x</sub> were effectively consumed, leading indirectly to the reduction of the initial processes of O<sub>3</sub> production (Monks, 2005; Thornton et al., 2002).

$$OH + NO_2 \rightarrow HNO_3$$
 (9)

To get an insight into the different influence of detailed VOCs groups on  $O_3$  formation, we calculated the total S values for different VOCs groups according to their carbon number, shown in Fig. 12. As for  $C_2 \sim C_5$ VOCs, the dominant contributor to S value was alkene, suggesting the increase in low carbon olefins could increase the chemical formation of  $O_3$ . As indicated by the study of Zhang et al. (2015) and Simayi et al. (2020), low carbon alkenes were tracers of gasoline vehicles. Among  $C_5$ VOCs, isoprene contributed more than 95% of the total S. Since isoprene were mainly from biogenic emission, emission from local vegetation could strongly affect the local  $O_3$  formation. Aromatics contributed the most to the total S value for  $C_6 \sim C_9$  VOCs, since most of the  $C_6 \sim C_9$  species detected in this study were aromatics. Among  $C_6 \sim C_9$  VOCs, toluene, m, p-xylene and 1,3,5-trimethylbenzene were three key species. As suggested by previous studies, these VOCs were usually related to solvent use (Simayi et al., 2020; Yenisoy-Karakaş et al., 2020). High carbon VOCs (such as n-decane, n-undecane, and n-dodecane) were tracers of asphalt application (Liu et al., 2008). Total S values of high carbon VOCs were around 0 since those VOC species were relatively inert. Among all VOCs, the maximum S value (0.19%/%) was observed when carbon number was 5, while the minimum S value occurred when carbon number was 11. This indicated that the O<sub>3</sub> formation from the oxidization process of isoprene was remarkable at this site.

Fig. 13 exhibited the S values for the top 10 abundant VOC species at DSL. Isoprene was found to have the largest S value (0.18%/%) among all VOC species. That was quite different with the results in PRD (He et al., 2019) and Wuhan (Lyu et al., 2016). Isoprene is often used as a tracer of biogenic emissions and given that the vegetation coverage was relatively high around DSL site, O<sub>3</sub> formation is supposed to be sensitive to biogenic emissions. In addition, aromatics, especially m, p-xylene, toluene, ethylbenzene and o-xylene, exhibited relatively higher S value. In order to better quantify the influence of each VOC species on O<sub>3</sub>



Fig. 12. The S value for different kinds of VOCs (by carbon number).



Fig. 13. (A) The S value for individual VOC species, and (B) the S-weighted concentration for individual VOC species.

production, we adopted the S-weighted concentration, which considers both S value and mixing ratio of VOCs (Lyu et al., 2016). The S-weighted concentration of each VOC can be calculated by multiplying its S value with its mixing ratio. The top 10 VOC species in S-weighted concentration is exhibited in Fig. 13 (B). Although toluene only ranked third in terms of S value, it had the most significant influence on the formation of  $O_3$ , with a S-weighted concentration of 6.67  $\times$  10<sup>-2</sup> ppbv. As for isoprene, even it had the biggest S value, it ranked only second in terms of S-weighted concentration, resulting from the low concentrations in DSL. The S-weighted concentration further revealed that the effect of m, p-xylene and ethylene on ozone formation cannot be neglected, with S-weighted concentration of  $3.58 \times 10^{-2}$  ppbv and  $3.55 \times 10^{-2}$  ppbv, respectively. Since toluene, isoprene, and ethylene were often used as the tracer for solvent-using sources, biogenic sources, and gasoline vehicles sources (Zheng et al., 2009), VOCs-control strategies at DSL site should be targeted for aforementioned sources (excluding biogenic sources).

