



Strong regional transport of volatile organic compounds (VOCs) during wintertime in Shanghai megacity of China

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H I G H L I G H T S

- Meteorological conditions strongly influenced VOCs characteristics in winter.
- PPE and VPE were two kinds of typical pollution episodes in winter.
- Regional transport-related combustion from the northwest played important roles during PPE.
- Local emissions dominated the increase of VOCs during VPE.

A R T I C L E I N F O

Keywords:

Volatile organic compounds (VOCs)
Pollution periods
Source apportionment
VOCs concentration Weighted trajectory
Regional transport

A B S T R A C T

Measurements of volatile organic compounds (VOCs) were performed as well as other pollutants in Shanghai in winter. The whole measurements were classified into three types of periods, including particulate pollution episodes (PPE), VOC pollution episodes (VPE), and relatively clean periods based on the pollution characteristics. Of these types, PPE have the highest fine particulate matter (PM_{2.5}) mass concentrations and second-highest VOC concentrations, mainly impacted by the regional transport of aged air masses from the northwest. VPE generally concern long-lasting high concentrations of VOCs under stagnant atmospheric conditions due to the accumulation of local emissions. Five sources of VOCs were identified by the positive matrix factorization (PMF) model, and furthermore, the analysis of VOCs concentration weighted trajectory (CWT) was employed to investigate the potential source region and even to validate the source identification to some extent. As a result, VOCs in Shanghai in winter were mainly from solvent usage (23.9%), vehicle emissions mixed with some petrochemical emissions (24.7%), natural gas and background (23.6%), combustion-related to regional transport (22.1%), and secondary formation (5.7%). The regional transport, usually with large combustion sources, played more important roles (41.9%) in VOCs during PPE compared to VPE and clean periods. The contribution of local emissions like vehicle exhaust and petrochemical emissions increased during VPE compared to PPE and clean periods. Clean periods have low PM_{2.5} and low VOC concentrations, with a large contribution from the regional background. The present study highlighted the regional transport of VOCs should be taken into account for policymakers when making the city scale controlling measures.

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1. Introduction

Volatile organic compounds (VOCs), consisting of a variety of atmospheric organic chemicals that have both numerous sources and well demonstrated toxic effects, play a key role in the formation of ground ozone (O₃) and secondary organic aerosols (SOA) (Atkinson, 2000; Seinfeld and Pandis, 2016). Atmospheric photochemical reactions of anthropogenic and biogenic VOCs with oxidants (e.g., O₃ & NO_x) and OH radicals can generate SOA, and even further aggravate fine particulate matter (PM_{2.5}) to cause air pollution (e.g., haze) under stagnant meteorological conditions in the troposphere (Ahern et al., 2019; Hodzic et al., 2016; Johnson et al., 2006).

Shanghai, a megacity in the Yangtze River Delta (YRD) region of China, with a population of over 24.1 million and more than 3.5 million motor vehicles (Shanghai Municipal Statistics Bureau, 2018), is still suffering from ozone or PM_{2.5} pollution (Chang et al., 2019; Ling et al., 2019; Ran et al., 2012; Wang et al., 2015). In our companion paper, we have described how the regional transport of air mass affects local VOC concentrations in summer (Liu et al., 2019). The massive pollutants transported from central and northern China often contribute considerably to PM_{2.5} in Shanghai during winter (Li et al., 2011; Ming et al., 2017; Zhao et al., 2015). These previous studies have mostly focused only on PM_{2.5} (Shu et al., 2019), but in recent years with worsening secondary pollution, more attention should be paid to the interaction of VOCs and PM_{2.5}.

Vehicle exhaust has been considered the most important source of VOC emissions in Shanghai urban, with a relative contribution rate of 25%–34% (Cai et al., 2010; Liu et al., 2019; Wang et al., 2013), followed by solvent usage, chemical industry, fuel evaporation, petroleum industry, and biogenic emission, etc. However, studies on the characteristics and sources of VOCs during VOC pollution episodes are still limited. Therefore, an integrated analysis to improve the understanding of VOCs characteristics during wintertime (PM_{2.5} pollution season) in Shanghai is needed.

In this study, we present comparisons of VOC speciation during PM pollution episodes and VOC pollution episodes in Shanghai during winter. The data collected include 113 VOC species, PM_{2.5}, gaseous pollutants, and meteorological variables. The characteristics and sources of VOCs associated with two types of pollution are reported here. The aim is to understand the major characteristics of winter VOCs in urban areas, especially VOC sources, and the effects of local emissions and regional transport, to provide perspective for policy makers in suppressing or reducing pollutants.

2. Material and methods

2.1. Sampling site

The field measurements were carried out at an urban supersite at an interval of 1 h from December 5, 2017 to January 15, 2018, on the rooftop of a nine-story building in the Shanghai Academy of Environmental Sciences (SAES, 31°17'N, 121°43'E), located in the southwest portion of downtown Shanghai. The specific location and the environment surrounding the SAES supersite were described in detail elsewhere (Liu et al., 2019; Wang et al., 2015).

2.2. Measurements

The ambient C₂–C₁₀ VOCs were measured to simultaneously using a gas chromatography (GC)-mass spectrometry (MS) and flame ionization detector (FID) system (TH-PKU 300 B, Wuhan Tianhong Instruments Co., Wuhan, China), introduced in previous studies (Liu et al., 2019; Zhu et al., 2018). During the campaign, calibration of the GC-MS/FID was performed every day to ensure consistency and sensitivity using a 1.0 ppbv photochemical assessment monitoring station (PAMS) standard mixture (Spectra Gases Inc., USA). The deviation for most PAMS target

compounds is constrained within ±12%. Detailed information on quality assurance and quality control (QA/QC) procedures and their corresponding results are presented in Section S1 and Fig. S1.

