# Chemical loss of volatile organic compounds and its impact on the source analysis through a two-year continuous measurement

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## HIGHLIGHTS

- 35% initial VOCs had been consumed during the transport from sources to the receptor.
- Reactivity of VOCs was underestimated over 60% if the removal of VOCs was ignored.
- C3−C5 alkenes and C8 aromatics contributed over 60% of the chemical loss of VOCs.
- Seven sources of VOCs were identified and quantified in Shanghai urban.
- The regional transportation contributed ∼20% of VOCs in Shanghai urban from PMF.

## ARTICLE INFO

## ABSTRACT

Chemical loss of volatile organic compounds (VOCs) is more important than the observed VOCs, which is the real actor of the chemical process in the atmosphere. The chemical loss of VOCs might impact on the identification of VOCs sources in ambient. For this reason, VOCs with 56 species were continuously measured in the urban area of Shanghai from 2009 to 2010, and based on the measurement the chemical loss of VOCs was calculated. According to the result, the initial VOCs in Shanghai urban was $(34.8 \pm 20.7)$ ppbv, higher than the observed one by ∼35%, including alkanes (∼38%), aromatics (∼36%), alkenes (∼17%), and acetylene (∼8%). The chemical reactivity of VOCs would be underestimated by ∼60% if the chemical loss were ignored. The chemical loss of VOCs showed a good agreement with Ox ($O_3 + NO_2$). C7−C8 aromatics and C3−C5 alkenes contributed ∼60% of consumed VOCs. Seven sources were identified and quantified from positive matrix factorization (PMF) analysis. Vehicular emissions were the largest anthropogenic source of VOCs in Shanghai urban, accounting for 27.6% of VOCs, followed by solvent usage (19.4%), chemical industry (13.2%), petrochemical industry (9.1%), and coal burning (∼5%). The contribution of biogenic emissions to total VOCs was 5.8%. Besides the five local anthropogenic sources and one biogenic source, the regional transportation was identified as one important source, contributing about 20% of VOCs in Shanghai urban. Sources apportionment results from PMF analysis based on the initial VOCs showed some differences from those based on observed data and might be more appropriate to be applied into the formulation of air pollution control measures.

## 1. Introduction

Shanghai has been experiencing a rapid economic growth in the past decades. The increase of the energy consumption due to the rapid economic growth resulted in a dramatic increase of the pollutants emissions (Huang et al., 2011) and the deterioration of the air quality in Shanghai, in term of ozone and fine particles (Gao et al., 2009; Geng et al., 2009; Tie and Cao, 2009). Volatile organic compounds (VOCs) are important precursors of the photochemical process and have been paid a large amount attention to as their great contribution to the formation of troposphere ozone and secondary organic aerosols (SOA) (IPCC, 2007; Seinfeld and Pandis, 2006).

So far, many studies have been conducted to investigate the characterization of VOCs and the key VOCs components of ozone formation in Shanghai. However, identifying the important contributors to ozone formation potential (OFP) based solely on the observed data was problematic (Shao et al., 2011). The chemical loss

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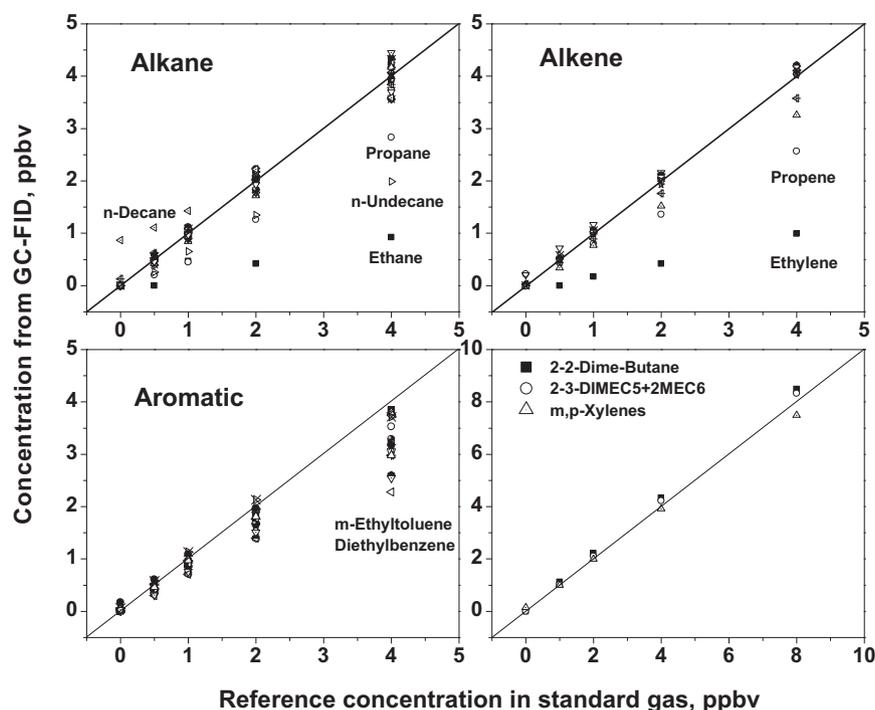
**Fig. 1.** Comparison of the manual calibration results and the reference concentrations in standard gas.

of the reactive VOC species during the transportation from emission sources to the receptor site played important role in the formation of ozone. As studied by Xie et al. (2008), the chemical loss of the reactive VOC species contributed more than one third of the OFP in Beijing urban. Actually, the consumed VOCs might be the real contributors to the ozone formation, which could not be taken into account by the observed data. The oxidants formation agreed better with the consumption of VOCs than with the observed VOCs in Beijing during the 2008 Olympic period (Shao et al., 2011). Furthermore, the source apportionment of VOCs would have large uncertainty for the reactive VOC species if the chemical loss was ignored (Wittig and Allen, 2008). The source apportionment of VOCs by Chemical Mass Balance model (CMB) considering the chemical loss differed a lot from that based on the observed data (Na and Kim, 2007; Shao et al., 2011). As reported by Na and Kim (2007), the contribution from vehicle exhaust was underestimated by 10% when the chemical loss effect was incorporated in the CMB calculation while the contribution from solvent usage and gasoline evaporation were overestimated. Generally, the contribution of sources with more reactive species would be underestimated based on the observed VOCs.

There were usually two kinds of methods using to estimate the consumption of VOCs in ambient. One was through estimating the photochemical age of air mass by the VOC species pairs from the same emission sources but having different reactivities with OH (McKeen et al., 1996). The other was based on the oxidation products measurement to estimate the consumption of their parent VOC species (Bertman et al., 1995; Wiedinmyer et al., 2001). The chemical loss of VOCs has been estimated previously in different regions (Shao et al., 2011; Shiu et al., 2007; Xie et al., 2008) but not in Shanghai.

In this study, the continuous measurement of C2–C12 VOC species were carried out for two years to investigate the characterization of VOCs in urban Shanghai, China. Based on the observed data, the chemical loss of VOCs was estimated. The high response temporal variation of VOCs through over the two years was

discussed in detail combining with the oxidants variations in Sections 3.2 and 3.3. Studies of VOCs in other cities were employed to compare with that in this study, and some special result in Shanghai was obtained in Section 3.4. According to the estimation result of the chemical loss, the sources contributions were quantified by receptor model, positive matrix factorization (PMF) (Paatero, 1997), in Section 3.5. Finally, in Section 4, the conclusions of the present study were summarized and the implications were discussed.

