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Characteristics of atmospheric volatile organic compounds (VOCs) at a mountainous forest site and two urban sites in the southeast of China



Zhenyu Hong ^{a,b,c,1}, Mengze Li ^{d,1}, Hong Wang ^e, Lingling Xu ^{a,b}, Youwei Hong ^{a,b}, Jinsheng Chen ^{a,b,*}, Junhuai Chen ^{a,b}, Han Zhang ^{a,b}, Yanru Zhang ^{a,b,c}, Xin Wu ^{a,b,c}, Baoye Hu ^{a,b,c}, Mengren Li ^{a,b,*}

^a Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

^b Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

^c University of Chinese Academy of Sciences, Beijing 100086, China

^d Max Planck Institute for Chemistry, 55128 Mainz, Germany

^e Fujian Institute of Meteorological Sciences, Fuzhou 350001, China

HIGHLIGHTS

GRAPHICAL ABSTRACT

- Comprehensive measurements of VOCs were conducted in southeastern China.
- Seasonal and diurnal patterns of VOCs were driven by variations of OH radicals.
- The VOCs of remote site were strongly influenced by anthropogenic sources in winter.
- High targeted VOCs emissions in urban sites probably due to the widely use of LPG.



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ABSTRACT

Volatile organic compounds (VOCs) are important trace gases in the atmosphere, affecting air quality (e.g. ozone and secondary organic aerosol formation) and human health. To understand the emission, transport and chemistry of VOCs in the southeast of China (Fujian Province), a campaign was conducted in summer and winter of 2016 at three contrasting sites in close proximity. One measurement site (Mt. Wuyi) is a mountainous forest site (1139 m a.s.l.) located in a natural reserve, while the other two sites (Fuzhou, Xiamen) are coastal urban sites with high population and vehicle density. Comparison of VOCs at these three sites provides a valuable perspective on regional air pollution and transport. Many of the measured alkanes, alkenes and aromatics exhibited clear seasonal and diurnal patterns, driven by variations of hydroxyl (OH) radicals, which is the predominant oxidant of VOCs in the atmosphere. By examining tracer-tracer correlations for VOCs, variability-lifetime analysis and 36 h backward trajectories, strong emissions from vehicular exhaust, liquefied petroleum gas (LPG) and solvent usage were identified as key sources in Fuzhou and Xiamen, whereas at Mt. Wuyi the main emission sources were local emissions (e.g. biomass burning) in summer and long-range transport in winter. The results indicate that natural sites could be impacted strongly by surrounding urbanization. Isoprene and propylene in summer and propylene in winter contributed the most to ozone formation.

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* Corresponding authors at: Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China. E-mail addresses: jschen@iue.ac.cn (J. Chen), mrli@iue.ac.cn (M. Li).

¹ These authors contributed equally to this work.

1. Introduction

Volatile organic compounds (VOCs) play an important role in the atmospheric chemistry because they affect air quality, climate change and even human health (Borbon et al., 2013). For instance, the degradation of VOCs contributes to the formation of secondary organic aerosols (SOA) (Lai et al., 2011). Besides, in polluted regions with high nitrogen oxides (NOx = NO + NO₂), photochemical smog type mechanisms can be initiated by the oxidation of VOCs and result in ozone formation (Atkinson, 2003; Lelieveld et al., 2004).

Atmospheric VOCs are present in the atmosphere mostly at partsper-billion (ppb, 10^{-9}) level or even lower and their lifetimes vary from minutes to years (Williams, 2004). The emissions of VOCs into the atmosphere are anthropogenic sources (solvent usage, biomass burning, vehicles combustion, etc.) and natural sources (soil, ocean, vegetation, etc.) (Barletta et al., 2005). The major sink of most VOCs in the troposphere is the removal by OH radical, other minor sinks can be oxidation by nitrate (NO₃) radical during night (for some biogenic VOCs), reactions with chlorine (Cl) radical and ozone (O₃), photolysis and deposition (de de Gouw et al., 2005).

