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Characteristics and sources of atmospheric volatile organic compounds (VOCs) along the mid-lower Yangtze River in China

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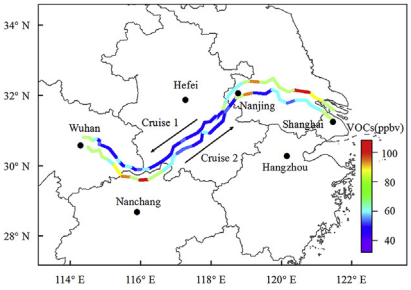
GRAPHICAL ABSTRACT



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ABSTRACT

The Yangtze River Delta (YRD), one of the most important developed urban regions in eastern China, has been experiencing severe air pollution due to the rapid economic development. VOCs characterization and sources were studied based on ship-based measurements along the mid-lower Yangtze River (MLYR). The measured VOCs mean concentration was (65.5 ± 16.8) ppbv, among which alkanes, alkenes, oxygenated VOCs (OVOCs), aromatics and halogenated hydrocarbons (XVOCs) are (26.4 ± 7.2) ppbv, (11.3 ± 3.6) ppbv, (11.3 ± 4.6) ppbv, (6.3 ± 2.6) ppbv, (5.9 ± 2.7) ppbv, and (4.4 ± 1.8) ppbv, respectively. Interestingly, the present result shows much lower aromatics fractions and higher long-lived species fractions than those in YRD's urban and suburban areas, which is similar to those in rural areas, but higher ship emissions-related species fraction than those in rural areas. The positive matrix factorization (PMF) model is used to identify and apportion the possible sources of ambient VOCs along the MLYR. According to source apportionment, the shipping emission takes up (23.5 ± 20.0)% of total VOCs on average. Moreover, the other three sources are also identified for VOCs with somewhat spatial variability, including chemical and petrochemical industries (12.9 ± 9.2%), combustion-related emissions (36.1 ± 17.9%), and regional aged air mass (27.5 ± 16.2%). In general, the VOCs sources in

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the waterway are very different from those published results over urban and suburban areas in the YRD. The present study highlights that rural VOCs pollution should be paid attentions to, and common differentiated controlling measures are essential to reduce emissions in the whole YRD.

1. Introduction

Volatile organic compounds (VOCs), as the key precursors of tropospheric ozone (O_3) and secondary organic aerosols (SOA) (Atkinson, 2000; Chameides and Walker, 1976; Seinfeld and Pandis, 2006; Volkamer et al., 2006), have received increasing attention in recent years. Because of a large amount of anthropogenic emissions, now VOCs become an open question to prevent and mitigate air pollution in China. To date, many studies have been conducted to explore the characteristics, activities, and emission sources of VOCs at various locations throughout China over the past several years (Guo et al., 2011; Li et al., 2015; Liu et al., 2008b, 2016; Song et al., 2012; Wang et al., 2013; Xia et al., 2014; Zhang et al., 2015). Li et al. (2015) revealed that alkenes and aromatics are the largest contributors to total ozone formation potential (OFP) of VOCs in Beijing. Meanwhile, over urban areas of the Pearl River Delta (PRD), propane was observed to be the major VOCs species (Lai et al., 2009; Liu et al., 2008b; Yuan et al., 2012a). The receptor models, such as positive matrix factorization (PMF), chemical mass balance (CMB) and principal component analysis/absolute principal component scores (PCA/APCS), have been used to assess VOC sources qualitatively and quantitatively (Baudic et al., 2016; Geng et al., 2009b; Na and Kim, 2007; Xia et al., 2014). Based on these methods, vehicular emission was identified as the largest anthropogenic source of atmospheric VOCs in urban areas of Beijing and Shanghai (Geng et al., 2009b; Liu et al., 2016; Shao et al., 2011).

The Yangtze River Delta (YRD), one of most important city clusters in eastern China, has been experiencing severe air pollution in recent years, especially the increasing ozone (O_3) and the high mass fractions of secondary components in fine particles (Ding et al., 2013; Gao et al., 2009; Geng et al., 2009a; Wang et al., 2015, 2016). Widespread chemical and petrochemical industries, high energy consumption, and busy traffics (both on-road and off-road) have been believed as potential contributors to air pollutions in both local urban and surrounding rural regions due to large emissions of VOCs and other air pollutants (Fan et al., 2015; Huang et al., 2011). Recent studies have focused on the concentrations, compositions, sources, and impacts on ozone formation of VOCs in both urban and suburban areas (Cai et al., 2010; Wang et al., 2013; Xia et al., 2014), however few studies are on rural areas. In fact, the studies over rural areas are helpful for us to understand the transportation of VOCs originating from urban areas (Li et al., 2015; Tang et al., 2007). Particularly, it is critical to investigate the formation of regional air pollutions caused by ozone or secondary particles. We are also aware that the pollutants associated with shipping emissions can significantly impact air quality over the entire YRD (Fan et al., 2015).

In this study, the ship-based measurements are presented to characterize VOCs and analyze their possible sources on the middle and lower reaches of the Yangtze River (MLYR). MLYR mentioned in this study is mostly located in YRD region, along which there located the most developed cities of YRD region. Thus, measurements of VOCs along the MLYR are critical important to study the characterization and sources of VOCs in YRD region and are especially important for the understanding of VOCs regional characteristics which is not easy to study at the stationary sites.