Formaldehyde was detected using a commercial Hantzsch monitor (AL4021, Aero-Laser GmbH, Garmisch-Partenkirchen, Germany) with a time resolution of 1 min and a detection limit of 0.02 ppbv, which was manually calibrated by the six-point calibration every week, including a zero-concentration point and five other points distributed proportionally (i.e., 5, 10, 20, 40, 80 µg L⁻¹ standard formaldehyde solution, respectively). Zero adjustments were automatically performed every 8 h per day. All the measured VOC species were listed in Table S1.

Gaseous pollutants (NO–NO₂–NO_x, CO, SO₂ and O₃), peroxyacetyl nitrate (PAN), PM_{2.5} and photolysis rate constant (j_{NO2}) were measured at the supersite simultaneously. Meteorological variables, such as temperature (T), relative humidity (RH), wind speed (WS) and wind direction (WD), were acquired from a weather station approximately 10 km northwest of the supersite.

2.3. Concentration weighted trajectory (CWT)

In this study, CWT was used to apportion the potential source areas for VOCs in Shanghai. Briefly, CWT is a function of VOC concentrations that were measured every 1 h and the residence time in each grid cell (*i, j*) of a trajectory arriving at the receptor site. The 24 h back trajectories of air masses at height of 100 m a.g.l. (above ground level) corresponding to the sampling cycle of VOC measurement per hour were generated using the HYSPLIT4 model (Draxler et al., 1999; Stein et al., 2015).

Based on the maximum distance traveled by air mass back trajectories over the measurement period, a geographical domain of 26–40° N × 110–130° E was found to be suitable for calculation of CWT, with a grid resolution of 0.1° × 0.1°. Also, a smoothing factor of 5, the strength of Gaussian smoothing for the attributed VOC contributions, was applied considering the uncertainties of back trajectory paths.

2.4. Positive matrix factorization (PMF)

The US EPA PMF 5.0 (Norris et al., 2014) was used to qualitatively identify sources of VOCs measured at a receptor site (Liu et al., 2019; Shao et al., 2016; Sun et al., 2016). Each PMF model, consisting of 4–8 factors, was run 100 times to ascertain the optimum solution. The diagnostic parameters for the PMF application are summarized in Table S2.

2.5. VOC reactivity

The R_{OH} for certain VOC species (VOC_{*i*}) can be calculated by the rate constant of the species reaction with OH radicals (k_{OH,VOC_{*i*}}):

$$R_{OH} = \text{VOC}_i \times k_{OH,VOC_i}$$

k_{OH} values at 298 K were derived from previous studies by Atkinson and Arey (2003), Atkinson et al. (2006), Burkholder et al. (2015), and Abeira et al. (2017), as summarized in Table S1.

3. Results and discussion

3.1. Overview of the measurements

The time series of the measurements are presented in Fig. 1. During the campaign, several rainfall events affected Shanghai. Hourly temperatures varied between –4 °C and 18 °C with an average of 6.5 ± 3.9 °C (Table S3), while prevailing winds shifted between northerly and northwesterly with a mean WS of 3.8 ± 1.9 m s⁻¹ (Fig. S2). The whole observation can be classified into three comparable periods: PM_{2.5} pollution episodes (PPE), VOC pollution episodes (VPE) and clean