Several field campaigns have been conducted in China to understand the chemistry and transport of VOCs. Emission rates and chemistry are being strongly impacted by rapid urbanization. It is therefore important to characterize and contrast both rural and urban emissions so that future air quality models can be used effectively. Xue et al. (2013) discussed the seasonal and diurnal patterns and photochemistry of VOCs at rural Mt. Waliguan in the southwestern China in 2003. In contrast, Yuan et al. (2010) discussed source profiles of solvent use related VOCs in Beijing and found that toluene and C8-aromatics were the most abundant species in paint applications, while Barletta et al. (2008) reported 50 non-methane hydrocarbons (NMHCs) in the Pearl River Delta (PRD) region and identified strong industrial emission sources.

For this study, we conducted measurement campaigns at three sites, namely Mt. Wuyi, Fuzhou (FZ) and Xiamen (XM), which are located in Fujian Province in the southeast of China, in the summer and winter 2016. Mt. Wuyi Nature Reserve is a UNESCO World Heritage Site and represents for this study a background and remote site, whereas FZ and XM are urban cities with population of 7 million and 3.5 million, respectively. Thus different VOCs characteristics are expected among the three sites. To assess that, 70 species of VOC including alkanes, alkenes, halogenated hydrocarbons and aromatics were measured in samples taken continuously over 4 days with 3 h intervals at three sites in each season. As exemplified above, most studies on VOCs chemistry in China have focused on either remote sites or megacities, mostly in the PRD region, Beijing-Tianjin-Hebei (BTH) region, or Yangtze River Delta (YRD) region. Relatively few studies have been made in the southeast of China. Many cities in this region are growing coastal cities, close to Taiwan Province and the Pacific Ocean. This region can be affected by air masses from East China Sea and South China Sea. This study provides a validated and comprehensive data of VOCs in this region at three sites over two seasons. The seasonal and diurnal patterns of the VOCs, their sources profiles and transport pathways, and their contributions towards ozone formation were determined. Furthermore, the results among remote and urban sites were compared. The results can be helpful to future air quality studies and policy making for local air pollution control.

2. Materials and methods

2.1. Site description and sampling collection

Three sampling sites (Fig. 1) in the southeast of China (Fujian Province) were selected in this study.

The Mt. Wuyi (27.35°N, 117.43°E, 1139 m a.s.l.) observation site is located in Mt. Wuyi Nature Reserve in the northern part of Fujian Province. As a UNESCO World Heritage Site since 1999, Mt. Wuyi Nature Reserve has a total area of 99,975 ha with the highest peak at 2158 m. Due to its enormous biodiversity values, it serves as an intact forest in the subtropical region of China. The annual precipitation excesses 2000 mm and the annual relative humidity is around 85%, with the



Fig. 1. Location of sampling site on Mt. Wuyi, FZ and XM in the southeastern China.



Fig. 2. Trajectory cluster analysis of three sites during sampling time (a, c, e: summer Mt. Wuyi, FZ and XM; b, d, f: winter Mt. Wuyi, FZ and XM).

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 Table 1

 Mixing ratios (ppbv) and contributions (in brackets, %) of different kinds of VOCs at three sites.

Sites	Halocarbons	Alkanes	Alkenes	Aromatics	TVOCs
Mt. Wuyi	1.82 (30.0)	1.89 (31.2)	1.06 (17.5)	1.30 (21.4)	6.06
FZ	2.54 (18.1)	6.79 (48.2)	1.66 (11.8)	3.07 (21.8)	14.08
XM	2.62 (14.6)	9.14 (51.0)	2.07 (11.6)	4.09 (22.8)	17.91

open surrounding area and high wind speed (annual average ~ 7.5 km/h). Mt. Wuyi observation site is one of the 15 atmospheric background monitoring sites in China, representing the atmospheric remote background of the forests and mountains in East China. Without significant local anthropogenic sources of air pollutants, Mt. Wuyi is able to reflect the influence of anthropogenic pollutants transported from surrounding area.