2. Experiment and methodology

2.1. Ship cruises and sampling

Air samples were collected using an auto VOC sampler (model 1800; Entech Instruments Inc., Simi Vally, CA, USA) with stainless-steel canisters (SUMMA canisters, 3.2L, Entech Instruments Inc., Simi Vally, CA, USA) every 3 h, lasting for 180 min. The sampler container (length × width × height: 10 × 4 × 2.5 m) was placed on top of a Mobile Real-Time Haze Monitoring Platform aboard a scientific research ship (length × width: 20 × 6m). The sampling tube was installed on the upwind side to minimize contamination caused by pollutants from the observation ship self-emission. All SUMMA canisters were cleaned using high-purity nitrogen and were vacuumed before sampling.

The observation ship cruises along the middle and lower Yangtze River (MLYR) are shown in Fig. 1, during which the voyages traversed Shanghai, Jiangsu, Anhui, Jiangxi and Hubei Provinces. Cruise 1 was defined as that the observation ship departed from the Waigaoqiao Terminal of Shanghai Port (31.42°N, 121.49°E) on November 22 and cruised upstream to the Wuhan Port(30.65°N, 114.37°E) on November 29 in 2015. Cruise 2 began after ship's berthing for one night at Wuhan Port. The observation ship went back to Shanghai, following the same voyage as cruise 1 on December 4, 2015.

2.2. Chemical analysis of VOCs

Air samples were analyzed using high-performance gas chromatography combined with a mass spectrometer system and flame ionization detector (GC-MS/FID, TH-PKU 300B, Wuhan Tianhong Instruments Co., Wuhan, China). Sampled air (300 ml) was drawn through a cryogenic trap and cooled to −160 °C for pre-concentration. After being trapped, the sample was heated up to 100 °C, and all target compounds were transferred by high-purity helium (He) to the secondary trap. C2−C5 hydrocarbons were separated on a PLOT (Al_2O_3/KCl) column (15 m × 0.32 mm × 6.0 μm, Dikma Technologies, Beijing, China) and detected by a FID, while other species were separated on a DB-624 column (60 m × 0.25 mm × 1.4 μm, Agilent Technologies, Santa Clara, CA, USA) and detected using an MSD with Dean's switch.

PAMS species, listed in Table S1 (ID 1–56), were calibrated using PAMS (photochemical assessment monitoring stations) standard gas mixture (Spectra Gas Inc., NY, USA). Other VOC species were quantified by oxygen standard mixture gas (reference compendium method TO-15, US EPA, 2001) and classified into oxygenated volatile organic compounds (OVOCs) and halogenated hydrocarbons (XVOCs). Bromo-

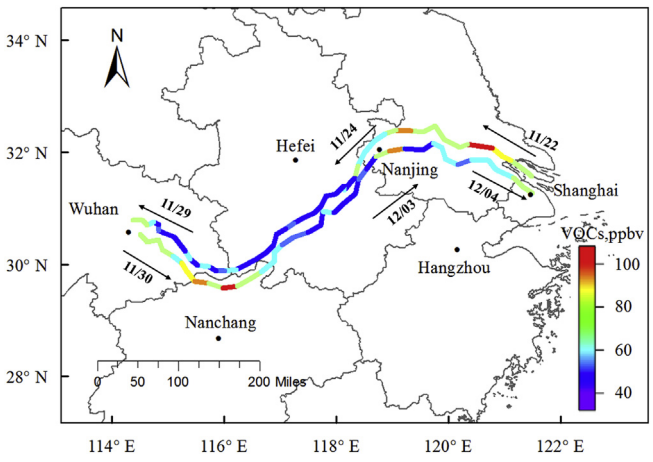

Fig. 1. VOCs concentrations along ship cruises. The cruise 1 is upstream shipping from Shanghai to Wuhan between 22 and 29 November. The cruise 2 is downstream shipping back to Shanghai from 30 November to 4 December.

chloromethane, 1,4-difluorobenzene, chlorobenzene and 4-bromofluorobenzene were used as internal standards for calibrating the analytical system. In addition, 1 ppbv PAMS standard gas and N_2 were added to the analytical system every 10 samples to check the stability and ensure no residual substances present, respectively.

2.3. Influence of self-emission from observation ship on samples

The emission of the ships is a significant type of off-road transportation source of VOCs (Fan et al., 2015). To avoid direct contamination by the self-emission of observation ship, the sampling tube was installed in upwind direction. In addition, we collected the contaminated samples near diesel generator and at diesel engine port, and compared them with air samples to estimate the potential contribution of the observation ship self-emission to ambient VOCs. Fig. 2 shows the averaged VOC profiles of contaminated and air samples. The predominant VOCs species in contaminated samples was ethylene (193.4 ± 74.3 ppbv, 36.8 ± 1.3%), whereas ethane (7.1 ± 0.9 ppbv, 10.9 ± 2.2%), acetylene (5.9 ± 2.7 ppbv, 9.0 ± 3.3%) and propane (5.7 ± 2.2 ppbv, 8.6 ± 2.0%) were most abundant in air samples. A F-test indicated that these two profiles were significantly different ($p < 0.05$). Hence, the measured atmospheric VOCs were not contaminated by the observation ship self-emission, and basically reflected the levels of atmospheric gaseous organic compounds on the mid-lower Yangtze River.

2.4. PMF model analysis

PMF is a mathematical approach for analyzing and quantifying the contribution of sources to samples based on the chemical composition or the fingerprint of targeted sources (Paatero and Tapper, 1994). As shown in Equation (1), given the factor p, the mass amount of a species can be calculated from the contribution of sources to samples and the species profile of each source:

$$\mathrm{xij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad (1)$$

where x_{ij} is measured *jth* species concentration in the *ith* sample, g_{ik} is the contribution of the *kth* source to the *ith* sample, f_{kj} is the fraction of the *jth* species from the *kth* source, and e_{ij} is the residual of the *jth* species in the *ith* sample. In this study, the PMF model was used to analyze all of the 89 collected samples based on 17 VOC species (Table S2).