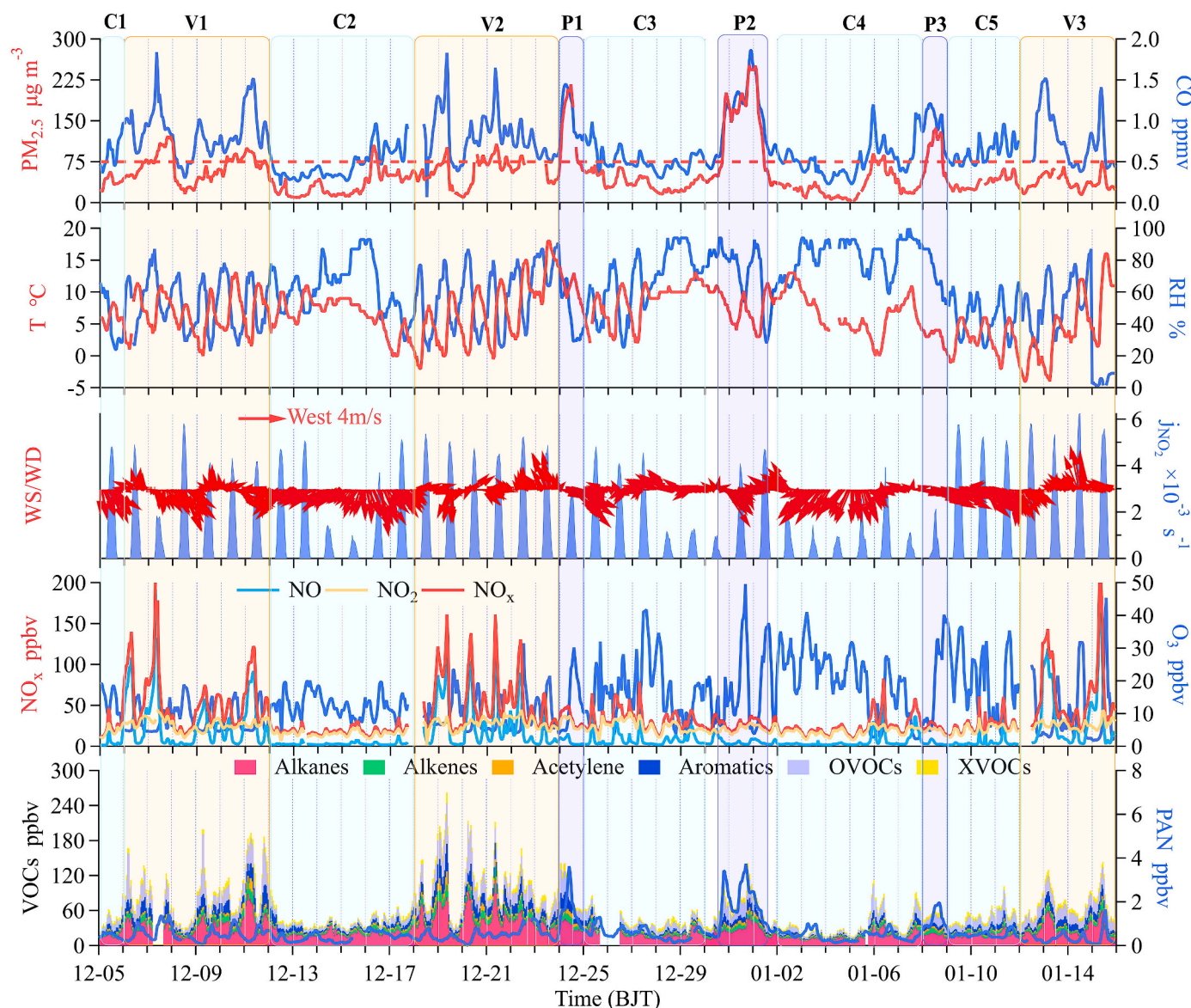


Fig. 1. Time series of particulate matter mass concentrations ($PM_{2.5}$), meteorology parameters (T , RH , WS and WD), photolysis frequencies j_{NO_2} , gaseous pollutants (NO – NO_2 – NO_x , CO , PAN and O_3) and VOC species. Blue area represented $PM_{2.5}$ pollution episodes (PPE, P1–P3), yellow area represented VOC pollution episodes (VPE, V1–V3), and pale area represented clean periods (clean, C1–C5). Time is given in Beijing Time. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

periods, as shown in Fig. 1, mainly based on the meteorology as well as the pollution characteristics.

PPE generally occur with a large drop of temperature and strong transport from the north-to-northwest of Shanghai indicated by the rapid increase and decrease of aged pollutants, like PAN and CO, at the beginning and end of PPE. Generally, the duration of PPE ranged from few to dozens of hours. PPE result in particularly high $PM_{2.5}$ mass concentrations, such as $252 \mu g m^{-3}$ (Table S3). The average mass concentration of $PM_{2.5}$ during PPE is $142 \mu g m^{-3}$. The concentrations of VOCs and CO are 73.3 ppbv and 1.12 ppmv, respectively. Time series for CO correlate well with $PM_{2.5}$ (correlation coefficient $r = 0.89$, $p < 0.01$), while NO, NO_2 and SO_2 have low concentrations and completely different time series compared with $PM_{2.5}$. Regional transport from north-northwest of Shanghai may be the most plausible contributor of increasing $PM_{2.5}$ and VOCs.

By comparisons, long-lasting high concentrations of VOCs, such as during 6–11 December 2017, 18–23 December 2017 and 12–15 January 2018, with mixing ratios over 60 ppbv, are observed along with high

concentrations of NO and NO_x during the winter campaign (Fig. 1). These periods are defined as VPE. VPE usually have a long duration, the longest lasting 6 days. The concentrations of VOCs vary greatly, from 24.5 to 262.5 ppbv, with an average of 91.0 ± 42.7 ppbv (Table S3). The time-averaged and maximum hourly concentrations of NO_x are 57.6 ppbv and 221.1 ppbv for VPE, respectively. The time-averaged WS ($2.8 m s^{-1}$), T (6.2 °C) and RH (52.3%) during VPE are much lower than those in PPE ($5.0 m s^{-1}$, 6.9 °C, 67.3%), indicating that more stagnant atmospheric conditions favor the accumulation of VOC pollution in VPE. Increases in total VOCs correlate with NO and CO ($r = 0.67$ and 0.75 , respectively; $p < 0.01$), suggesting that the time variation for VOCs during VPE is driven to a large extent by traffic-related sources.

Out of a total of 42 days, the remainder can be classified as clean periods, during which many pollutant concentrations are much lower than those in PPE and VPE, with $PM_{2.5}$, VOCs, and NO_x averages of $34 \mu g m^{-3}$, 41.9 ppbv, and 25.3 ppbv, respectively. Clean periods generally exhibit relatively high WS that favors the diffusion and dilution of air pollutants.

3.2. CWT analysis of VOCs

As mentioned in Sect. 3.1, PPE episodes tend to accompany with strong wind, indicating a potential contribution from regional transport. Fig. 2 shows the 24 h back trajectories of air masses at a height of 100 m, at hourly intervals and the corresponding potential source areas contributing to VOCs. This demonstrates that during PPE episodes VOCs are largely influenced by north-northwest air masses (Fig. 2a), which pass through Anhui and Jiangsu provinces with high-density emissions before reaching Shanghai (Fig. 2b).

During VPE, the average WS is 3.0 m s^{-1} , significantly lower than those during PPE and clean periods (Table S3), which suggests that the weather pattern during VPE remains relatively stagnant. As shown in Fig. 2d, the local emissions played dominant roles in VOC concentrations during VPE. Additionally, the contribution from the southeastern, mainly Hangzhou Bay and Ningbo-Zhoushan Port where have large emissions from the petrochemical industry and ship exhausts (Liu et al., 2019), is also considerable.

Compared to the back trajectories during PPE and VPE, many of those during clean periods are from the relatively clean areas over the eastern sea of China (Fig. 2e and f). Meanwhile, trajectories from the north-to-northwest of Shanghai are longer than those during PPE and VPE, suggesting more favorable dilution conditions during clean periods.

3.3. VOC concentrations and reactivity

Fig. 3 (a,b) shows the variation in VOC concentrations and their compositions during different episodes. As presented in Table S3, the hourly VOC concentration during VPE averaged $91.0 \pm 42.7 \text{ ppbv}$, significantly higher than $73.3 \pm 27.3 \text{ ppbv}$ during PPE and $41.9 \pm 16.7 \text{ ppbv}$ on clean days. The most abundant species are alkanes, followed by oxygenated volatile organic compounds (OVOCs), alkenes, aromatics,

halogenated hydrocarbon (XVOCs) and acetylene, and their average fractions are 35.5%, 28.0%, 15.4%, 9.7%, 7.2% and 4.3%, respectively, during the whole measurement.