#### 3.5. Control strategies for ozone episodes

The above analysis demonstrated that O<sub>3</sub> formation was quite sensitive to NO<sub>x</sub> and VOCs. However, it was unclear how much VOCs or NO<sub>x</sub> should be reduced to achieve effective O3 improvement, considering the non-linear response of O<sub>3</sub> to changes in VOCs and NO<sub>x</sub> emissions. To answer this question, we further conducted series of simulations to calculate the increment of maximum O3 concentration (Max-O3) by adjusting input  $NO_x$  and VOC ratios. In Fig. 14, the horizontal and vertical axis corresponded to the reduction percentages of NO<sub>x</sub> and the increment in Max-O<sub>3</sub> (positive and negative values means the increase and decrease in Max-O<sub>3</sub> compared to the base case), respectively. Each curve in Fig. 14 represents the reduction percentage of VOCs. Results show that the increment of Max-O3 increased as NOx reduction increased from 0 to 40%, regardless of the reduction of VOCs. The Max- $O_3$  decreased gradually when NO<sub>r</sub> was cut by >40% in most scenarios, suggesting a transition from VOC-control regime to NO<sub>x</sub>-control regime. As for VOCs, a higher cutdown of VOCs always results in more decrease



Fig. 14. Reduction of maximum as a function of reduction percentages of  $NO_x$  and VOCs.

of Max-O<sub>3</sub> regardless of NO<sub>x</sub>. Therefore, when an improper abatement ratio of VOC/NO<sub>x</sub> was applied (i.e., when the cut of VOCs is 20%, the increment of Max-O3 could be negative, positive and again negative when NO<sub>x</sub> reduction increased), ozone concentrations could actually go up. Similar pattern was also found in the study of (He et al., 2019). Although great reduction of Max-O3 could be achieved when VOCs cut was over 60% or  $NO_x$  cut was over 70%, it may not be practical in the current stage. Therefore, we focused on the reduction range of 0%-40% for VOCs and 0-70% for NO<sub>x</sub> in order to choose optimum control strategies. It was determined that when  $NO_x$  reduction was 0–70%, the minimum abatement ratio of VOCs/NOx for zero Max-O3 increment (the ratios of VOCs/NOx at the intersections of the curves and horizontal axis) changed from  $\sim 0.38$  to  $\sim 0.72$ , suggesting that the minimum abatement ratio of VOCs/NO<sub>x</sub> should be higher than 0.72 to prevent the increase in Max-O<sub>3</sub> at the DSL site. That result was relatively lower than that for Wuhan, which was 1.1 (Lyu et al., 2019), suggesting the O<sub>3</sub> formation was less sensitive to the change in  $NO_x$  at DSL. In addition, maximum reduction of Max-O<sub>3</sub> (18.94 ppb) could be achieved when the reduction percentages of NO<sub>x</sub> and VOCs were 0 and 40%, respectively.

## 4. Conclusions and policy implications

Based on ground-level observations from April to September 2018 at DSL in YRD, the potential sources of VOCs, ozone formation sensitivities, and the control strategies during  $O_3$  episodes were investigated. The main conclusions are as follows. Strong photochemical losses of VOCs, especially alkenes, were found when  $O_x$  concentrations were high. Zhejiang province was found to be the most important potential source region of VOCs at DSL site. Based on the results of scenario analysis, alkenes and  $NO_2$  exhibited the most significant positive and negative influences on  $O_3$  production, respectively. As for individual VOCs, toluene and isoprene were the top two factors promoting  $O_3$  formation.

According to the scenario analysis, reduction of VOCs could lead to a monotonous decrease of Max-O<sub>3</sub>. However, improper abatement ratio of NOx and VOCs could lead to the increase of Max-O<sub>3</sub>. Therefore, unsuitable control strategies could run counter to what the policymakers want to achieve. Although the results suggest that separate controls on VOCs could bring obvious reductions of Max-O<sub>3</sub>, VOCs and NO<sub>x</sub> are frequently controlled simultaneously at present. Therefore, the abatement ratio of VOCs/NO<sub>x</sub> should be no less than 0.72, considering the policy feasibility, to prevent the increase of O<sub>3</sub> at the DSL site. In addition, the S-weighted concentrations of individual VOCs indicate that the control of solvent-use sources and gasoline vehicles sources could be the most efficient method to reduce O<sub>3</sub> at the DSL site. Overall, this study will be helpful for local and regional policymakers to design appropriate control strategies for O<sub>3</sub> pollution in YRD or other regions of China.