Equation (1) usually leads to uncertainty due to the error fraction of species concentrations and the method detection limit (MDL, ppbv). Na and Kim (2007) estimated the error of calculated VOCs to be approximately 20%. The PMF analysis depends on the objective function (Q) to minimize the residual and uncertainty:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right] \right]^2 \quad (2)$$

where n and m are number of species and samples, respectively, and u_{ij} is uncertainty of the *jth* species in the *ith* sample. Here, Q (true) is the goodness-of-fit parameter that is calculated with all the points included, whereas Q (robust) is calculated using the points excluded by the model because they did not fit. The Q values can be used to choose the mathematically best result.

3. Results and discussion

3.1. Spatial variation of VOCs levels

Fig. 1 shows the variation of total VOCs concentration measured during the cruise 1 and the cruise 2. During the cruise 1, VOCs concentration was high in the Shanghai-Jiangsu section of the MLYR (SJ-1, 82.1 ± 13.4 ppbv), moderate in the Hubei-Jiangxi section (HJ-1, 59.2 ± 12.9 ppbv), and relatively low in the Anhui section (AH-1, 48.6 ± 9.8 ppbv). During cruise 2, VOCs concentration was high in the Hubei -Jiangxi section (HJ-2, 78.9 ± 14.0 ppbv), moderate in the Shanghai-Jiangsu section (SJ-2, 67.4 ± 12.0 ppbv), and low in the Anhui section (AH-2, 54.1 ± 4.2 ppbv). These results are roughly consistent with the spatial distribution of VOC emission intensity throughout the entire MLYR reaches (Wu and Xie, 2017). The level of PAMS species in the SJ section (56.7 ± 11.0 ppbv) was higher than those in the urban Shanghai (30.8 ± 21.2 ppbv) and the suburban Nanjing (36.5 ppbv) (Wang et al., 2013; Xia et al., 2014). The VOCs concentration in the Wuhan waterway (79.3 ± 6.3 ppbv) is significantly higher than the previous results from urban Wuhan (23.3 ppbv) (Lyu et al., 2016). Overall, the VOCs concentration is generally higher along the MLYR than that in neighboring cities and suburbs.

3.2. VOC composition

In general, the main compositions of VOCs are alkanes (26.4 ± 7.2 ppbv, 40.3 ± 4.4%), alkenes (11.3 ± 3.6 ppbv, 17.2 ± 3.2%), OVOCs (11.3 ± 4.6 ppbv, 17.2 ± 4.5%), aromatics (6.3 ± 2.6 ppbv, 9.5 ± 2.7%), acetylene (5.9 ± 2.7 ppbv, 9.1 ± 3.3%) and XVOCs (4.4 ± 1.8 ppbv, 6.7 ± 2.2%).

Fig. 3 shows the time-series of VOCs and their main compositions along the MLYR. During the campaign, the VOCs compositions vary slightly, except for acetylene which shows a larger fraction during the cruise 2 than cruise 1. On average, alkanes are the most abundant species (29.9–47.9%), followed by alkenes (9.9–26.4%), OVOCs (7.1–34.5%), aromatics (5.5–26.3%), acetylene (3.5–16.6%) and XVOCs (3.2–12.3%).

Fig. 4a presents a comparison of VOCs compositions between this study and previous studies (Li et al., 2015; Wang et al., 2013; Xia et al., 2014). It is obvious that the VOCs compositions of ship self-emission are different from those of atmospheric air. The fraction of alkenes takes up (43.6 ± 1.37)% for ship-emission. In contrast, alkanes are the most abundant components along the MLYR and in urban, suburban and rural environments. In the three cities mentioned above (Shanghai, Nanjing and Beijing) and at two rural sites (Gucheng and Quzhou), alkanes account for 46.7%, 47.5%, 45.8%, 48.9% and 56.8%, of total VOCs, respectively (Li et al., 2015; Wang et al., 2013; Xia et al., 2014). With the exception of "others" compositions, the proportion of alkanes in PAMS species is higher on the MLYR (53.0 ± 4.0%) than those in Shanghai (46.6%) and Nanjing (47.5%) (Fig. 4b). Meanwhile, the fraction of acetylene in this study (11.8 ± 4.0%) is also higher than those in Shanghai (9.0%), Nanjing (8.2%) and Beijing (9.2%), but the fractions of aromatics (12.6 ± 3.7%) are lower in these three sites

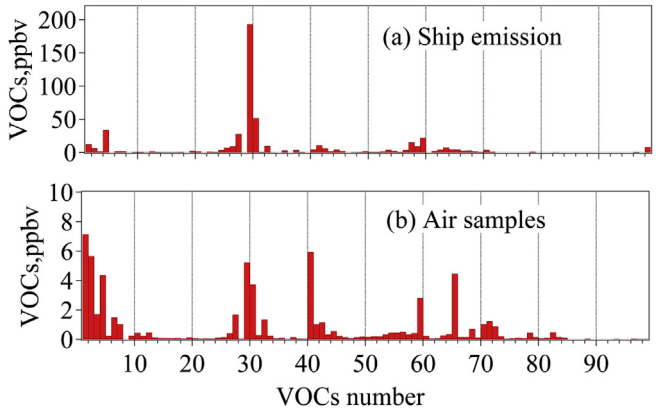

Fig. 2. Average concentrations of VOCs (a) by ship own exhaust and (b) in air samples. The numbers at x-axis are the ID of compounds listed in Table S1.