VOCs compositions during the three periods have some differences. Specifically, alkanes, especially $\text{C}_2\text{-C}_3$ alkanes with a longer lifetime, give higher contributions during clean periods compared to those during PPE and VPE. It can be expected that clean periods usually happen with favorable dilution meteorology, which is mostly impacted by the aged and regional air masses. The contributions of alkenes during three periods are comparable. Acetylene is 5.9% during PPE and higher than those during other periods, mainly associated with combustion processes (Liu et al., 2008), suggesting that the importance of coal combustion from the transport of northwest of Shanghai during PPE. Aromatics has the highest proportion (11.0%) during VPE among all the periods, which indicates large emissions of solvent usage in Shanghai considering air masses during VPE are mainly from the local area.

The calculated R_{OH} for all measured VOC species during the whole measurement, PPE, VPE, and clean periods are on average 8.1 s^{-1} , 8.3 s^{-1} , 11.7 s^{-1} and 5.5 s^{-1} (Fig. 3c), respectively. The contribution from alkenes is dominant, accounting for 33.9–36.0% (Fig. 3d), due to high k_{OH} values for alkenes. The average k_{OH} (divide total R_{OH} by total VOC concentration) during VPE ($0.114 \text{ ppbv}^{-1} \text{ s}^{-1}$) is slightly higher than during PPE ($0.103 \text{ ppbv}^{-1} \text{ s}^{-1}$) and clean periods ($0.106 \text{ ppbv}^{-1} \text{ s}^{-1}$), indicating that VOC species during VPE are relatively more reactive than during PPE.

The ratios of ethylbenzene to m,p-xylene (E/X) can serve as indicators of the photochemical aging of air masses (de Gouw, 2005), since they have similar sources in urban environments (Miller et al., 2012; Wang et al., 2013) and m/p-xylene has a faster rate constant for oxidation by OH radicals than ethylbenzene (Atkinson and Arey, 2003). The ratios of E/X during PPE (0.67) are much higher than during VPE (0.53) and clean periods (0.59). The higher ratio during PPE highlights the potential impact of a more aged VOC mixture from regional

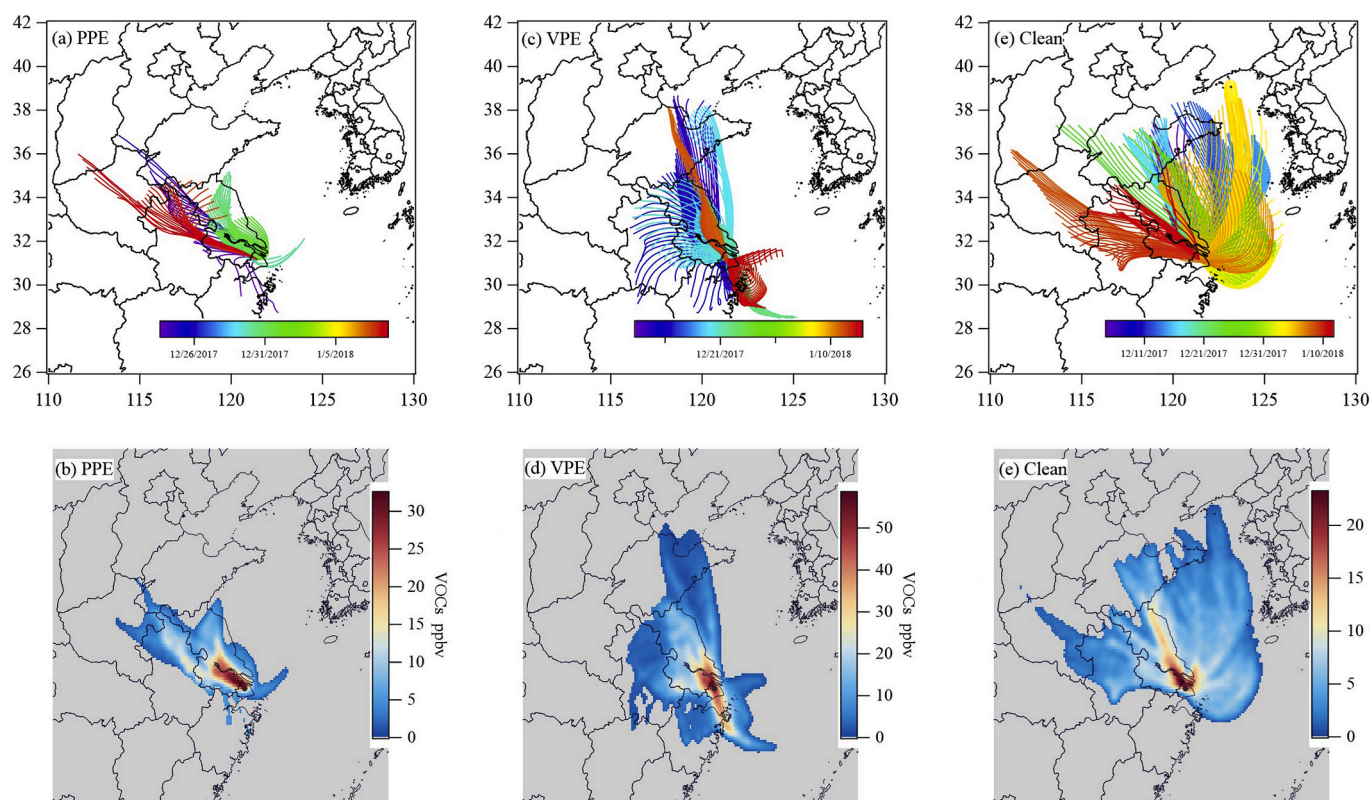


Fig. 2. (a,c,e) Clustered 24-h air mass backtrajectories starting at 100 m height for PPE, VPE, and clean periods, respectively; (b,d,f) concentration weighted trajectory (CWT) map for total VOCs for PPE, VPE, and clean periods, respectively.