## 2. Experiment

### 2.1. Monitoring sites

The monitoring site locates in the southwest of the urban area in Shanghai, China. It is about 8 km away from the city center. The sample inlet is on the roof of a 5-floor building at Shanghai Academy of Environmental Science (31.17°N, 121.43°E), about 15 m above the ground. There are no other large VOCs sources except the vehicular and domestic emissions in the urban area. In the south and southwest around 50 km away from the monitoring site, there are some petrochemical and chemical industrial factories in the rural area (Cai et al., 2010; Huang et al., 2011), which may have effects on the VOCs measured results at the monitoring site in the special meteorological conditions.

### 2.2. Measurement of VOCs

Individual VOC species were continuously measured every 30 min from January 2009 to December 2010 by two on-line high performance gas chromatograph with flame ionization detector (GC-FID) systems (Chromato-sud airmoVOC C2–C6 #5250308 and airmoVOC C6–C12 #2260308, France). For C2–C6 VOCs, the sample is preconcentrated through a trap, a fine tube containing porous substances. Three trap phases, including Carbotrap C, Carbopack B and Carboxen, are chosen so as to trap from the selected

compounds. The trap is cooled by a cell with Peltier effect during the sampling. The temperature for the cold is set at −8 °C. Then, the tube is heated and thermodesorption is fixed at 220 °C, followed by separation on an ultimetal column (id = 0.53 mm, length: 25 m). A flame ionization detector (FID) is used for quantification. The air sample volume for C2−C6 analysis is around 80 mL. For C6−C12 VOCs, the sample is preconcentrated through a trap, and the trap phase (Carbotrap B) is chosen so as to trap C6−C12 compounds. Then, the thermodesorption is fixed to 380 °C, followed by separation on an ultimetal column (id = 0.28 mm, length: 30 m, MXT30 CE, 1 μm), and the detector is also FID. The air sample volume is around 105 mL. This instrument includes one auto-calibration unit, which uses three internal permeation tubes with standard compounds, to make auto-calibration every 24 h. The detection limits for VOC species are between several tens to hundreds pptv (Liu et al., 2012).

Additionally, the manual calibration by standard gas (Spectra, USA) was also performed periodically. The measured results by GC-FID were used to compare with the reference concentrations of the standard gas diluted by dynamic gas calibrator. Fig. 1 shows that for the species of C2−C3, there were large differences between the two results, and the results from GC-FID were only half of the reference concentrations in standard gas. This was mainly because the adsorption efficiencies of C2−C3 species in the trap were low due to the high volatility of these species. By contrast, in terms of ethyltoluene, diethylbenzene and n-undecane, their desorption efficiencies were low due to their low volatility, which resulted in the underestimation of their concentrations by ∼30%, as shown in Fig. 1. In addition, it seems that the correlation of n-decane had a significant intercept, probably due to the high concentration of n-decane in zero gas. In this study, the measured concentrations of C3 species and n-decane were recalculated according to their calibration curves, because the concentrations of these species in ambient were considerable and meanwhile the measured results and the reference concentrations in standard gas had strong correlations ($R^2 > 0.99$). The concentrations of ethane, ethylene, ethyltoluene, diethylbenzene and n-undecane in this text were the measured results from GC-FID. For the other 46 kinds of VOC species, the correlations between the measured results from GC-FID and the reference concentrations in standard gas were good ($R^2 > 0.99$), and the average slope of the correlation was $0.95 \pm 0.10$.

## 2.3. Estimation of the initial mixing ratio of VOCs

VOCs are usually composed of species with high chemical reactivity, and their lifetimes range from several hours to several hundred hours dependent on their reactivity and the concentration of OH radical. For example, the chemical lifetime of isoprene is only ∼1 h in the condition of OH radical concentration of $5.0 \times 10^6$ molecule cm$^{-3}$, while the lifetime of propane is about 100 h under the same condition. Consequently, the photochemical loss of VOCs is more significant for the VOC species with larger OH reaction rate constant. The sum of chemical loss and the observed mixing ratio of VOC species was considered as the initial mixing ratio.

Several methods used for calculating the initial mixing ratio of VOCs have been developed previously (McKeen et al., 1996; Wiedinmeyer et al., 2001). In the study of Wiedinmeyer et al. (2001), VOCs initial mixing ratio was calculated according to the isoprene conversion process, using the observed data of isoprene and its oxidation products (Xie et al., 2008). Because the products of isoprene were not observed from the measurements, we used the method mentioned in McKeen et al. (1996) to calculate the initial mixing ratio of VOCs. General description of the method is mentioned as below.

The major loss of VOCs is assumed due to their reactions with OH radicals in daytime. To estimate the initial mixing ratio of the VOCs, two hydrocarbons from the same emission sources but having different reactivities with OH are generally used as a measure of photochemical oxidation by OH radicals (de Gouw et al., 2005; Goldan et al., 2000; Jobson et al., 1999; McKeen and Liu, 1993; Kramp and Volz-Thomas, 1997). In this study, we choose ethylbenzene (E) and m,p-xylenes (X), for this purpose (Nelson and Quigley, 1983). The initial mixing ratio can be calculated by the equations below (McKeen et al., 1996):

$$[VOC_i]_t = [VOC_i]_0 \times \exp(-k_i[OH]\Delta t) \tag{1}$$

$$\Delta t = \frac{1}{[OH](k_E - k_X)} \times \left( \ln\left\{ \frac{[E]}{[X]}\Big|_{t=t_0} \right\} - \ln\left\{ \frac{[E]}{[X]}\Big|_{t=t} \right\} \right) \tag{2}$$

Where $[VOC_i]_t$ and $[VOC_i]_0$ are the observed and initial mixing ratio of VOC$_i$, respectively. $k_i$ is the reaction rate constant of VOC$_i$ with OH radicals, and $k_E$ and $k_X$ are the reaction rate constants of ethylbenzene (E) and m,p-xylenes (X) with OH radicals. [OH] is the mixing ratio of OH radicals. $\Delta t$ is the reaction time or the photochemical age. It should be noted that these results do not depend on the OH mixing ratio assumed: if a lower value of [OH] is assumed, then the photochemical age according to Equation (2) increases, and the product [OH]$\Delta t$ in Equation (1) remains the same. $([E]/[X])_{t=t_0}$ is the ratio between the initial mixing ratios of ethylbenzene and m,p-xylenes, and in other words, is the ratio of [E] to [X] in the VOCs emission sources. $([E]/[X])_{t=t}$ is the ratio of [E] to [X] at time $t$. Given the assumption that the removal of VOCs is governed by the reactions with OH radicals, the initial mixing ratios of VOCs were only estimated in daytime (i.e. 8:00−18:00) in the present study.