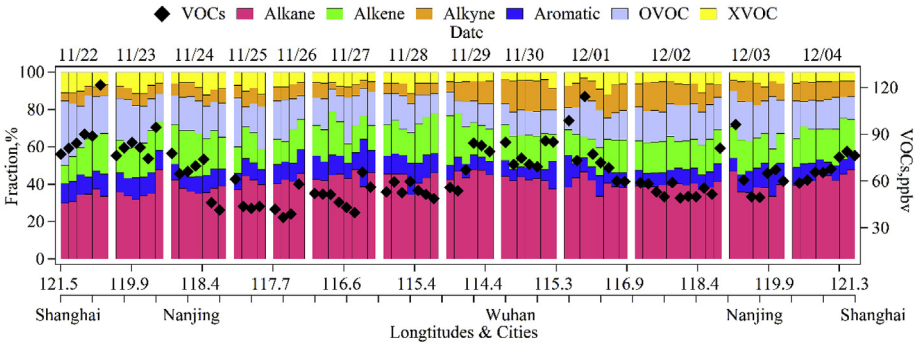

Fig. 3. Fractions of major VOC compositions and VOCs concentrations along the ship cruises. The numbers at x-axis correspond to the longitudes of ship cruise and main cites.

(Fig. 4b). VOCs compositions are relatively similar among MLYR and rural areas of Gucheng and Quzhou, as shown in Fig. 4b. However, VOCs concentration is much lower in Gucheng and Quzhou. One possible reason is different sampling seasons, that is, the present study was carried out in winter with frequent unfavorable diffusion conditions to pollutants and more VOCs emissions due to heating in northern China, while the studies in Gucheng and Quzhou were carried out in summer with relatively favorable meteorological conditions (Li et al., 2015). The other reason is that the YRD region is one of the strongest VOCs emission areas in China. There are more VOCs emissions in YRD region, compared with Hubei Province which Gucheng and Quzhou are located in (Wu and Xie, 2017).

The top 10 species measured in this study are presented in Table 1. In comparison with those from nearby major cities along the MLYR and other regions in China (Li et al., 2015; Liu et al., 2008b; Lyu et al., 2016; Wang et al., 2013; Xia et al., 2014), the content of aromatics is less along the MLYR than those in Shanghai and Wuhan. In addition, the relatively unreactive species with long life time (Atkinson and Arey, 2003) are more abundant along the MLYR than those in urban cities. The result suggests that VOCs is the possible representative of regional characteristics along the MLYR.

3.3. Ozone formation potential (OFP)

The OFP is usually used to evaluate the capacity of VOCs to form ozone (Carter, 1994), which can be calculated by the maximum incremental reactivity (MIR) (Carter, 2008):

$$\mathrm{OFP_i} = VOC_i \times \mathrm{MIR_i} \quad (3)$$

The top 10 contributors to total OFP on the MLYR are propylene, ethylene, methylmethacrylate, 1-butene, 1,2,3-trimehylbenzene, m/p-xylene, *m*-diethylbenzene, toluene, 1,2,4-trimehylbenzene and n-butane, accounting for (63.1 ± 4.0)% of total OFP. As shown in Table 1, in term of concentration and OFP contribution, 5 compounds are identified as key VOC species, including ethylene, propylene, n-butane, toluene and m/p-xylene. They are used as key species in source analysis in next section.

3.4. Sources of VOCs

3.4.1. Species ratio

Following the method of Zhang et al. (2016), we found that the ratio of benzene, toluene and ethylbenzene (B:T:E) is useful to classify VOC sources as industrial, traffic-related or combustion-related emissions (e.g., biomass, biofuel, or coal burning). Based on recently reported source profiles (e.g., Liu et al., 2008a; Wang et al., 2014a; b; Wang et al., 2017; Yuan et al., 2010; Zhang et al., 2015), these three type emissions can be grouped into combustion source characterized by an extremely high proportion of benzene, into traffic source characterized by high toluene and benzene, and into industry source characterized by higher toluene and ethylbenzene and lower benzene. Accordingly, the mean B:T:E ratios are 0.69:0.27:0.04 for combustion source, 0.31:0.59:0.10 for traffic source, and 0.06:0.59:0.35 for industrial sources (Zhang et al., 2016).

In this study, higher levels of benzene (0.41) and toluene (0.56), and

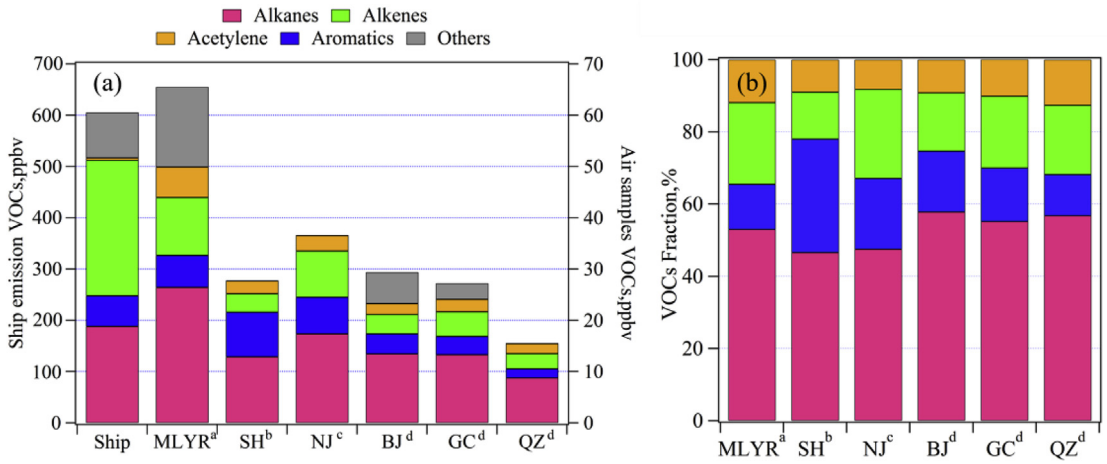

Fig. 4. (A) Concentrations of major VOC types in samples polluted by observation ship exhaust, and in air samples on the MLYR, at the cities such as Shanghai (SH), Nanjing (NJ) and Beijing (BJ) and at the rural sites such as Gucheng (GC), Quzhou (QZ); and (b) fractions of major VOCs types in air samples on the MLYR, at the cities such as Shanghai (SH), Nanjing (NJ) and Beijing (BJ) and at the rural sites such as Gucheng (GC), Quzhou (QZ). (superscript: a: the middle and lower Yangtze River; b: Wang et al., 2013; c: Xia et al., 2014; d: Li et al., 2015).