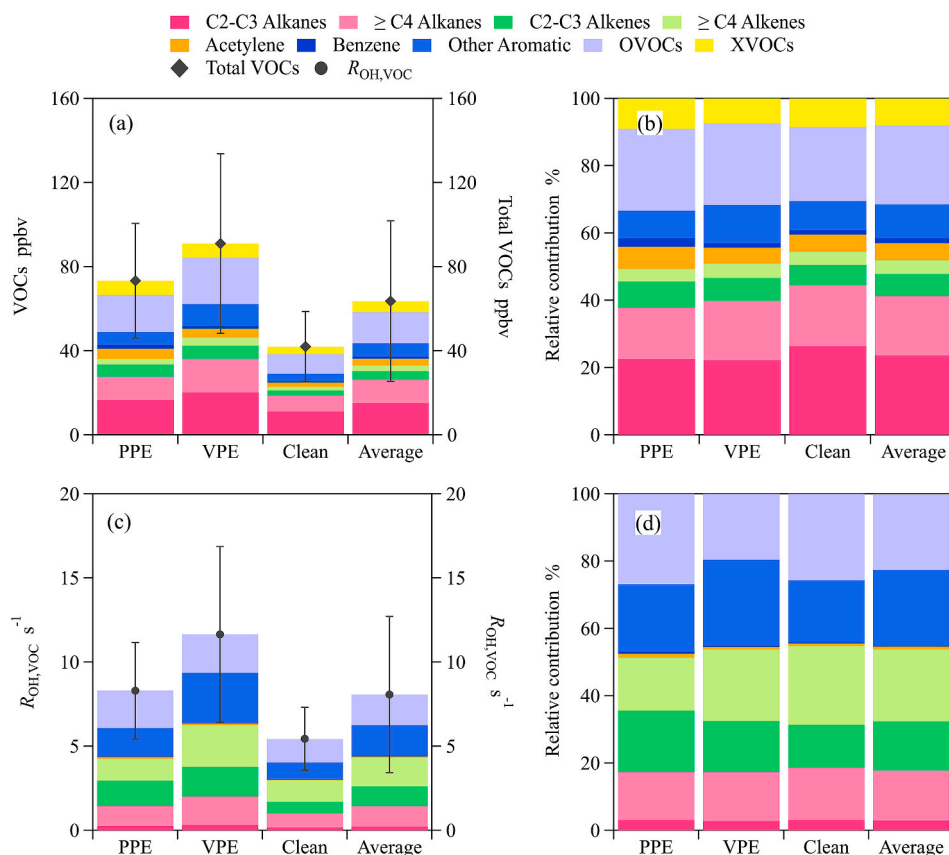


Fig. 3. The VOC concentrations and chemical compositions (a, b), and average reactivity (c, d) of major VOC groups during PPE, VPE, clean periods and the whole measurement, respectively.

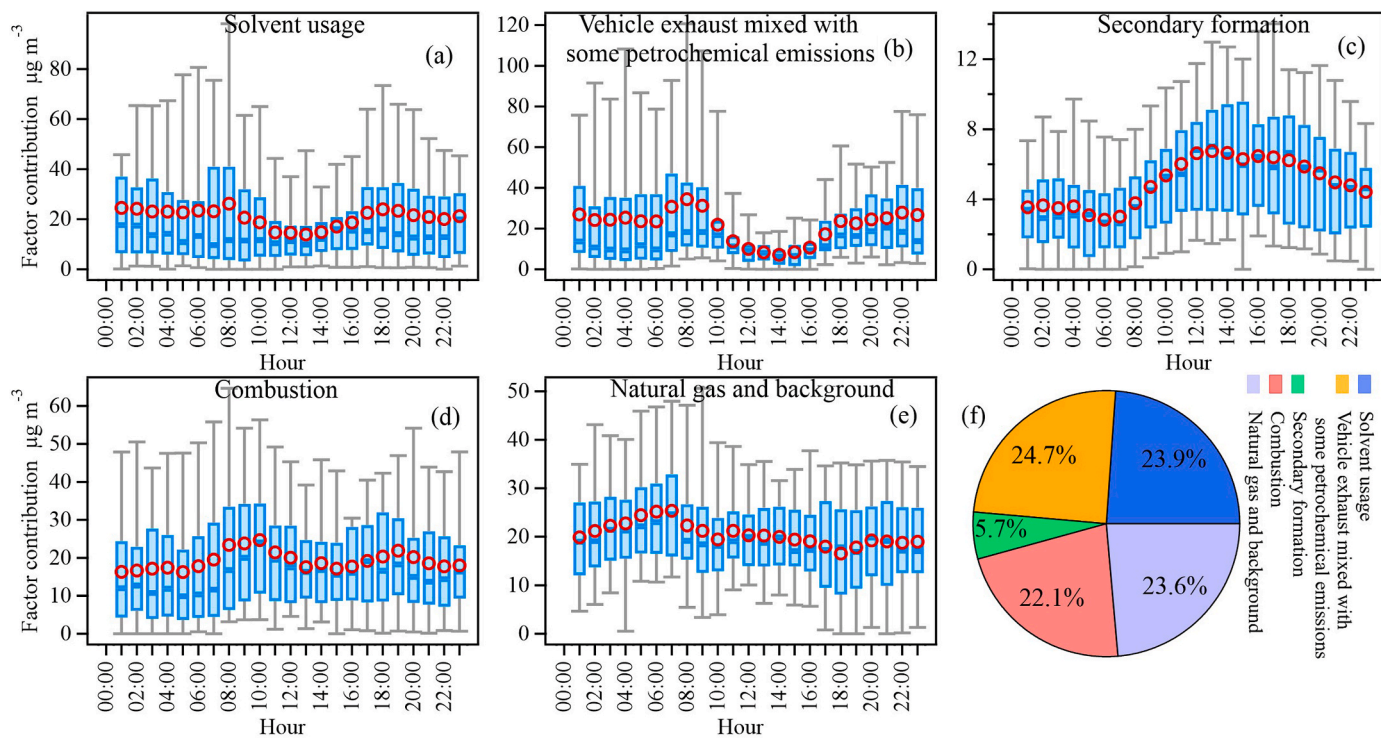


Fig. 4. a~e, diurnal patterns of five factors from the PMF results, 25th and 75th percentile for deep sky-blue boxes, 5th and 95th percentile for whiskers, dashed lines for the median values, and solid red dots for the mean values. f, Source contribution of VOCs during the whole measurements. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