As reported in the previous studies, the values of $([E]/[X])_{t=t_0}$ for the sources related to the vehicular emission and the coal combustion are 0.3−0.4 (Liu et al., 2008), and is around 0.4−0.5 for solvent use (Wang et al., 2013; Yuan et al., 2010), and is about 0.65 for the biomass burning (Liu et al., 2008), and for the petrochemical and chemical processes this value is around 0.5−0.7 (Liu et al., 2008). According to the VOCs emission inventory in Shanghai, the petrochemical and chemical processes, painting and printing and vehicle contributed more than 80% of VOCs in 2007 (Huang et al., 2011). Therefore, we chose the value of $([E]/[X])_{t=t_0}$ as 0.5 in this study. In addition, higher (0.7) and lower (0.3) $([E]/[X])_{t=t_0}$ were used to carried out the sensitivity analysis and to test the uncertainties of estimation of initial mixing ratios. As a result, the relative changes of initial mixing ratios of different species ranged from 5% to 122% and from 1% to −48% for lower and higher $([E]/[X])_{t=t_0}$, respectively. Generally, initial mixing ratios of reactive VOC species were more sensitivity to $([E]/[X])_{t=t_0}$, and consequently their uncertainties were relatively high.

Additionally, the uncertainty of estimating the initial mixing ratio by hydrocarbons ratio method has been pointed out previously (McKeen and Liu, 1993). For example, the mixing of qualitatively different air masses could also have similar effects as chemical reactions on the atmospheric composition (Parrish et al., 2007). McKeen et al. (1996) showed that the time for dilution with background air was about 2.5 days, which was longer than the processes focused on in this study. Nevertheless, the assumption that the effects of mixing could be ignored should be treated with some caution.

In addition, there were some limitations for estimating initial mixing ratios of reactive species using the method above. de Gouw et al. (2005) estimated the rate coefficients for the reaction of all primary anthropogenic VOCs with OH radical using the method

**Fig. 2.** Mixing ratio, $L^{OH}$, and the OFP of each chemical VOC group in 2009 and 2010 (Obs-N: the observed mixing ratio during nighttime, Obs-D: the observed mixing ratio during daytime, Ini-D: the initial mixing ratio during daytime.).

their small observed mixing ratios and very fast removal processes. Given that, for the VOC species with larger rate coefficients than that of m,p-xylene, their initial mixing ratios were estimated using the rate coefficient of m,p-xylene in Equation (1) rather than themselves' in this study. Therefore, the initial mixing ratio of reactive species obtained in this study was a lower estimate.

## 3. Results and discussion

### 3.1. Characteristics of VOCs

#### 3.1.1. Mixing ratio

Fig. 2 summarized the observed and initial mixing ratios of each chemical VOC groups both in 2009 and 2010. In order to better understand the difference between the observed and the initial mixing ratio of each group, we divided the observed data into two groups, i.e. daytime (8:00—18:00) and nighttime (0:00—7:00 and 19:00—23:00). The observed mixing ratios of total VOCs (TVOC) during nighttime were (30.8 ± 21.2) ppbv in 2009 and (28.7 ± 21.5) ppbv in 2010 averaged daily, respectively, compared to (26.4 ± 16.0) ppbv and (24.5 ± 13.6) ppbv, respectively during daytime, mainly due to the lower height of mixing layer during night. The initial mixing ratios of TVOC during daytime were (35.4 ± 21.6) ppbv in 2009 and (34.1 ± 19.8) ppbv in 2010, respectively, higher than the observed ones by ~35%. A larger amount of VOCs had been consumed in atmosphere before measured.

According to the observed data, alkanes were the largest group of VOCs, with a mixing ratio around (12.9 ± 8.1) ppbv, followed by aromatics ((8.7 ± 6.2) ppbv), alkenes ((3.6 ± 2.6) ppbv) and acetylene ((2.5 ± 1.9) ppbv). Further examination showed that toluene, acetylene and C2—C3 alkanes were the most abundant species, accounting for more than ~35% of the total observed VOCs, followed by C8 aromatics and C4—C5 alkanes. C2—C3 alkenes were the largest composition of observed alkenes. These VOC species are almost related to the traffic emission (Liu et al., 2008), and industrial processes such as solvent usage are also important sources of toluene and C8 aromatics (Yuan et al., 2010).

Compared to the speciation of observed VOCs in daytime, the contribution of reactive VOC species to the initial VOCs was higher. The contributions of aromatics and alkenes to initial VOCs increased to ~36% and ~17%, and especially the proportion of C8 aromatics, toluene, and C2—C3 alkenes were more than 40% of the initial VOCs, followed by C4—C5 alkenes. Correspondingly, the proportion of alkanes and acetylene decreased to about ~38% and ~8% in initial mixing ratio of VOCs.

#### 3.1.2. Reactivity: the OH loss rate and the ozone formation potential

The OH loss rate ($L^{OH}$) and OFP of each VOC species was calculated to evaluate the VOC reactivity combining with the constant of OH loss rate ($k_{OH}$) and maximum incremental reactivity (MIR) (Atkinson et al., 2006; Carter, 2008). The average reactivity of VOCs was calculated as the ratio of the total $L^{OH}$ or OFP to the mixing ratio.

For the reactivity of observed VOCs, no significant differences were observed between 2009 and 2010. The total $L^{OH}$ in these two years was ~6 s$^{-1}$, and the OFP was ~120 ppbv. The reactivity during nighttime was higher than that in daytime by ~20% for both $L^{OH}$ and OFP, mainly because of the higher mixing ratio of VOCs in nighttime. The average $k_{OH}$ and MIR were 8.7 × 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and 4.2 (mol O$_3$/mol VOCs), respectively. These values are comparable to those of ethylene (Atkinson et al., 2006; Carter, 2008), respectively.

In the case of the initial reactivity, the total $L^{OH}$ in these two years was ~10 s$^{-1}$ and the OFP was ~186 ppbv. Compared to the observed reactivity in daytime, the initial $L^{OH}$ and OFP increased by

above by the ratios of toluene/benzene and o-xylene/toluene, and found that their results agreed well with the literature rate coefficients until the rate coefficient of toluene (in the case of using toluene/benzene ratio) or o-xylene (in the case of using toluene/o-xylene). For the VOC species with faster removal than that of toluene (in the case of using toluene/benzene ratio) or o-xylene (in the case of using toluene/o-xylene), the rate coefficients became constant according to de Gouw et al. (2005) results, and the rate coefficients of alkenes were determined with large uncertainties as

67% and 55%, respectively. The average $k_{OH}$ and MIR of the initial VOCs was $11.6 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and 5.4 (mol O$_3$/mol VOCs), respectively. Most of the increment resulted from alkenes and aromatics as indicated in Fig. 2.

Further examination showed that the largest contributing species to $L^{OH}$ were C4–C5 alkenes, C8 aromatics, C2–C3 alkenes and toluene. These species took up about 75% of the total $L^{OH}$ of observed VOCs and this proportion increased to 81% for the initial $L^{OH}$. Specifically, C4–C5 alkenes and C8 aromatics contributed about 44% and 26% of the increment part ($L^{OH}$ of consumed VOCs), followed by C2–C3 alkenes (14%). In the case of OFP, C8 aromatics and toluene contributed 48% of the observed OFP, followed by alkenes. The contribution of these reactive species to the initial VOCs OFP increased at different extent dependent on their reactivities. Most of the increment OFP was attributed to C8 aromatics (44%), and toluene and the other aromatics accounted for 22%, followed by C4–C5 and C2–C3 alkenes.