# 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.

#### CRediT authorship contribution statement

Kun Zhang: Formal analysis, Writing - original draft. Li Li: Writing review & editing. Ling Huang: Formal analysis. Yangjun Wang: Formal analysis. Juntao Huo: Formal analysis. Yusen Duan: Formal analysis. Yuhang Wang: Formal analysis. Qingyan Fu: Formal analysis.

## Acknowledgements

This study was financially supported by the National Natural Science Foundation of China (NO. 41875161), Shanghai International Science and Technology Cooperation Fund (NO.19230742500) and Shanghai Science and Technology Fund (NO.19DZ1205007). We thank Shanghai Environmental Monitoring Center (SEMC) for conducting the measurement and sharing the data.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2020.117511.

#### References

- Atkinson, R., Arey, J., 2003. Atmospheric degradation of volatile organic compounds. Chem. Rev. 103, 4605–4638.
- Bari, M.A., Kindzierski, W.B., 2018a. Ambient volatile organic compounds (VOCs) in Calgary, Alberta: sources and screening health risk assessment. Sci. Total Environ. 631–632, 627–640.
- Bari, M.A., Kindzierski, W.B., 2018b. Ambient volatile organic compounds (VOCs) in communities of the Athabasca oil sands region: sources and screening health risk assessment. Environ. Pollut. 235, 602–614.
- Draxler, R.R., Rolph, G.D., 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model Access via NOAA ARL READY. NOAA Air Resources Laboratory, Silver Spring. Md website. http://www.arl.noaa.gov/ready/hysplit4.html.
- El-Said, E.M.S., Abdelaziz, G.B., 2020. Experimental investigation and economic assessment of a solar still performance using high-frequency ultrasound waves atomizer. J. Clean. Prod. 256.
- Gu, Y., Li, K., Xu, J., Liao, H., Zhou, G., 2020. Observed dependence of surface ozone on increasing temperature in Shanghai, China. Atmos. Environ. 221, 117108.
- He, Z., Wang, X., Ling, Z., Zhao, J., Guo, H., Shao, M., Wang, Z., 2019. Contributions of different anthropogenic volatile organic compound sources to ozone formation at a receptor site in the Pearl River Delta region and its policy implications. Atmos. Chem. Phys. 19, 8801–8816.
- Ismail, M., Abdullah, S., Yuen, F.S., Ghazali, N.A., 2016. A ten-year investigation on ozone and it precursors at Kemaman, terengganu, Malaysia. Environment 9 (1), 1–8.
- Kramp, F., Volz-Thomas, A., 1997. On the budget of OH radicals and ozone in an urban plume from the decay of C5-C8 hydrocarbons and NO(x). J. Atmos. Chem. 28, 263–282.
- Li, L., An, J., Shi, Y., Zhou, M., Yan, R., Huang, C., Wang, H., Lou, S., Wang, Q., Lu, Q., 2016. Source apportionment of surface ozone in the Yangtze River Delta, China in the summer of 2013. Atmos. Environ. 144, 194–207.
- Li, K., Jacob, D.J., Liao, H., Shen, L., Zhang, Q., Bates, K.H., 2019. Anthropogenic drivers of 2013–2017 trends in summer surface ozone in China. Proc. Natl. Acad. Sci. Unit. States Am. 116, 422–427.