transport, which is consistent with given trajectories (Fig. 2a, b). Such haze day characteristics have been found in previous studies (Hui et al., 2019; Zhang et al., 2014). In contrast, a lower ratio during VPE reflects a greater influence from local fresh emissions.

3.4. Source apportionment

3.4.1. Identification of PMF factors

Overall, five factors are resolved by the PMF model, as shown in Fig. S3, which will be identified based on their source profiles as well as their diurnal patterns (Fig. 4) and region contributions (Fig. 5) as follows.

3.4.1.1. Solvent usage. More than 60% of total toluene and the sum of C₈ aromatics (i.e., ethylbenzene, xylenes and styrene) are explained by factor 1 (Fig. S3a). Among these, toluene, xylenes and ethylbenzene contribute most (33%, 21%, 10%, respectively) to the total measured VOC mass of factor 1. These species (TEX) have industrial sources as they are widely used solvents and/or reactants in various processes, and can also be emitted from vehicle exhaust and coal combustion (Guo et al., 2011; Kwon et al., 2007; Wang et al., 2010; Yuan et al., 2010). Aromatic emissions from vehicle exhaust and coal combustion are usually accompanied by high abundances of short-chain hydrocarbons ($\leq C_6$) (Liu et al., 2017). However, the abundance of C₂–C₆ in factor 1 is low, suggesting that the contribution of the two sources can be excluded. Therefore, this factor is solvent usage, and its average relative contribution is 23.9% (Fig. 4f).

3.4.1.2. Vehicle exhaust mixed with some petrochemical emissions. Factor 2 explains high percentages of alkenes (Fig. S3b) such as trans-2-pentene (91%), cis-2-pentene (74%), isoprene (62%), 1,3-butadiene (54%), 1-pentene (54%), propylene (51%). Among these, trans/cis-2-pentenes

and 1,3-butadiene are the most adequate tracers of vehicle exhaust (Borbon et al., 2001; Liu et al., 2008). 42% of total MTBE, a typical tracer of fuel additive almost exclusively used in motor gasoline (Markus et al., 2010), is explained by this factor. These strongly suggest that this factor is linked to traffic emissions and especially, the factor contribution correlates well with CO and NO_x concentrations ($r = 0.54$ and 0.85 , respectively; $p < 0.01$). While, there are some characteristics not related to vehicles in this factor, such as high contributions to styrene, isoprene, and xylenes, which are more related to industrial emissions. Isoprene has been reported also from vehicle emissions (Barletta et al., 2005; Hellén et al., 2012), which, however, is not important for Shanghai (Liu et al., 2019; Wang et al., 2013). As shown by the region contribution (Fig. 5b), this factor is contributed largely from the emissions in the southeast of Shanghai where located abundant petrochemical industries and Ningbo-Zhoushan Port and emitted both high VOCs and NO_x (Liu et al., 2019). This can, to some extent, explain the good correlations of factor 2 with NO_x, even though factor 2 is mixed with emissions from the southwest of Shanghai. Thus, factor 2 is vehicle exhaust mixed with some petrochemical emissions, the average relative contribution is 24.7% (Fig. 4f).

3.4.1.3. Secondary formation. Factor 3 includes a predominance of carbonyl compounds. n-Hexanal and acetaldehyde make the largest contributions to the total measured VOC mass of this factor, 19% and 14%, respectively, while formaldehyde, MVK, n-butanal, and propanal together contribute 27%, with individual contributions of 7%, 7%, 5%, and 3%, respectively, as shown in Fig. S3c. Factor 3 explains more of the total MACR and MVK mass than any of the other factors, 57% and 52%, respectively, secondary products from the photooxidation of isoprene (Akimoto, 2016; Liu et al., 2013). Besides, 56% of n-pentanal, 55% of n-hexanal, 53% of n-butanal, and 40% of both acetaldehyde and propanal are explained by this factor. Meanwhile, factor 3 has the peak