Table 1
Top-10VOC species measured in this study and at various urban sites in China (ppbv).

MLYR[a]		Shanghai[b]		Nanjing[c]		Wuhan[d]		Beijing[e]		Gucheng[e]		Quzhou[e]	
2015		009-2010		2011-2012		2013-2014		2014		2014		2014	
Ethane	7.44 ± 0.94	Toluene	12.8	Ethane	5.69 ± 4.45	Ethane	5.2	Ethane	4.37 ± 1.65	Ethane	4.43 ± 1.93	Ethane	3.53 ± 1.51
Acetylene	5.93 ± 2.70	Acetylene	8.7	Ethylene	4.5 ± 2.3	Ethylene	3.3	Propane	2.44 ± 1.57	Ethene	3.04 ± 2.39	Acetylene	1.94 ± 1.12
Propane	5.66 ± 2.15	Propane	3.6	Acetylene	3.0 ± 1.7	Toluene	2	Ethylene	2.33 ± 1.58	Propane	2.61 ± 1.65	Ethene	1.92 ± 1.61
Ethylene	5.24 ± 1.78	Ethane	3.5	Propane	3.0 ± 1.4	Acetylene	1.9	Acetylene	2.17 ± 1.42	Acetylene	2.45 ± 1.66	Propane	1.31 ± 0.95
n-Butane	4.36 ± 1.89	Ethylene	2.6	Benzene	2.7 ± 2.1	Propane	1.9	n-Butane	1.43 ± 1.04	n-Butane	1.43 ± 1.07	Benzene	0.81 ± 0.48
Propylene	3.78 ± 1.37	n-Butane	1.9	1-Butene	1.9 ± 1.0	Benzene	1.7	Toluene	1.33 ± 1.12	Toluene	1.31 ± 1.46	iso-Pentane	0.60 ± 0.57
iso-Butane	1.72 ± 1.04	iso-Pentane	1.7	Propylene	1.9 ± 1.2	n-Butane	1.3	iso-Butane	1.03 ± 0.83	0.83 iso-Butane	1.21 ± 0.87	n-Butane	0.59 ± 0.46
iso-Pentane	1.50 ± 0.66	m/p-xylene	1.5	Toluene	1.7 ± 1.1	iso-Butane	1.1	iso-Pentane	0.99 ± 0.69	Benzene	1.08 ± 0.68	n-Pentane	0.50 ± 0.98
Toluene	1.09 ± 0.68	Benzene	1.4	n-Butane	1.5 ± 0.8	Propylene	0.5	Benzene	0.82 ± 0.52	iso-Pentane	1.07 ± 0.82	Toluene	0.48 ± 0.35
n-Pentane	1.04 ± 0.57	iso-Butane	1.4	iso-Butane	1.3 ± 0.6	Ethylbenzene	0.5	n-Pentane	0.56 ± 0.43	Propylene	0.84 ± 1.66	Isoprene	0.47 ± 0.68

Superscript: a, MLYR: this study; b, Wang et al., 2013; c, Xia et al., 2014; d, Lyu et al., 2016; e, Li et al., 2015; f, Liu et al., 2008b.

low proportion of ethylbenzene (0.13) are observed, and the compositions of most samples scatter within or near areas of traffic and combustion emissions (Fig. 5). A ternary plot of the samples reveals that traffic and combustion emissions are the dominant sources of VOCs on the MLYR. In particular, the traffic emission probably originates from shipping in the river and on-road traffic near the river. Interestingly, 2,2-dimethylbutane, as a typical tracer of gasoline vehicle source (Cai et al., 2010), was lower than the detection limit of GC-MS/FID system. Therefore, on-road traffic emission has a negligible influence on atmospheric VOCs on the MLYR in this study. In comparison, 2,2-dimethylbutane concentration was 0.49 ppbv in suburban Nanjing (Xia et al., 2014). Meanwhile, the averaged proportion is scattered in the composition scope of industrial emission in rural YRD (Fig. 5), with a B:T:E ratio of 0.17:0.51:0.32 (Zhang et al., 2016). In urban Shanghai, industrial and traffic emissions are dominant VOC sources (Cai et al., 2010). In urban Wuhan, the mean ratio is different from both aforementioned domains and more closer to that of traffic and combustion emissions, suggesting that each of three emissions types is of considerable importance, particularly vehicular exhaust and combustion (Lyu et al., 2016). In suburban Nanjing, the mean ratio is relatively similar to that in the MLYR (Xia et al., 2014).

3.4.2. *Major sources identified by PMF*

The PMF analysis is used to identify four sources of VOCs, such as industry emission, shipping emission, combustion-related emission and regional aged air mass. Fig. 6 shows the percentages and distributions of VOC species among four factors.

The first factor is dominated by toluene, ethylbenzene and xylenes (Fig. 6a) and identified as industry emissions, including m/p-xylene (82.0%), ethylbenzene (80.5%), o-xylene (74.8%) and toluene (56.4%) that mainly originate from industry and solvent usage (Borbon et al., 2002; Guo et al., 2011; Wang et al., 2014b). The next contributor is propylene (45.6%) from petrochemical industry (Wei et al., 2014).