In contrast to Mt. Wuyi site, FZ and XM act as typical urban sites in Fujian Province. The population (area) of FZ and XM are about 7 million (12,177 km²) and 4.0 million (1699 km²) in 2017, respectively. The FZ site (26.06°N, 119.17°E, 20 m a.s.l.) is located in central Fuzhou (the capital city of Fujian Province) and near to a main road. The railway station is 3 km from the site. As one of the first four Special Economic Zones in China, Xiamen is also a major economic center of Fujian province. The XM site (24.28°N, 118.09°E, 20 m a.s.l.) is located in a commercial center, surrounded by commercial plaza and near to a heavy traffic road. Both the FZ and XM sites included a mix of condensed residential areas. As can be seen in Fig. 1, FZ and XM sites are open to the Pacific Ocean.

The campaigns were conducted simultaneously in Mt. Wuyi, FZ and XM in August 22–25th 2016 (summer) and December 27–30th 2016 (winter). In order to study the diurnal variations, VOCs samples were intensively collected (8 samples a day with 3 h intervals) using 3.2 L Summa stainless steel canisters. The canisters were flushed at least three times using ultra-pure N_2 (>99.999%) through a Canister Cleaner (model 3100A, Entech Instruments Inc., USA) and evacuated before sampling. 150 samples (including 6 field blanks) were collected during the whole sampling period. After sampling, canisters were delivered to the lab in Chinese Academy of Science in Xiamen immediately and analysis was completed within a week.

2.2. Chemical analysis

70 VOCs species (Table S1) were quantitatively determined for each sample by a gas chromatography (GC, Shimadzu GC-2010) equipped with a mass spectrometer (MS, Shimadzu QP2010 plus) (GC-MS). The GC-MS column has a capillary of 60 m length, 0.25 mm diameter, and 1.0 µm film thickness coated with 6% nitrile propyl phenyl and 94% dimethyl polysiloxane (DB-624). Specific cryogenically concentration procedures have been described elsewhere (Zhang et al., 2012; Wang and Wu, 2008). In short, all samples were preconcentrated by a Model 7100A VOC pre-concentrator (Entech Instruments Inc., USA) before the GC-MS. VOCs were initially condensed by liquid-nitrogen glass beads cryogenic trap at -150 °C and then transferred through pure helium to a next trap at -30 °C with Tenax as absorbent. After these trapping steps, most of H₂O and CO₂ were removed. Then VOCs were heated up and transferred with helium to a third capillary cryo-focus trap at -160 °C. After the concentration step, the trap was quickly heated and the VOCs were transferred to GC-MS system. The initial oven temperature was 35 °C for one minute, increasing to 50 °C at 3 °C·min⁻¹, then to 55 °C at 1 °C·min⁻¹, and then raised to 180 °C at 3 °C·min⁻¹, finally rising to 240 °C at 40 °C·min⁻¹, where it remained for 2 min. The selected ion monitoring mode was applied in data collection, and the ionization technique was electron impacting (EI, 70 eV) with a source temperature of 200 °C.



Fig. 3. The seasonal and diurnal variations of benzene (B), toluene (T), ethylbenzene (E) and *m*,*p*-Xylene (X) at three sites. Box plot gives the 25% and 75% percentiles with the median (horizontal solid line) and the mean (square) in the box and whisker indicates 10% and 90% percentiles.



Fig. 4. The seasonal and diurnal variations of propane at three sites. Box plot gives the 25% and 75% percentiles with the median (horizontal solid line) and the mean (square) in the box and whisker indicates 10% and 90% percentiles.