- Ling, Z., Zhao, J., Fan, S., Wang, X., 2017. Sources of formaldehyde and their contributions to photochemical O<sub>3</sub> formation at an urban site in the Pearl River Delta, southern China. Chemosphere 168, 1293–1301.
- Liu, Y., Shao, M., Fu, L., Lu, S., Zeng, L., Tang, D., 2008. Source profiles of volatile organic compounds (VOCs) measured in China: Part I. Atmos. Environ. 42, 6247–6260.
- Liu, Y., Song, M., Liu, X., Zhang, Y., Hui, L., Kong, L., Zhang, Y., Zhang, C., Qu, Y., An, J., 2019. Characterization and sources of volatile organic compounds (VOCs) and their related changes during ozone pollution days in 2016 in Beijing, China. Environ. Pollut. 257, 113599.
- Lyu, X.P., Chen, N., Guo, H., Zhang, W.H., Wang, N., Wang, Y., Liu, M., 2016. Ambient volatile organic compounds and their effect on ozone production in Wuhan, central China. Sci. Total Environ. 541, 200–209.
- Lyu, X., Wang, N., Guo, H., Xue, L., Jiang, F., Zeren, Y., Cheng, H., Cai, Z., Han, L., Zhou, Y., 2019. Causes of a continuous summertime O<sub>3</sub> pollution event in Jinan, a central city in the North China Plain. Atmos. Chem. Phys. 19, 3025–3042.
- McKeen, S.A., Liu, S.C., Hsie, E.Y., Lin, X., Bradshaw, J.D., Smyth, S., Gregory, G.L., Blake, D.R., 1996. Hydrocarbon ratios during PEM-WEST A: a model perspective. J. Geophys. Res. Atmos. 101, 2087–2109.
- Monks, P.S., 2005. Gas-phase radical chemistry in the troposphere. Chem. Soc. Rev. 34, 376–395.
- National Research Council, 1991. Rethinking the Ozone Problem in Urban and Regional Air Pollution. National Academy Press, Washington, D.C, pp. 186–221.
- Paoletti, E., De Marco, A., Beddows, D.C., Harrison, R.M., Manning, W.J., 2014. Ozone levels in European and USA cities are increasing more than at rural sites, while peak values are decreasing. Environ. Pollut. 192, 295–299.
- Parra, R., Cadena, E., Flores, C., 2019. Maximum UV index records (2010-2014) in Quito (Ecuador) and its trend inferred from remote sensing data (1979-2018). Atmosphere 10 (12), 787.
- Parrish, D.D., Stohl, A., Forster, C., Atlas, E.L., Blake, D.R., Goldan, P.D., Kuster, W.C., de Gouw, J.A., 2007. Effects of mixing on evolution of hydrocarbon ratios in the troposphere. J. Geophys. Res. Atmos. 112 (10).
- Simayi, M., Shi, Y., Xi, Z., Li, J., Yu, X., Liu, H., Tan, Q., Song, D., Zeng, L., Lu, S., Xie, S., 2020. Understanding the sources and spatiotemporal characteristics of VOCs in the Chengdu Plain, China, through measurement and emission inventory. Sci. Total Environ. 714.
- Song, C., Liu, B., Dai, Q., Li, H., Mao, H., 2019. Temperature dependence and source apportionment of volatile organic compounds (VOCs) at an urban site on the north China plain. Atmos. Environ. 207, 167–181.
- Thornton, J.A., Wooldridge, P.J., Cohen, R.C., Martinez, M., Harder, H., Brune, W.H., Williams, E.J., Roberts, J.M., Fehsenfeld, F.C., Hall, S.R., Shetter, R.E., Wert, B.P.,