The second factor is composed mainly of ethylene (44.9%) and n-undecane (54.3%), identified as shipping emission (Section 2.3 and Fig. 2). The n-undecane has already been found in pollutants associated with diesel vehicular exhaust (Liu et al., 2008a), in particular of ship operated by diesel engines (Fan et al., 2015). Therefore, the second factor is related to shipping emission, which is a unique and significant source on the river.

The third factor is characterized by high percentages of acetylene and propylene, which are typical species from combustion emission (Baker et al., 2008; Barletta et al., 2005; Wu et al., 2016). In addition, iso-pentane, iso-butane, n-butane and propane are also emitted from combustion processes and liquefied petroleum gas (LPG) (Guo et al., 2011; Lai et al., 2009). In this study, the ship cruised a long distance across urban, suburban and rural regions, each of which were influenced by a variety of combustion (e.g., biomass burning) and LPG usage (e.g., household) (Guo et al., 2004; Li et al., 2017; Lyu et al., 2016). Although it is difficult to resolve individual source for third factor, the third factor can be considered as a combustion-related emission.

The fourth factor is mainly dominated by acetone (53.5%),

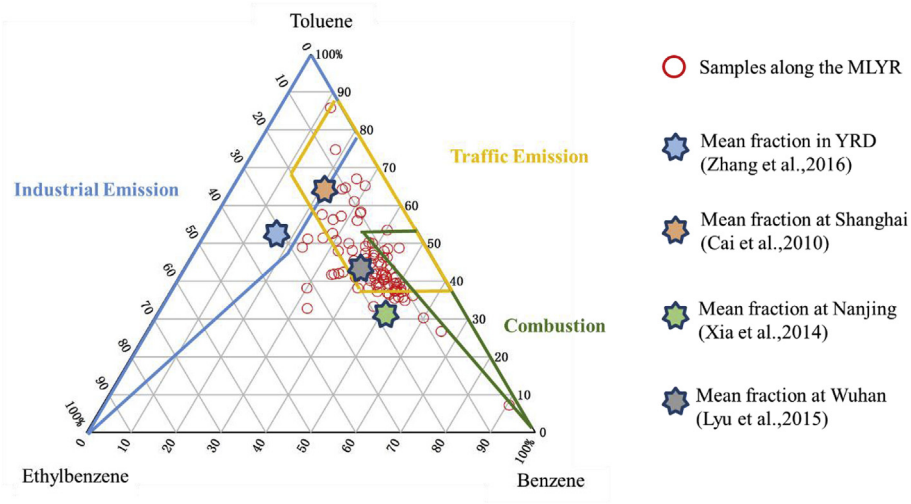

Fig. 5. Proportions of benzene, toluene and ethylbenzene from combustion, traffic and industrial emissions along the MLYR waterway, in the Yangtze River Delta (YRD, Zhang et al., 2015), and at the cities of Shanghai (Cai et al., 2010), Nanjing (Xia et al., 2014) and Wuhan (Lyu et al., 2016).

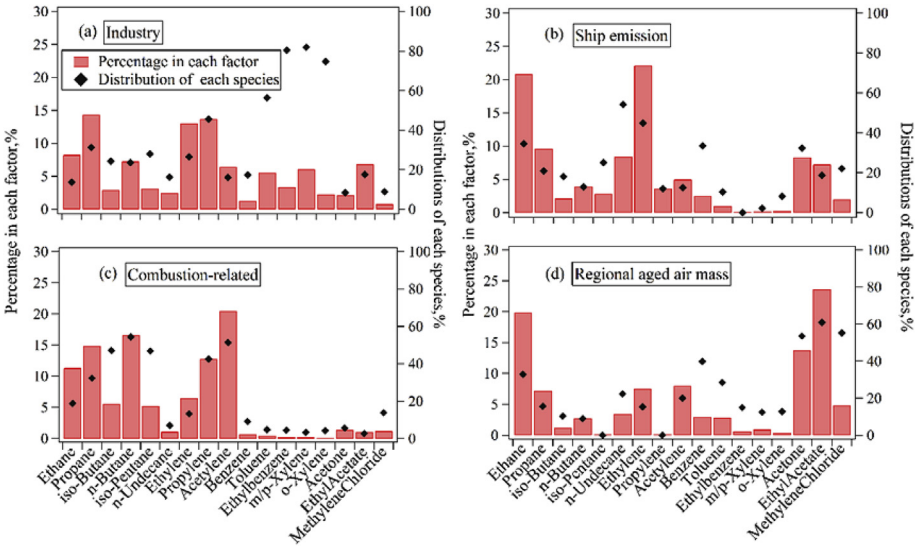

Fig. 6. Source composition profiles (percentage) and distributions by emission among the factors of PMF solution, such as (a) *industry*, (b) *ship emission*, (c) *combustion-related emission and* (d) regional *aged air mass.*

ethylacetate (60.9%), benzene (39.9%) and ethane (32.9%), with relatively long lifetimes of 64, 9, 9, and 48 days in the atmosphere assuming OH radical concentration as 2.0×10^6 molecules cm^{-3}, respectively (Atkinson et al., 2006). Because of low reactivity of above species, the fourth factor can be defined as regional aged air mass, indicative of local background and long-range transport. Generally, the factor fraction of aged air mass increases as VOCs become more unreactive, and the correlation between factor fraction of each species and its k_{OH} value is expected (Bon et al., 2011; Yuan et al., 2012b). The scatterplots of factor fractions versus OH rate (k_{OH}) for VOC species are shown in Fig. 7 (Atkinson et al., 2006). Only a polynomial fit to the data point (blue line) is noted for "regional aged air mass", which is a mixing source in the above analysis, in Fig. 7d. While other three factors do not show any correlation in Fig. 7a, b and c. Moreover, the regional aged air mass factor decreases as the VOCs become relatively unreactive because of the dominant contributions of the relatively low reactive species (i.e., acetone and ethylacetate).