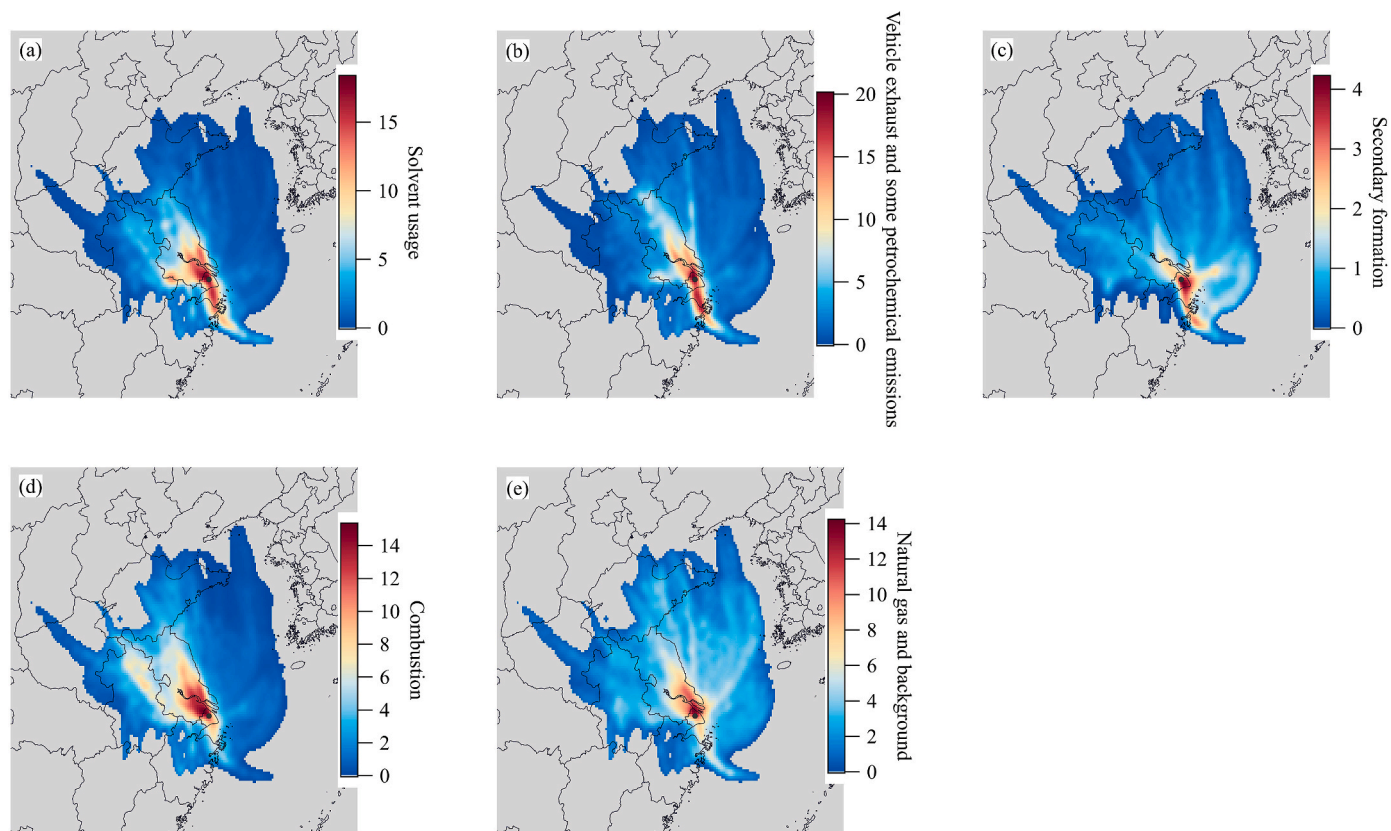


Fig. 5. CWT maps for all source factors resolved by PMF (the unit of the color bar is $\mu\text{g m}^{-3}$). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

during noontime and correlates well with PAN ($r = 0.96$, $p < 0.01$), suggesting a large contribution of photochemical formation. The average relative contribution of this factor is 5.7% during the whole measurement (Fig. 4f).

3.4.1.4. Combustion. Approximately 57% of total benzene, 51% of total ethylene and 47% of total acetylene are explained by factor 4 (Fig. S3d). The profile of this factor largely consists of propane, ethane, ethylene, toluene, benzene, acetylene, n-butane, formaldehyde and MEK, together accounting for 79% of this factor, possibly being related to combustion (Liu et al., 2008; Parrish et al., 2012; Yáñez-Serrano et al., 2016). The contribution of factor exhibits good correlation with CO ($r = 0.79$, $p < 0.01$) but poor with NO_x ($r = 0.31$), in contrast to the results of factor 2. Thus, this factor is mainly associated with combustion, especially the regional combustion from northwest of Shanghai shown in Fig. 5d. The average relative contribution of this factor in winter is 22.1% during the whole measurement (Fig. 4f).

3.4.1.5. Mixture of natural gas and background. Factor 5 has abundant C₂–C₃ alkanes (Fig. S2e), ethane and propane, which contributes 25% and 23%, respectively. This factor explains 49% of total ethane and 37% of total propane. Since ethane and propane are two major components of natural gas (Baudic et al., 2016), they are likely emitted in the production and use of natural gas. Therefore, this factor is attributed to natural gas. Poor correlation with the reactivities of NO_x and CO ($r = 0.11$ and 0.16 , respectively), imply that this factor has no relationship to traffic sources. Additionally, factor 5 also contributes considerably to some carbonyls, as shown in Fig. S3e, suggesting there exists some aged air mass in factor 5. In comparison with factor 2, a flat diurnal pattern is observed for factor 5, as shown in Fig. 4e. It means the aged air mass in factor 5 may be more likely to be regional background rather than the local formation, which can also be seen from the region distribution (Fig. 5e). Thus, we define factor 5 as a mixture of natural gas and background. The average relative contribution of this factor is 23.6% during the whole measurement (Fig. 4f).

3.4.2. VOC sources

Accordingly, the major VOCs sources in Shanghai include solvent usages, vehicle emissions, petrochemical industry, natural gas, combustion mainly related to regional transport from the northwest of Shanghai, as well as regional background. The local secondary photochemical is also considerable in winter with an average contribution of 5.7%.

Solvent usage, generally more significant in warm seasons due to the higher temperature, is the largest source even in the winter of Shanghai, which is mainly from the local emissions as shown in Fig. 5a. Vehicle emissions and petrochemical emissions in Shanghai are the second-largest source with a together contribution of 24.7%, and it is not easy to separate these two sources due to two possible reasons in the present study. One is the similar speciation, like C₂–C₅ alkenes and C₄–C₇ alkanes. The other one is the petrochemical industries located in the southeast of Shanghai, where also has a large port with large vehicle-related emissions. Generally, these two large sources impact the urban area simultaneously under suitable meteorology. Combustion related emissions, mostly from the regional transport of the northwest, play an important role (22.1%) in VOCs in winter in Shanghai, which, however, is negligible in summer (Liu et al., 2019). Natural gas-related emissions have become one important source of VOCs in Shanghai with the increased consumption of natural gas in recent years (Shanghai Municipal Statistics Bureau: Shanghai Statistical Yearbook (2009–2015), China Statistics Press, Beijing, China), which are characterized by ethane and propane. Unfortunately, some species with a long lifetime, like acetylene and benzene, correlate well with ethane/propane, resulting in a mixture of natural gas and aged air mass. Combining with the regional distribution of the emissions, it can be further

concluded that the natural gas emissions are mixed with the regional background to some extent.