### 3.2. Monthly variations

Two peak periods of the initial VOC mixing ratio were observed through the whole year as shown in Fig. 3. One period was from October to the next January, and the average initial VOCs was 30–50 ppbv, which was generally resulted from the unfavorable meteorological condition, such as inversion layer, the effect of cold front or uniform pressure field in winter (Zhang et al., 2010). The second one was from June to July. The peak value of the average initial VOCs was ∼30 ppbv, slightly lower than that of the previous period. During the second period, the frontal inverted trough or stagnant high pressure system with the southwest flow occurred frequently, which always resulted in the poor diffusion condition (Zhang et al., 2010). Besides the effect of meteorological conditions, chemical and petrochemical industrial factories locating in the

southwest and south of the monitoring site (Huang et al., 2011) had large impact on the VOC level at the monitoring site in summer, especially in June and July, and winter, but less impact in spring and autumn (Cai et al., 2010).

Monthly variations of consumed VOCs were also shown in Fig. 3, as well as its speciation and the oxidants (Ox = O$_3$ + NO$_2$) levels (Ox data were not available until March in 2010). The consumed VOCs were likely responsible for the production of oxidants, which was indicated by the modest correlation between Ox and consumed VOCs as shown in Fig. 3. The similar variation trends of consumed and initial VOCs suggested the large impact of the meteorological conditions on consumed VOCs mixing ratio. The speciation of consumed VOCs was shown in Fig. 3(c) and Fig. 3(d). Most of the consumed VOCs were C8 aromatics, C2–C3 alkenes, C4–C5 alkenes and toluene, taking up ∼60% of consumed VOCs on average through the whole year.

Although toluene was one important contributor of the consumed VOCs, the consumed toluene took up only ∼28% of the initial toluene, which was lower than that of total VOCs, because toluene was not very reactive (Atkinson et al., 2006). Both the consumed and initial toluene appeared the similar variation trends with those of total VOCs, as shown in Fig. 4. By contrast, consumed isoprene accounted for less than 2% of total consumed VOCs but contributed more than 60% of initial isoprene because of its large rate coefficient and the fast removal. In particular, the monthly variation of isoprene showed a totally different trend from those of total VOCs and toluene, which agreed well with the ambient temperature, as shown in Fig. 4(d).

### 3.3. Diurnal variations

The diurnal variation of VOCs was investigated in this section aiming to provide some insights into the effect of VOC consumption
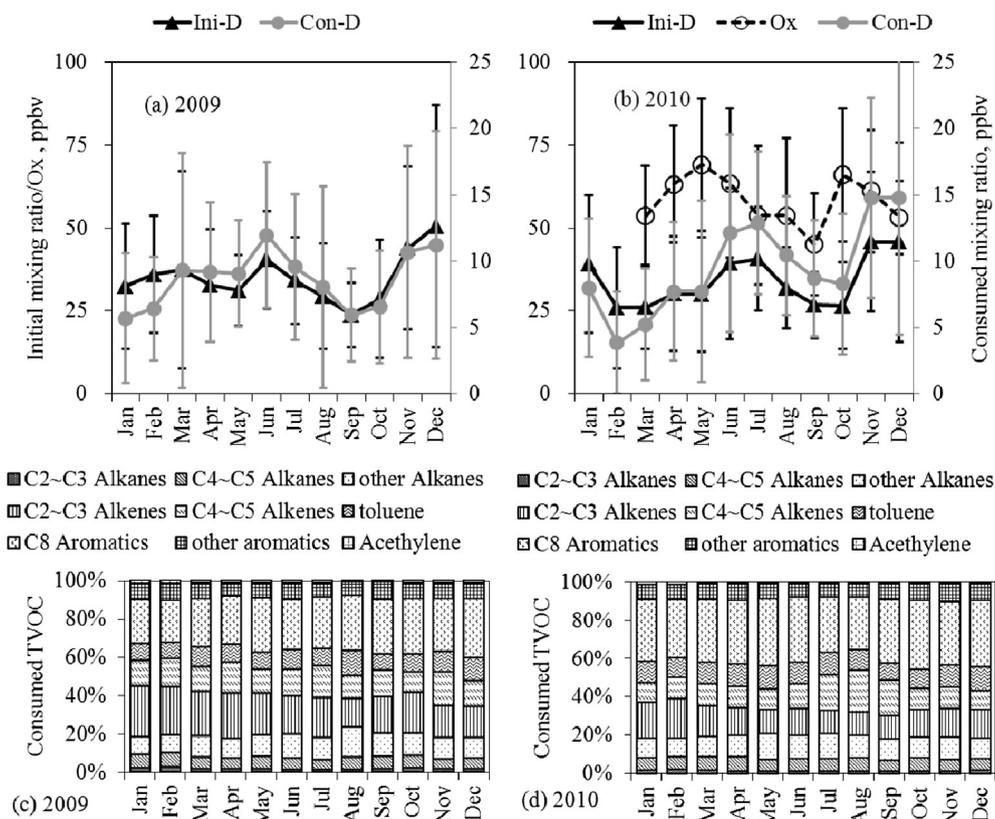


Fig. 3. The monthly variation of VOCs and its composition (Ini-D: initial VOCs during daytime, Con-D: consumed VOCs during daytime, Ox: O$_3$ + NO$_2$).
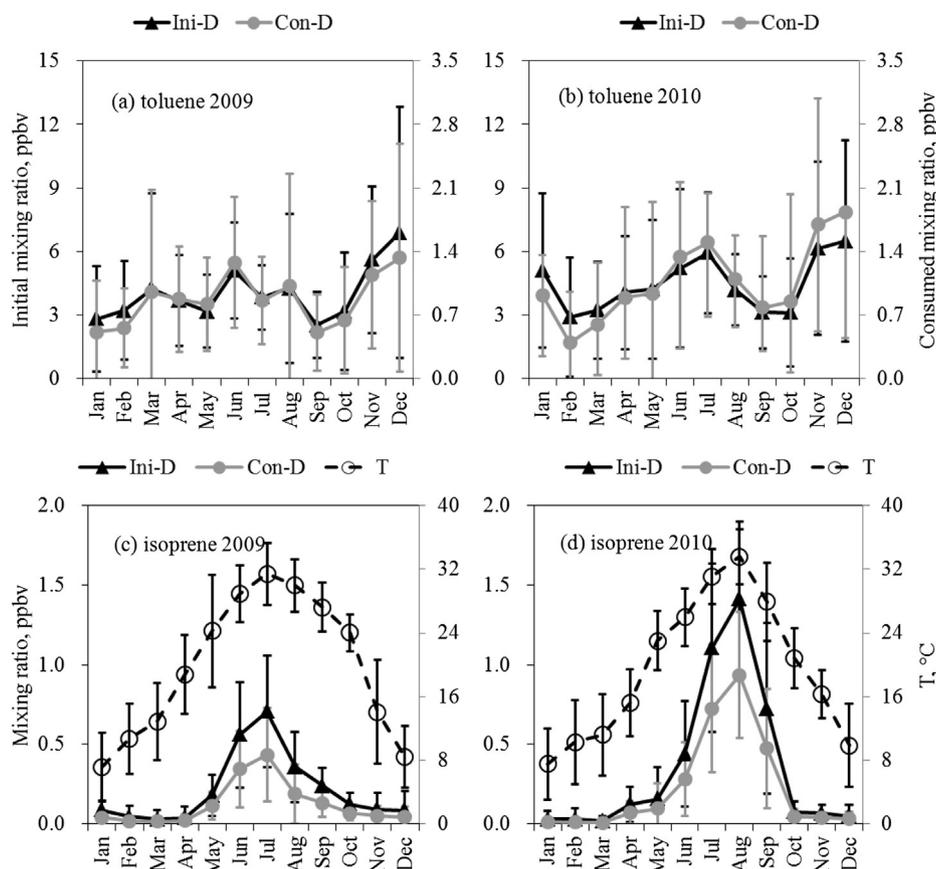
**Fig. 4.** The monthly variation of toluene (a, b), isoprene (c, d) and temperature (Ini-D: initial VOCs during daytime, Con-D: consumed VOCs during daytime, T: temperature).

on oxidants production and the factors that impacted the chemical loss of typical VOC species.