2.3. Quality control and quality assurance

To check whether there was contamination or not, all canisters were evacuated after the cleaning steps, refilled with ultra-pure N₂, kept in the lab for at least 24 h, and then they were measured in the same way as field samples to ensure that no objective targeted VOC present. The targeted VOC species were identified based on their retention times and mass spectra with reference to standard mass spectra (NIST98) and quantified through external calibration methods. A multicomponent pressurized standard gas mix was used (Spectra Gases, USA), with each component volume fraction was approximately 1 $\times 10^{-6}$ (1 ppm). The calibration curves were obtained by running five diluted standards (3 duplicates for each standard) with humidified zero air, in the same way as the field samples. The analytical system was calibrated every 12 samples by a one-point calibration. If the response was in excess of $\pm 15\%$ of the original calibration curve, it was then recalibrated. The correlation coefficients (R^2) of standard curves fluctuated between 0.990 and 1.000. By repeatedly injecting a standard gas with mixing ratios of 1 ppb, the precision of the system was checked. Data below detection limits was excluded from further discussion.

2.4. Lifetime-variability analysis

The variability (standard deviation) of trace gases from a dataset has an inverse relationship with its atmospheric lifetime, this was first observed by Junge (1974) for long-lived trace gases and Jobson et al. (1998) (Jobson et al., 1998) extended it for NMHCs (short-lived trace gases) with the following equation:

$$S_{\ln X} = A \tau^{-b} \tag{1}$$

where S_{inX} is the standard deviation of natural logarithm of mixing ratio of a dataset, τ is the lifetime, *A* and *b* are fitting parameters and differ in regions and time scales. This relationship is a useful analytical tool for examining sources and sinks and it was applied in several studies (Jobson et al., 1999; Pollmann et al., 2016; Williams et al., 2000; Williams et al., 2001). The b-value has been shown to indicate the remoteness of emission sources. When b > 0.5, samples are remote from sources and chemistry has a significant impact on the variability; when b < 0.3, the variability of the samples is influenced by nearby emission sources (Pollmann et al., 2016).

2.5. Ozone formation potential (OFP)

Ozone formation potential (OFP) method has been widely used to describe the chemical reactivity of VOCs (Carter, 1994). According to the corresponding maximum incremental reactivity (MIR) coefficient, the OFP can be calculated using the following equation:

$$OFP_i = Conc_i \times MIR_i$$
 (2)

where OFP_i is the ozone formation potential of each VOC_i, Conc_i is the concentration of compound i, MIR_i is the maximum incremental reactivity coefficient of compound i (Carter, 1994; Carter, 2008; Roger Atkinson and Arey, 2003).

2.6. Backward trajectory analyses

In order to study the long-range transport of air masses at three sites, backward trajectories were calculated by Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) with inputs from the NCEP/GDAS meteorological dataset (horizontal resolution of 1° longitude \times 1° latitude) and a temporal resolution of 2 h. 36 h air mass backward trajectories were calculated with the height of 500 m above ground level at Mt. Wuyi, FZ and XM, starting at 10:00 a.m. (local time) each day during the sampling period. Cluster analysis was then performed by HYSPLIT model, which can result in sub-sets of trajectories with those calculated backward trajectories (Stein et al., 2015; Rolph et al., 2017).



Fig. 5. The seasonal and diurnal variations of *n*-pentane and *i*-pentane at three sites. Box plot gives the 25% and 75% percentiles with the median (horizontal solid line) and the mean (square) in the box and whisker indicates 10% and 90% percentiles.



Fig. 6. The seasonal and diurnal variations of chlorormethane at three sites during summer and winter. Box plot gives the 25% and 75% percentiles with the median (horizontal solid line) and the mean (square) in the box and whisker indicates 10% and 90% percentiles.