Different sources show varied time series, as shown in Fig. S4, resulting in different patterns of source contributions during three kinds of episodes which are presented in Fig. 6. During the PPE, combustion mainly related regional transport is the largest source of VOCs, with a contribution of 41.9%, which is much higher than those during VPE (18.8%) and clean periods (20.5%). This is consistent with the back trajectories of air masses (Fig. 2a) during PPE, which are mainly from the northwest of Shanghai where locates many coal power plants and industries (Chen et al., 2019). Solvent usage and natural gas mixed with background take up 23.6% and 20.7% of VOCs during PPE, respectively. Vehicle emissions mixed with petrochemical emissions contribute 8.9% to VOCs during PPE, much lower than those during VPE (30.5%) and clean periods (20.8%). This is due to vehicle emissions mixed with petrochemical emissions mainly from local emissions and the transport from southeastern (Fig. 5b), which is very different from the back trajectories of PPE (Fig. 2a). Secondary formation takes up 4.8% during PPE, which is comparable to that during VPE (4.2%) and lower than that of clean periods (8.2%).

In terms of VPE, vehicle emissions mixed with petrochemical emissions and solvent usage are the two largest sources of VOCs, accounting for 30.5% and 28.9%, respectively. Combustion related to regional transport and natural gas mixing with background contributes 18.8% and 17.6% during VPE, respectively. Interestingly, the mixture of natural gas-related background is the largest source of VOCs during clean periods, as the CWT map of this source is very similar to that of total VOCs during clean periods. This is expected because clean periods usually happens with favorable dilution meteorology, and thus the local emissions would not accumulate in the near ground.

4. Conclusions

This study presents measurements of VOC species and other pollutants performed at the SAES supersite in Shanghai from December 5, 2017 to January 15, 2018. The entire intensive field campaign was classified into three contrasting episodes on the basis of chemical emission signatures. The characteristics and sources of VOCs are compared during PPE, VPE and clean periods, as well as the impact of regional transport.

Measurements of the two types of pollution episodes (PPE and VPE) are compared during winter. During PPE, the main factor affecting VOC concentrations is from the strong north-northwest winds, originating from Anhui and Jiangsu Provinces and northwest Shanghai areas, carrying high-density emissions to the receptor site. During VPE, high local emissions are intensified as well as some transport of petrochemical emissions from southeast of Shanghai, resulting in the highest and longest VOC pollution days under stagnant atmospheric conditions. Clean periods generally happen when cold air dominates and Shanghai is under the influence of clean air from the north, northeast, and east. Generally, VOCs during VPE are fresher due to local emissions, and those during clean periods are more aged and characterized by a large abundance of long lifetime species.

Five VOC sources are extracted using the PMF model with the combination of CWT analysis, consisting of solvent usage (23.9%), vehicle exhaust mixed with some petrochemical emissions (24.7%), secondary formation (5.7%), combustion-related to regional transport (22.1%), natural gas and background (23.6%). Combustion-related to regional transport is found to be a large contributor (41.9%) to ambient VOC concentrations during PPE, and the solvent usage, vehicle exhaust mixed with some petrochemical emissions contribute 59.4% during VPE, and the natural gas and background contribute to 34.6% during clean periods.

The present study investigates the characteristics and sources of VOCs in the winter of Shanghai as well as the impact of regional transport through the PMF model and the CWT analysis. The results

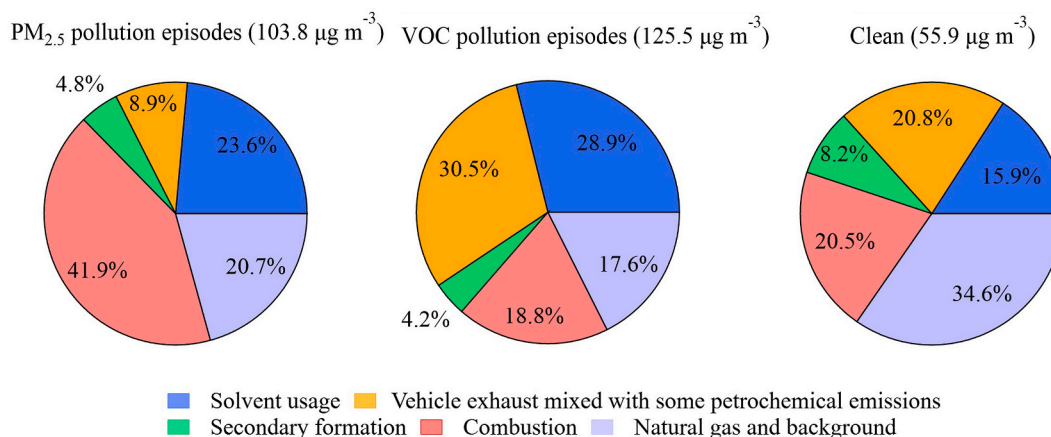


Fig. 6. Relative contribution of VOC factors during PPE, VPE, and clean periods.

highlight the importance of regional transport to the levels and compositions of VOCs in winter of the YRD region, which is recognized to be small considering the shorter lifetime of VOCs compared to ozone and particles. The regional transport of VOCs would impact the characteristics of precursors in the atmosphere in each city, which further impacts the secondary transformation of air pollution. It is very critical for the policy makers to take the regional transport of VOCs into account besides the local emissions.

Data availability

The data used in this paper is available on request from the corresponding author (wanghl@saes.sh.cn).

Author statement

We affirm that all authors have read and approved the submission of this paper and that none of the material in the paper has been published or is under consideration for publication elsewhere. There are no any ethical/legal conflicts involved in the article.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2020.117940>.

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