As shown in Fig. 5(a) and (b), the lowest initial mixing ratio appeared during 13:00 to 14:00 in the diurnal variation of initial VOCs, which was generally caused by the higher mixing layer during this period. Higher initial mixing ratios could be observed at early morning and late afternoon, which was the product of large vehicle emissions and lower mixing layer during these periods. The ratio of chemical loss to initial VOCs (Con/Ini) and Ox mixing ratio were also shown in Fig. 5(b), and their diurnal variations were in good agreement with each other, indicating more Ox production from more chemical loss of VOCs. As a marker of anthropogenic emissions, toluene displayed the similar diurnal variation trend with that of initial VOCs, as well as that of Con/Ini ratio but with a lower ratio of 0.23 compared to 0.27 for VOCs, which was due to the relatively low reactivity of toluene.

Different from toluene, the initial mixing ratio of isoprene increased from 8:00 due to the increase emissions caused by the temperature rise (Guenther et al., 2006) and arrived at the peak value until 10:00. After 10:00 the initial isoprene decreased slowly due to the high mixing layer and the decrease became faster after 14:00, which might be because of the less emissions due to the decrease of temperature, as shown in Fig. 5(e) and (f). The temperature might be also responsible for the chemical loss of isoprene, because the Con/Ini of isoprene agreed well with the temperature, as indicated in Fig. 5(e) and (f).

### 3.4. Comparison with other regions

The top ten abundant species measured in Shanghai and another four cities were listed in Table 1. Nagoya and Dallas were

selected because VOCs in these two cities were measured continuously by on-line GC-FID and the measurement periods covered one year at least (Qin et al., 2007; Saito et al., 2009), which was very similar to this study. Moreover, the VOCs measurement in another two megacities in China, Guangzhou and Beijing, and the previous study in Shanghai were also listed.

As shown in Table 1, there was some difference between this study and the previous study in Shanghai (Cai et al., 2010). Besides the three C2 species (i.e. ethane, ethylene, and acetylene) not reported in the study by Cai et al. (2010), the other seven species listed in the top ten abundant species in this study were also reported by Cai et al. (2010). However, the mixing ratios of these species were higher in the study by Cai et al. (2010), especially for propane, i-pentane, and butane which were recognized as the indicators of vehicular emission (Blake and Rowland, 1995; Liu et al., 2008). This was probably because the samples taken by Cai et al. (2010) were mostly collected during the rush hours (6:00–9:00).

Compared to other cities, the VOCs mixing ratio in Shanghai was similar to that in Nagoya, and much lower than those in Dallas and Guangzhou. Alkanes were the dominant VOCs species for all the listed cities, followed by aromatics and alkenes. The percentage of aromatics in Shanghai was higher than those in other cities, maybe due to the large industry in Shanghai (Huang et al., 2011). Further examination showed that Shanghai had the highest percentage of toluene among these cities, mainly due to the large chemical industry in Shanghai; Guangzhou had the highest mixing ratio of propane (6.83 ppbv), due to the widespread usage of liquid petrol gas (LPG) in domestic and vehicles sectors (Yuan et al., 2012a). Compared to the other cities, isoprene concentration in Shanghai was the lowest.

The ratio of toluene to benzene (T/B) is usually used to evaluate the contribution from the vehicular emissions. In general, the ratio
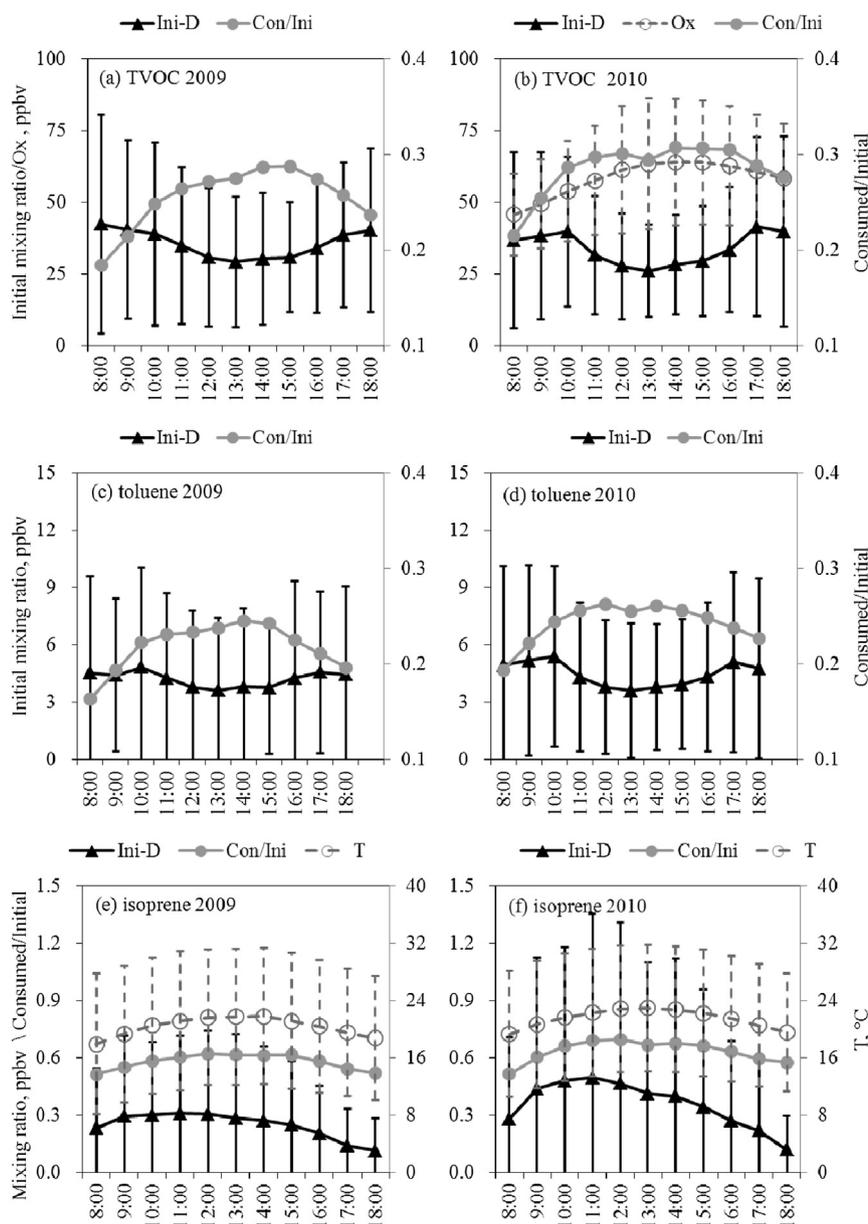
**Fig. 5.** The diurnal variation of TVOC (a, b), toluene (c, d), and isoprene (e, f) (Ini-D: initial VOCs during daytime, Con/Ini: the ratio of consumed mixing ratio to initial mixing ratio during daytime, Ox: $O_3 + NO_2$, T: temperature).