3. Results and discussion

3.1. Air transport patterns

Long-range transport of air masses from other areas can impact both the composition and concentration of VOCs at the sampling sites. As shown in Fig. 2, in summer, the air masses reaching Mt. Wuyi were all from the nearby surrounding area, thus the VOCs of Mt. Wuyi were mainly influenced by local sources. Relatively low mixing ratios of anthropogenic VOCs (such as benzene, toluene, *m*,*p*-Xylene and ethylbenzene, Table 2) in summer Mt. Wuyi were evident for local sources. In summer, the FZ and XM sites were mainly affected by the air masses originating from the East China Sea which were advected along the coast before reaching the FZ and XM. In winter, the air masses that influenced Mt. Wuyi were originated from Hunan province (cluster 2, 55%), Yunnan province (cluster 3, 29%) and Thimphu (Kingdom of Bhutan) (cluster 1, 18%). Such long-range transportation of pollutants led to relatively high mixing ratios of VOCs observed in Mt. Wuyi (Table 1). The backward trajectories of winter air masses affecting FZ were similar to those of Mt. Wuyi, and associated with air masses from the west. Unlike Mt. Wuyi and FZ, XM was mainly affected by the air masses coming from southeast China, which were first transported to FZ and then on to XM. Such long-range transport of air masses over several cities in conjunction with the local sources, resulted in the highest mixing ratios of VOCs at XM.

3.2. General overview of observed VOCs

Table S1 in the supplementary material shows the statistical values (mean and one standard deviation) of all seventy identified VOCs at three sites in two seasons. Instead of discussing details of every VOCs observed, we have selected some VOCs, which are anthropogenic and whose patterns are representative, to understand the influence of urbanization on the remote site and source profiles and transportation at three sites. In the following sections, we will show seasonal and diurnal patterns of these selected VOCs, compare the temporal patterns and concentration differences between mountainous site and urban sites, discuss air transport and source profiles with VOC mixing ratios, VOC-VOC ratios, lifetime-variability analysis and backward trajectory analysis.

Table 1 summarizes the mixing ratios of four VOC groups (i.e. halocarbons, alkanes, alkenes and aromatics) and their contributions to the total VOCs (TVOCs) at three sites. The highest mixing ratio of TVOCs was observed in XM (17.91 ppbv), followed by FZ (14.08 ppbv) and smallest concentration at Mt. Wuyi (6.06 ppbv). Among the four groups, alkanes (31.2%) were the most abundant species at Mt. Wuyi, followed by halocarbons (30.0%), aromatics (21.4%) and alkenes (17.5%). Similar patterns (with aromatics and halocarbons dominant) were also found in Mt. Waliguan (Xue et al., 2013). Alkanes and aromatics were the dominant groups in FZ and XM, both accounted for >69% of the total VOCs concentrations, indicating that variation of the TVOCs were mainly affected by alkanes and aromatics, whereas alkenes contributed at the same level (~11.5%) at FZ and XM.

3.3. Seasonal and diurnal variations of selected VOCs species

Figs. 3–6 show the diurnal patterns (daytime: from 8 am to 5 pm, nighttime: from 8 pm to 5 am) of selected representative VOC species at three sites in summer and winter of 2016. Table 2 compares mixing ratios of selected VOCs with literature, with emphasis on comparison with other Chinese observation sites.

Table 2

Comparison of 10 selected VOCs (mean and one standard deviation) at three sites in this study with observations at other sites.