#### K. Zhang et al.

Fried, A., 2002. Ozone production rates as a function of  $NO_x$  abundances and  $HO_x$  production rates in the Nashville urban plume. J. Geophys. Res. Atmos. 107 (12).

Wang, T., Wei, X., Ding, A., Poon, S.C., Lam, K., Li, Y., Chan, L., Anson, M., 2009a. Increasing surface ozone concentrations in the background atmosphere of Southern China, 1994-2007. Atmos. Chem. Phys. 9 (16), 6217–6227.

- Wang, Y., Zhang, X., Draxler, R.R., 2009b. TrajStat: GIS-based software that uses various trajectory statistical analysis methods to identify potential sources from long-term air pollution measurement data. Environ. Model. Software 24, 938–939.
- Wang, H., Chen, C., Wang, Q., Huang, C., Su, L., Huang, H., Lou, S., Zhou, M., Li, L., Qiao, L., 2013. Chemical loss of volatile organic compounds and its impact on the source analysis through a two-year continuous measurement. Atmos. Environ. 80, 488–498.
- Wang, P., Chen, Y., Hu, J., Zhang, H., Ying, Q., 2018. Attribution of tropospheric ozone to NO x and VOC emissions: considering ozone formation in the transition regime. Environ. Sci. Technol. 53, 1404–1412.
- Wiedinmyer, C., Friedfeld, S., Baugh, W., Greenberg, J., Guenther, A., Fraser, M., Allen, D., 2001. Measurement and analysis of atmospheric concentrations of isoprene and its reaction products in central Texas. Atmos. Environ. 35, 1001–1013.
- Wolfe, G.M., Marvin, M.R., Roberts, S.J., Travis, K.R., Liao, J., 2016. The Framework for 0-D atmospheric modeling (F0AM) v3.1. Geosci. Model Dev. (GMD) 9, 3309–3319.
- Xing, C., Liu, C., Wang, S., Chan, K., Gao, Y., Huang, X., Su, W., Zhang, C., Dong, Y., Fan, G., 2017. Observations of the summertime atmospheric pollutants vertical distributions and the corresponding ozone production in Shanghai, China. Atmos. Chem. Phys. Discuss. 1–31, 2017.
- Xu, J., Ma, J.Z., Zhang, X.L., Xu, X.B., Xu, X.F., Lin, W.L., Wang, Y., Meng, W., Ma, Z.Q., 2011. Measurements of ozone and its precursors in Beijing during summertime: impact of urban plumes on ozone pollution in downwind rural areas. Atmos. Chem. Phys. 11, 12241–12252.

- Xu, J., Tie, X., Gao, W., Lin, Y., Fu, Q., 2019. Measurement and model analyses of the ozone variation during 2006 to 2015 and its response to emission change in megacity Shanghai, China. Atmos. Chem. Phys. 19, 9017–9035.
- Xue, L., Wang, T., Gao, J., Ding, A., Zhou, X., Blake, D., Wang, X., Saunders, S., Fan, S., Zuo, H., 2014. Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes. Atmos. Chem. Phys. 14, 13175–13188.
- Yenisoy-Karakaş, S., Dörter, M., Odabasi, M., 2020. Intraday and interday variations of 69 volatile organic compounds (BVOCs and AVOCs) and their source profiles at a semi-urban site. Sci. Total Environ. 723.
- Zeng, P., Lyu, X.P., Guo, H., Cheng, H.R., Jiang, F., Pan, W.Z., Wang, Z.W., Liang, S.W., Hu, Y.Q., 2018. Causes of ozone pollution in summer in Wuhan, Central China. Environ. Pollut. 241, 852–861.
- Zhang, Y., Wang, X., Zhang, Z., Lü, S., Huang, Z., Li, L., 2015. Sources of C2-C4 alkenes, the most important ozone nonmethane hydrocarbon precursors in the Pearl River Delta region. Sci. Total Environ. 502, 236–245.
- Zhang, K., Xiu, G., Lei, Z., Bian, Q., Duan, Y., Fei, D., Wang, D., Fu, Q., 2018. Vertical distribution of volatile organic compounds within the lower troposphere in late spring of Shanghai. Atmos. Environ. 186, 150–157.
- Zhang, K., Zhou, L., Fu, Q., Yan, L., Bian, Q., Wang, D., Xiu, G., 2019a. Vertical distribution of ozone over Shanghai during late spring: a balloon-borne observation. Atmos. Environ. 208, 48–60.
- Zhang, X., Yin, Y., Wen, J., Huang, S., Han, D., Chen, X., Cheng, J., 2019b. Characteristics, reactivity and source apportionment of ambient volatile organic compounds (VOCs) in a typical tourist city. Atmos. Environ. 215, 116898.
- Zheng, J., Shao, M., Che, W., Zhang, L., Zhong, L., Zhang, Y., Streets, D., 2009. Speciated VOC emission inventory and spatial patterns of ozone formation potential in the Pearl River Delta, China. Environ. Sci. Technol. 43, 8580–8586.
- Zhu, H., Wang, H., Jing, S., Wang, Y., Cheng, T., Tao, S., Lou, S., Qiao, L., Li, L., Chen, J., 2018. Characteristics and sources of atmospheric volatile organic compounds (VOCs) along the mid-lower Yangtze River in China. Atmos. Environ. 190, 232–240.