of T/B between 1.5 and 2.0 is the typical value of the vehicle emissions (Nelson and Quigley, 1984; Schauer et al., 2002; Sigsby et al., 1987), and the ratio of T/B will increase with the increase of the contribution from non-vehicular emissions. Table 1 summarized the ratio of T/B in different areas. From Table 1, we can see that the ratios of T/B in three Chinese megacities were lower than that in the other cities, suggesting that in megacities of China, the contribution from the vehicular emission were more important. In detail, Beijing and Guangzhou had the lowest T/B ratio (Wang et al., 2010; Yuan et al., 2012a), and suggested that the vehicular emission was the dominant contributor of VOCs. The T/B ratio of Shanghai was larger than those of Beijing and Guangzhou, but lower than those of Dallas and Nagoya, suggesting the comparative importance of the vehicular and non-vehicular emissions in these two cities.

Notably, the T/B ratio here (sign as $T/B_{(Ct)}$) were obtained based on the observed toluene and benzene. While, 1.5–2.0 is the value of T/B ratio in vehicular emission, and actually, it is the ratio of the initial mixing ratio of toluene to that of benzene in vehicle source

(sign as $T/B_{(C0)}$). The chemical loss of toluene and benzene are quite different due to the different chemical reactivities. Directly comparing these two ratios would result in the misestimate of the source contribution.

Considering mentioned above, the $T/B_{(C0)}$ in Shanghai were calculated by the methods mentioned in section 2.3. As a result, $T/B_{(C0)}$ was 30% larger than $T/B_{(Ct)}$. In detail, in year 2009, the annual average of $T/B_{(Ct)}$ and $T/B_{(C0)}$ were (2.59 ± 0.54) and (3.33 ± 0.67), respectively, and for 2010, were (3.51 ± 0.87) and (4.62 ± 1.20), respectively. The increase from $T/B_{(Ct)}$ to $T/B_{(C0)}$ could be explained by the larger reactivity of toluene than benzene. Consequently, the contribution of non-vehicular source might be underestimated by using $T/B_{(Ct)}$.

### 3.5. Source apportionment of VOCs

The receptor model, PMF 3.0 (US-EPA), was applied to analyze the hourly VOCs data set. 34 VOC species were included in PMF

**Table 1**
The top 10 abundant species, isoprene, and the ratio of toluene to benzene (T/B) measured in different cities, ppbv.

| Shanghai[a] | | Nagoya Japan[b] | | Dallas USA[c] | | Shanghai[d,g] | | Guangzhou[e,g] | | Beijing[f,g] | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2009–2010 | | 2003.12–2004.12 | | 1996–2004 | | 2007–2010 | | 2006.7 | | 2008.6–2008.9 | |
| TVOC | 27.82 | TVOC | 28.60 | TVOC | 41.50 | TVOC | 25.42 | TVOC | 41.26 | TVOC | 27.38 |
| Alkane | 12.82 | Alkane | 16.59 | Alkane | 29.50 | Alkane | 13.91 | Alkane | 22.46 | Alkane | 14.66 |
| Aromatic | 8.72 | Aromatic | 5.43 | Aromatic | 7.06 | Aromatic | 9.70 | Aromatic | 8.24 | Aromatic | 4.63 |
| Alkene | 3.64 | Alkene | 4.86 | Alkene | 2.90 | Alkene | 1.94 | Alkene | 6.83 | Alkene | 5.37 |
| Toluene | 3.53 | Ethane | 3.86 | Ethane | 6.62 | Propane | 4.81 | Propane | 6.83 | Ethane | 3.17 |
| Acetylene | 2.63 | Propane | 3.34 | Propane | 5.82 | Toluene | 4.70 | Toluene | 4.03 | Propane | 2.82 |
| Propane | 2.52 | Ethylene | 2.89 | n-Butane | 4.26 | i-Pentane | 2.29 | Acetylene | 3.73 | Acetylene | 2.80 |
| Ethane | 1.92 | n-Butane | 2.66 | i-Pentane | 3.49 | n-Butane | 2.03 | n-Butane | 3.72 | Ethylene | 2.42 |
| Ethylene | 1.73 | Toluene | 2.54 | Toluene | 2.90 | Benzene | 1.81 | Ethylene | 3.08 | i-Pentane | 1.99 |
| n-Butane | 1.46 | Acetylene | 1.99 | n-Pentane | 1.87 | i-Butane | 1.43 | i-Butane | 2.43 | Toluene | 1.71 |
| i-Pentane | 1.40 | i-Butane | 1.40 | Ethylene | 1.66 | m,p-Xylenes | 1.40 | Benzene | 1.84 | n-Butane | 1.68 |
| m,p-Xylenes | 1.38 | i-Pentane | 1.33 | i-Butane | 1.57 | Ethylbenzene | 1.23 | i-Pentane | 1.73 | i-Butane | 1.60 |
| Benzene | 1.19 | n-Pentane | 0.70 | Acetylene | 1.33 | n-Hexane | 0.84 | Ethane | 1.60 | 1-Bitene | 1.08 |
| i-Butane | 1.15 | m,p-Xylenes | 0.68 | m,p-Xylenes | 1.32 | Propene | 0.84 | Isoprene | 1.14 | Benzene | 0.84 |
| Isoprene | 0.08 | Isoprene | 0.66 | Isoprene | 0.33 | Isoprene | 0.12 | Isoprene | 1.14 | Isoprene | 0.48 |
| T/B | 2.97 | T/B | 5.23 | T/B | 3.58 | T/B | 2.60 | T/B | 2.19 | T/B | 2.04 |

[a] This study.
[b] Saito et al., 2009.
[c] Qin et al., 2007.
[d] C2 VOC species were not included, Cai et al., 2010.
[e] Yuan et al., 2012a.
[f] Wang et al., 2010.
[g] Sampling by canister and detecting by GC–MS.

analysis, which had signal-to-noise ratios (SNR) larger than three. There were 3552 and 3906 samples included in PMF analysis for year 2009 and 2010, respectively. PMF factor numbers were explored from 5 to 10 for the best solution according to the previous studies (Cai et al., 2010; Huang et al., 2011). Bootstrap analysis was run for 100 times to calculated the uncertainties of PMF results. Finally, seven factors were selected according to the resulted stable Q values. The rotation ambiguity was explored by varying the F-Peak values from −3 to 3. As a result, results from rotation were generally consistent with the runs with non-rotation. The results shown below were from the runs with non-rotation.