Component	Lifetime ^h	Mt. Wuyi ^b		FZ ^b		XM ^b		Mt. Waliguan ^c	Mt. Tai ^d	Xi'an ^e	Shanghai ^f
		Summer	Winter	Summer	Winter	Summer	Winter	Summer	Summer	Summer	Winter
Propane	225.5 ⁱ	265 (164)	1090 (283)	2638 (2280)	4800 (1854)	3458 (2212)	6207 (1602)	147 (45)	NA ^a	1.84 (0.95)	5.16 (2.39)
n-Butane	104.2 ⁱ	52.9 (14.1)	335 (71)	336 (119)	1735 (1285)	720 (272)	1788 (884)	40.1 (19.9)	0.44 (0.44)	2 (0.8)	1.69 (0.9)
n-Pentane	64.7 ⁱ	16.1 (4.7)	126 (31)	139 (100)	315 (156)	147 (60)	386 (163)	16.9 (10.1)	0.15 (0.21)	1.41 (0.66)	0.87 (1.02)
i-Pentane	68.3 ⁱ	26.8 (9.3)	164 (35)	266 (131)	670 (353)	330 (168)	858 (454)	68.8 (81.5)	0.32 (0.46)	11.63 (7.88)	1.63 (0.82)
Isoprene	2.5 ^j	287 (206)	124 (167)	546 (405)	58 (39)	293 (264)	256 (171)	126 (287)	0.17 (0.12)	0.5 (0.18)	NA
Benzene	192.0 ^j	88.4 (15.9)	400 (115)	137 (66)	337 (108)	150 (47)	371 (93)	67.8 (41.8)	0.51 (0.43)	3.75 (2.31)	2.00 (1.28)
Toluene	39.9 ^j	69.1 (15.9)	331 (110)	477 (204)	1667 (1084)	874 (435)	1876 (649)	62.3 (62.5)	0.47 (0.28)	1.33 (0.83)	4.86 (3.46)
m,p-Xylene ^g	10.0 & 16.2 ^j	74.2 (26.3)	195 (73)	200 (88)	377 (165)	232 (71)	410 (194)	14.1 (10.2)	0.11 (0.08)	0.82 (0.5)	1.14 (NA)
Ethylbenzene	32.7 ^j	73.9 (24.3)	244 (88)	226 (115)	522 (230)	269 (131)	505 (224)	7.1 (6.1)	0.14 (0.16)	0.3 (0.17)	1.32 (0.92)
CH ₃ Cl	5638.1 ^j	698 (60)	1686 (449)	824 (123)	1902 (858)	765 (77)	1519 (220)	552 (33)	NA	NA	1.61 (0.99)

All data are mean values (one standard deviation) in pptv except for Mt. Tai, Xi'an and Shanghai, which is in ppbv.

^a "NA" means not available.

^b data in this study.

^c Mt. Waliguan: 36.28°N, 100.90°E, 3816 m a.s.l.; Summer: 15 July-12 August 2003 (Xue et al., 2013).

^d Mt. Tai: 36.26°N, 117.11°E, 1534 m a.s.l.; Summer: June 2006 (Mao, 2009).

^e Xi'an: Summer: 19 May–6 June 2016 (Li et al., 2017).

- ^f Shanghai, Winter: December 2006–February 2007 (Song et al., 2012).
- ^g *m*-Xylene and *p*-Xylene are co-eluted in the chromatographic separation.
- ^h Atmospheric OH-initiated lifetime (unit in hour) is calculated with a global OH radical concentration of 1.13 × 10⁶ molecules cm⁻³ (Lelieveld et al., 2016).
- ⁱ Reaction rate with OH radical is taken from (Atkinson, 2003) at 298 K.
- ^j Reaction rate with OH radical is taken from (Atkinson, 1986) at 298 K.

Table 3	
The VOCs ratios in Mt.	Wuyi, FZ and XM.

Ratio	Mt. Wuyi		FZ		XM	
	Summer	Winter	Summer	Winter	Summer	Winter
T/B ^a	0.55	0.76	3.14	3.93	4.65	4.23
X/E ^b	1.02	0.79	0.94	0.77	0.96	0.84
X/B ^c	0.54	0.41	1.21	0.87	1.27	0.88
P/B ^d	3.42	3.49	5.50	3.89	4.92	3.90
I/N ^e	1.72	1.33	2.08	2.05	2.13	2.19

 $^{a-e}$ The ratio of toluene to benzene (T/B), *m*,*p*-Xylene to ethylbenzene (X/E), *m*,*p*-Xylene to benzene (X/B), propane to benzene (P/B) and *i*-pentane to *n*-pentane (I/N), respectively.