3.4.3. Comparison with previous studies

Fig. 8 shows the results of VOCs source apportionment in previous

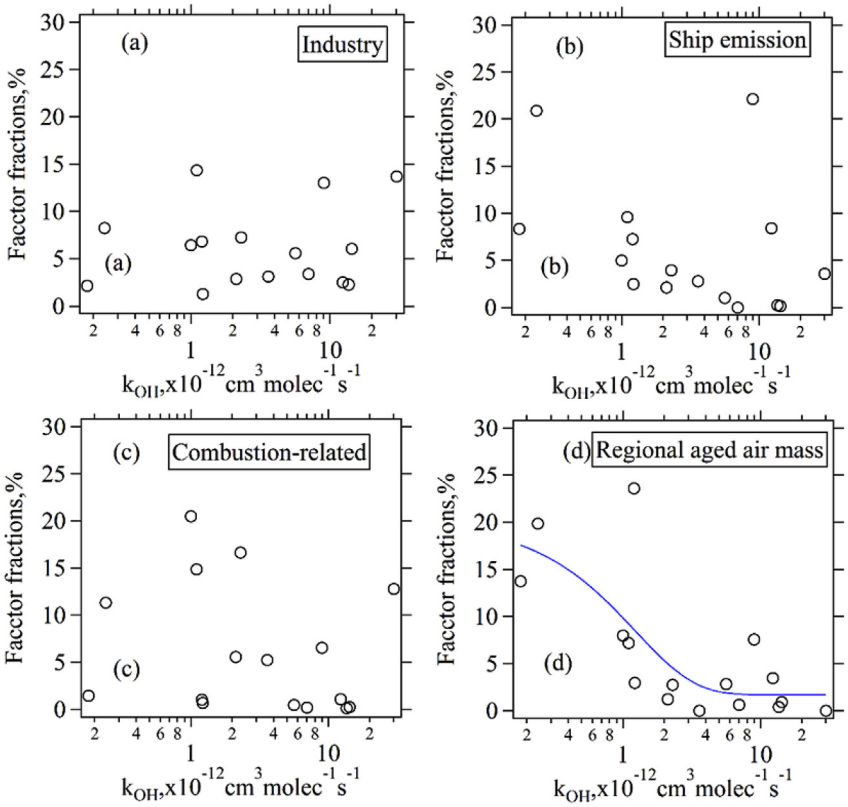

Fig. 7. Scattering points between factor fractions of VOC species and k_{OH} value for sources of (a) industry, (b) ship emission, (c) combustion-related emission and (d) regional aged air mass. k_{OH} respects OH rate constant.

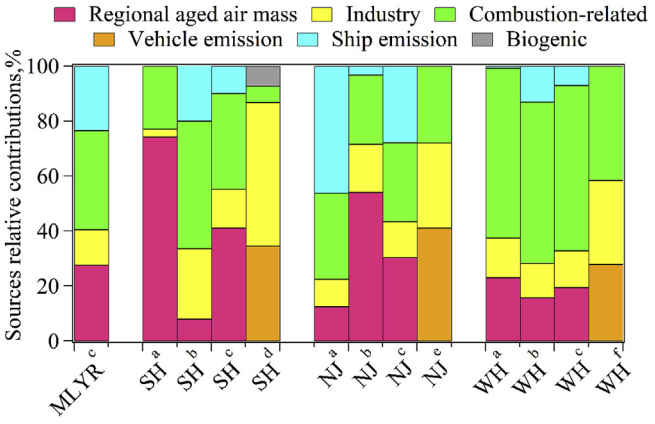

Fig. 8. Relative contributions of sources on the middle and lower Yangtze River (MLYR) and in the cities of Shanghai (SH), Nanjing (NJ), Wuhan (WH). The superscripts are (a) cruise 1 in this study, (b) cruise 2 in this study, (c) averaged along the MLYR, (d) Wang et al. (2013), (e) Xia et al. (2014), and (f) Lyu et al. (2016).

and the present studies, including in riverside Shanghai, Nanjing and Wuhan. On the MLYR on average, the predominant sources of VOCs were combustion-related emission (36.1 ± 17.9%), regional aged air mass (27.5 ± 16.2%), shipping emission (23.5 ± 20.0%) and industry emissions (12.9 ± 9.2%).

As shown in Fig. 9, in riverside Shanghai, the air mass transported from the East China Sea during cruise 1 but from southern Jiangsu Province during cruise 2. According to Fig. 8, the relative contribution of regional aged air mass during cruise 1 was much higher than that during cruise 2, which may result from the lack of local emissions in East China Sea. Also, the relative contribution of combustion-related emission during the cruise 2 was twice as much as that during the cruise 1. Based on Wu and Xie (2017), the combustion-related emission in Jiangsu Province was also twice as much as that in Shanghai, which indicates that the source relative contribution may be influenced by the regional transportation. In riverside Nanjing (Fig. 8), there was a high relative contribution of shipping emission during cruise 1. The air mass trajectory which passed through the Yangtze River during cruise 1, may be responsible for the difference of shipping emission contribution between cruise 1 and cruise 2. In riverside Wuhan, the source contributions of VOCs were relatively similar between the cruise 1 and the cruise 2 due to the weak regional transportation caused by low wind speeds (Fig. 9), which mainly reflected the high relative contribution of combustion-related of local emission (Lyu et al., 2016).