The factor 1 had high values of n-decane and n-nonane which were reported as the characteristic products of diesel exhaust (Liu et al., 2008). The C2–C6 alkanes and C3–C5 alkenes also showed considerable values in factor 1, which were associated with un-burned vehicular emissions and gasoline vehicular emissions (Guo et al., 2004). Thus, the physical meaning of factor 1 might be the mixtures of diesel and gasoline exhaust. The factor 2 had high contributions of ethylene, 1-butene, 1,3-butadiene and styrene which were known as the materials or products of chemical industries (Liu et al., 2008). Hence, the factor 2 was identified as the emissions from chemical industries. The factor 3 was characteristic by high isoprene values and had significant seasonal and diurnal variations as shown in Fig. 6 (a) and (c), whose peak value appeared at noontime and in summer. Thus, the factor 3 was biogenic emissions.

The major species of factor 4 were C4–C5 alkanes, and especially more than 50% of i-/n-pentane were attributed to factor 4. Additionally, the values of BTEX (benzene, toluene, ethylbenzene, xylenes) and 1,3-butadiene would not negligible. Therefore, the factor 4 was mainly considered as the mixtures of fuel evaporation and vehicular exhaust. The factor 5 contributed more than 50% of C7–C9 aromatics and showed significant diurnal variations with the higher values at noontime and in the early afternoon as shown in Fig. 6(c). C7–C9 aromatics were reported as major constituents of solvents and paints (Wang et al., 2013; Yuan et al., 2010). Thus, VOCs in the factor 5 was mainly from solvent usage and painting process.

The factor 6 was characteristic by high values of unreactive species, such as benzene, ethane, ethylene, acetylene, propane,

whose life times were several dozen hours in the condition of OH radical concentration of $5.0 \times 10^6$ molecule $cm^{-3}$. Yuan et al. (2012b) has considered this source as the aged air mass by PMF based on the observed VOCs in Beijing. However, this explanation might not be suitable in this study because the results here were on the basis of initial VOCs, and especially, the diurnal variations of its contribution to total VOCs were not significant, as shown in Fig. 6(c). Further examination indicated the contribution of factor 6 showed large seasonal variations, and specifically the factor 6 contributed much more to total VOCs in winter and early spring than that in summer, as indicated in Fig. 6(a). Additional analysis of the wind data (http://www.wunderground.com/) indicated that the larger contribution of factor 6 to total VOCs mainly appeared when the winds were from north and northwest direction, as shown in Fig. 7. As shown in Fig. 7 (right), the average wind speed from these directions was about 6 m s$^{-1}$, and on this condition the species mentioned above could be transported about several hundred kilometers because of their long lifetimes. Therefore, the factor 6 might not be the local emission source, and instead might be from the long transportation. During the air mass transportation, the reactive VOC species were largely consumed while these species with long lifetimes could be transported into Shanghai. In addition, some large steel factories and power plants located in the north and northwest of Shanghai (Cai et al., 2010; Huang et al., 2011), and VOCs emissions from coal burning in these factories might also contribute to the factor 6. Therefore, the physical meaning of the factor 6 was considered as the regional transportation from north and northwest and the local coal burning.

The major species of factor 7 were cyclohexane and C7 alkanes which were usually from the emission of fuel production processes (Liu et al., 2008). Thus, the factor 7 was primarily related to oil refinery in petrochemical industries.

According to the mentioned above, there were seven factors identified from PMF analysis. Among these factors, factor 1 and factor 4 were related to vehicular emissions. Thus, six sources of VOCs were identified. The source apportionment results were shown in Fig. 6(a) and (c), as well as the monthly and diurnal patterns of sources contributions. Generally, the largest local VOCs
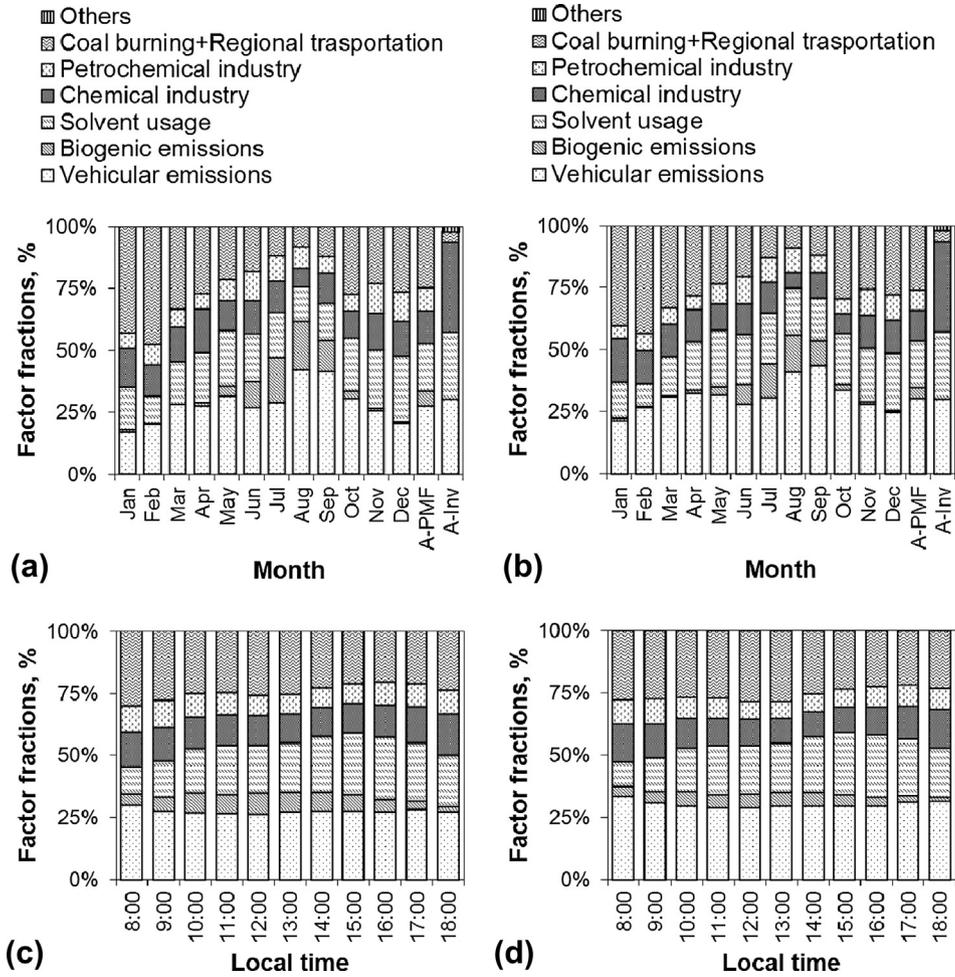
**Fig. 6.** Source apportionment results from PMF and the anthropogenic inventory in Shanghai urban (a,b), seasonal and diurnal patterns of source contributions from PMF (c,d). a and c, results based on initial VOCs; b and d, results based on observed VOCs; A-PMF, annually average source apportionment results in 2009 and 2010; A-Inv, anthropogenic VOCs inventory of Shanghai urban in 2010 and "Chemical industry" in A-Inv including both chemical and petrochemical industry (Huang et al., 2011; Personal communication with Dr. Huang, 2013).

source in Shanghai urban was vehicular emissions (including exhaust and fuel evaporation), taking up 27.6% of total VOCs, followed by solvent usage (19.4%), chemical industry (13.2%), petrochemical industry (9.1%), and biogenic emissions (5.8%). Besides the five local sources, the regional transportation and local coal burning contributed 24.9% of VOCs in Shanghai urban. For comparison, the anthropogenic VOCs inventory of Shanghai urban in 2010 (Huang

et al., 2011; Personal communication with Dr. Huang, 2013) was also shown in Fig. 6 (a). From the inventory, the local coal burning contributed less than 5% of total VOCs. Thus, the regional transportation accounted for about 20% of VOCs in Shanghai urban with the assumption of the consistent results from PMF and inventory. Except the biogenic contribution of 5.8%, about 75% of VOCs were from the local anthropogenic sources in Shanghai urban.
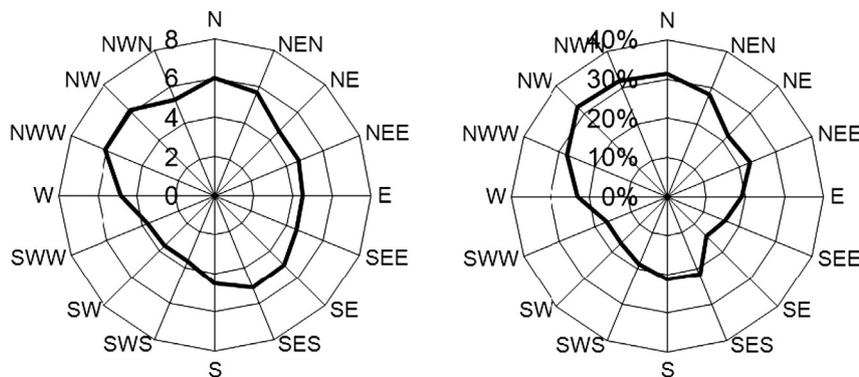


**Fig. 7.** Distributions of the wind speed (left) and the contribution of the factor 6 (right) under different wind directions.

Considering the analysis above, we amend the relative contributions of the local sources in inventory by a ratio of 0.75. Based on the comparison between the PMF results and the amended urban inventory, the solvent usage contributions by different methods matched very well; the vehicular contribution from the inventory was 22.7%, compared to 27.6% from PMF; correspondingly the industry (including chemical industry and petrochemical industry) contribution from the inventory was 27.0%, compared to 22.3% in PMF analysis. Probably, the surroundings of the sampling site might be partly responsible for the discrepancy. Meanwhile, large differences were observed between the PMF result and the anthropogenic inventory in the whole city of Shanghai. For example, the vehicular emissions contributed only 11.0% of total anthropogenic VOCs in Shanghai city, mainly because most of the vehicles were in the urban. However, the contributions of solvent usage and coal burning were 27.1% and 8.2% in city inventory (Huang et al., 2011; Personal communication with Dr. Huang, 2013), respectively, which were much larger than those in urban inventory or the PMF result. This was mainly because many industries and power plants widely spread in the rural of Shanghai (Cai et al., 2010; Huang et al., 2011), which emitted a large amount of VOCs during the industrial processes and coal burning.

For comparison, the source apportionment results of observed VOCs by PMF were also shown in Fig. 6(b) and (d). Similarly, seven factors were resolved by PMF and six similar sources were identified for the observed VOCs. Generally, the sources contributions trend was similar to that of initial VOCs. Further examination showed that the contributions of sources with more reactive species were underestimated in different extents, such as contributions of biogenic emissions (by ~30%) and chemical industry (by ~10%). In contrast, the contribution of regional transportation which was dominant by species with long lifetime was overestimated by ~10% based on the results of observed VOCs.

## 4. Conclusions and implications

A two-year monitoring result of VOCs in Shanghai urban was obtained through continuous measurement from 2009 to 2010. The initial mixing ratio of VOCs was estimated according to the photochemical evolution of the ratio between ethylbenzene and m,p-xylenes. As a result, the initial VOCs in Shanghai urban was (34.8 ± 20.7) ppbv, higher than the observed one by ~35%. The initial VOCs were composed of alkanes (~38%), aromatics (~36%), alkenes (~17%), and acetylene (~8%). C8 aromatics, toluene, and C2−C3 alkenes contributed more than 40% of the initial VOCs, followed by C4−C5 alkenes. Two pollution periods of initial VOCs, i.e. from October to next January, and from June to July, were observed through the monthly variations, which were mainly impacted by the unfavorable meteorological conditions and the large industrial emissions in south and southwest of Shanghai. The consumed VOCs showed similar monthly variation with that of Ox. While, the Ox diurnal variation was totally different from that of consumed VOCs mixing ratio, but instead agreed well with the consumed proportion of initial VOCs. Most of the consumed VOCs were C8 aromatics, C3−C5 alkenes and toluene, taking up ~60% of consumed VOCs.

$L^{OH}$ and OFP were calculated to evaluate the reactivity of VOCs. Based on the result, the total initial $L^{OH}$ was ~10 s$^{-1}$ and the OFP was ~186 ppbv, which were higher than those of observed ones by 67% and 55%, respectively. The increment part was mostly attributed to C4−C5 alkenes and C8 aromatics. C7−C8 aromatics and alkenes were dominant for the initial reactivity of VOCs. C4−C5 alkenes and C8 aromatics contributed about 44% and 26% of the increment $L^{OH}$, followed by propene and toluene. C8 aromatics proportioned 44% of the increment OFP, and toluene and the other aromatics accounted for 22%, followed by C4−C5 and propene.

A receptor model, PMF, was employed to quantify VOCs source contributions by checking the seasonal and diurnal variations of the sources. Seven VOCs sources were identified and quantified through comparing the source apportionment results from PMF analysis and the local VOCs inventory. As a result, vehicular emissions were the largest anthropogenic source of VOCs in Shanghai urban, accounting for 27.6% of VOCs, followed by solvent usage (19.4%), chemical industry (13.2%), petrochemical industry (9.1%), and coal burning (~5%). The contribution of biogenic emissions to total VOCs was 5.8%. Besides the five local anthropogenic sources and one biogenic source, the regional transportation contributed about 20% of the VOCs in Shanghai urban. The relative contributions of local anthropogenic sources from PMF analysis showed good agreement with those in local inventory. The source apportionment results based on the observed data showed some difference from those based on the initial data. Specifically, the contributions of relative reactive sources were underestimated in different extents, i.e. contributions of biogenic emissions (by ~30%) and chemical industry (by ~10%); in contrast, the contribution of regional transportation which was dominant by species with long lifetimes was overestimated by ~10%.

It should be pointed out that the initial mixing ratio of VOCs estimated in the present study was the lower limit, and especially the VOC species with faster removal than that of m,p-xylene might be underestimated a lot. Therefore, the real chemical loss of VOCs in Shanghai urban should be larger than the result of the present study. Still, very large difference between the observed data and the initial data were found according to the results of this study. Specifically, the key reactive species identified from initial or consumed VOCs were almost different from those of observed VOCs. The source apportionment results of initial VOCs also showed differences from those of observed data and were more appropriate to be applied into the formulation of air pollution control measures.

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