Present results of source apportionments are compared with those in the previous studies for those three major cities in YRD (Fig. 8). It is worth noting that solvent usage and the chemical and petrochemical industries are grouped into industry emissions; The fuel evaporation and the vehicular exhaust are grouped into vehicle emissions. In the riverside of Shanghai, the regional air mass (average of cruise 1 and 2) is the dominant source (41.0 ± 38.7%) (Fig. 8), which is quite different from that in urban Shanghai (Wang et al., 2013). In this study, the comparison shows that combustion-related emissions prevail among VOC sources in both suburban Nanjing (28%) (Xia et al., 2014) and riverside Nanjing (average of cruise 1 and 2) (28.6 ± 15.1%). However, the other sources showed differing contributions. Although combustion-related emissions are the most important contributor to VOCs in both riverside and urban Wuhan (Lyu et al., 2016), there is a discrepancy of 18.5% in contribution between these two results. The differences of source apportionments in Shanghai, Nanjing and Wuhan between this study and previously published studies probably result from differences in measurement periods and the influence of meteorological conditions.

The study reveals that different controlling measures need to be carried out to reduce VOCs emission in the MLYR and urban YRD regions. For the MLYR, controlling off-road vehicular emission is absolutely necessary. Large contribution of regional aged air mass in the MLYR shows that joint-control measures of VOCs on a cross-regional scale are essential in China.

4. Conclusions

Atmospheric VOCs were measured aboard ship over long distances along the Yangtze River in China to identify main VOC species and apportion their possible sources using the PMF model.

VOCs concentrations ranges from 30 ppbv to 120 ppbv during the sampling period with an average of 65.5 ppbv. They are higher in Shanghai-Jiangsu section than in Anhui section during cruise 1, and higher in Hubei-Jiangxi section than in Anhui section during cruise 2. The main components are alkanes (40.3 ± 4.4%), alkenes (17.2 ± 3.2%), OVOCs (17.2 ± 4.5%), aromatics (9.5 ± 2.7%), acetylene (9.1 ± 3.3%) and XVOCs (6.7 ± 2.2%). Ethylene, propylene, n-butane, toluene and m/p-xylene are key contributors to OFP of VOCs. Interestingly, VOCs characteristics along the MLYR differs significantly from those in previously published results in urban and suburban YRD region. According to the source apportionment, the shipping emission accounts for (23.5 ± 20.0)% of the measured VOCs along the MLYR region. Other three sources of VOCs are also identified, including chemical and petrochemical industries (12.9 ± 9.2%), combustion-related emissions (36.1 ± 17.9%), and regional aged air mass (27.5 ± 16.2%). These results for the MLYR region are different

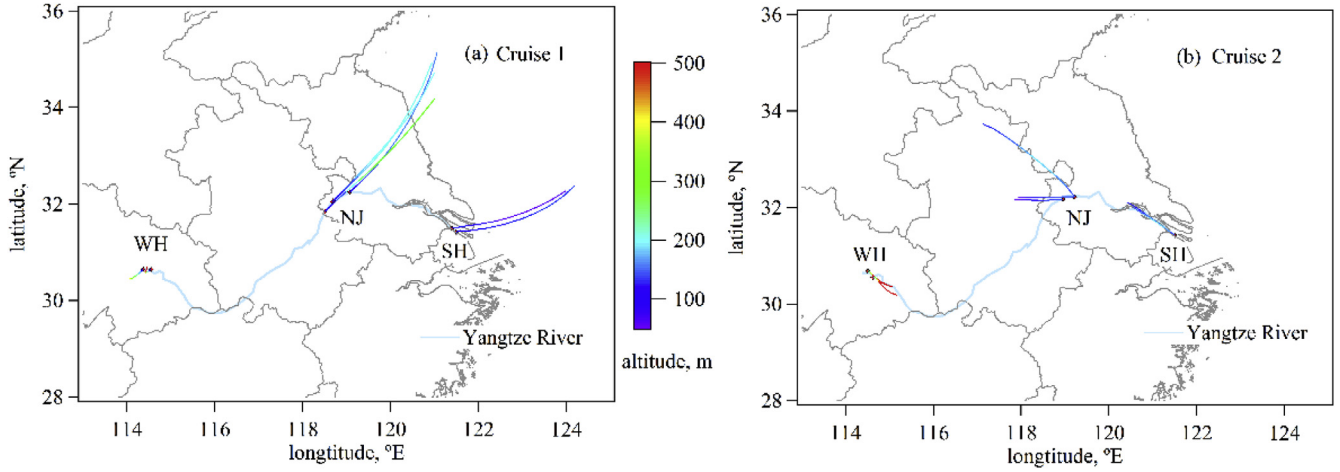

Fig. 9. 8-hour air mass backward trajectories arriving at 100 m in Shanghai (SH), Nanjing (NJ) and Wuhan (WH), (a) during cruise 1 and (b) during cruise 2.

from the published results for the urban suburban YRD region.

It is the first time to conduct the long-distance measurement to understand VOCs along the Yangtze River, an important waterway in a robust developing economic region in central/eastern China. The high contribution of regional aged air mass may have an important impact on the rural YRD where a strong pollution source hardly can be found. It suggests that more focus is needed on VOCs pollution in the rural YRD, and that different control measures are essential to reduce VOCs emissions in both rural and urban YRD regions. Controlling both vehicular emissions, including on-road and off-road vehicles, is equally important for urban and rural regions. Finally, the large contribution of regional aged air mass in MLYR underlines the importance of joint-control measures against VOCs on a cross-regional scale in China.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.atmosenv.2018.07.026.

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