3.3.1. BTEX

Benzene (B), toluene (T), ethylbenzene (E) and *m*,*p*-Xylene (X) are often called BTEX and they serve as indicators of air pollution. The carcinogenic compound, benzene has been shown to be from automobile exhausts in urban areas, and from biomass burning (Li et al., 2017). Toluene is mainly emitted from the evaporation of solvents used in paint, printing, coating, in additional to its use in fossil fuel (Yuan et al., 2010). Vehicle exhaust emissions and solvent usage are the major sources of *m*,*p*-Xylene and ethylbenzene (Garzón et al., 2015). For all BTEX species, similar seasonal profiles (Fig. 3), i.e. mixing ratios in winter are larger than those in summer at least by a factor of two, existed in this study. In each season, the differences between daytime and nighttime mixing ratios of BTEX were not apparent. The extreme high winter BTEX mixing ratios observed at Mt. Wuyi indicated a strong anthropogenic influence at the site which is confirmed by the variabilitylifetime analysis in Section 3.5. This is probably due to the longdistance transport of pollution from the west (Section 3.1). Compared with other polluted cities (Xi'an and Shanghai, Table 2), FZ and XM exhibit lower BTEX.

3.3.2. Propane

Propane is an abundant hydrocarbon in the troposphere and a precursor of the carbonyl compounds (e.g. propanol and acetone) and



Fig. 8. The contributions of VOCs groups to the total OFP (tOFP) at three sites.

organic peroxides (Hanst and Gay Jr, 1983). Propane is primarily emitted from natural gas losses, gasoline vapour, biomass burning and the petroleum industry (Rosado-Reves and Francisco, 2007). The observed propane mixing ratios (Fig. 4) exhibited a significant difference between the mountainous site and urban sites (XM > FZ > Mt. Wuyi). By comparing seasonal mean values, the propane concentrations in XM were higher than that at Mt. Wuyi by a factor of 6-10. At all three sites, the winter time propane mixing ratios were generally more than two times higher than summer time, which can be caused by higher local propane emission in winter or lower winter removal by OH radical due to the low winter OH concentration (Lelieveld et al., 2016). Opposite diurnal profiles, i.e. higher mixing ratios at night time in summer, higher daytime mixing ratios in winter, were found at all three sites. Since the OH radical reaches lowest concentration during nighttime, the loss of propane will be at minimum during night, thus higher mixing ratios at night are expected. As the main component of liquefied petroleum gas (LPG), the relative high mixing ratios of propane in FZ and XM



Fig. 7. The top 10 greatest contributions to total OFP in Mt. Wuyi, FZ and XM. Note: 1,3,5-TMB, 1,2,3-TMB, 1,2,4-TMB are the abbreviations of 1,3,5-Trimethylbenzene, 1,2,3-Trimethylbenzene, 1,2,4-Trimethylbenzene, 1,4,4-Trimethylbenzene, 1,4,4-Tr

indicated strong LPG emission, which is further supported by VOCs Characteristic Ratios in Section 3.4. The propane concentration in winter XM even exceeded 20% of that in winter Shanghai in 2007 (Table 2). It is to be noted that the XM site is close to a commercial plaza, thus heavy traffic pollution with high propane emission is expected.

3.3.3. Isomeric pentanes

As one of the most abundant VOCs associated with traffic-related sources, *i*-pentane is often used as a gasoline evaporation indicator (Morikawa, 1998; Liu et al., 2008; Wang et al., 2015). Gasoline-vehicle emission is the potential source of *n*-pentane (Jorquera and Rappenglück, 2004). Thus, *i*-pentane and *n*-pentane can indicate the



Fig. 9. Lifetime-variability plots of summer and winter for Mt. Wuyi (a), Fuzhou (b), and Xiamen (c). Linear regression fitting is applied for solid symbols in each season and the corresponding b-values are shown in the plots.

influences from gasoline evaporation and vehicular emissions. In general, daytime mixing ratios (Fig. 5) of both isomeric pentanes were comparable to or slightly lower than those at night time, with an exception in winter XM. Concentrations of *i*-pentane and *n*-pentane in XM were higher than those in FZ during the winter time, while in summer there was no big difference. It indicates high vehicular emission and gasoline evaporation in winter XM.

3.3.4. Chloromethane

Chloromethane (CH₃Cl) is a typical species emitted from biomass/ coal burning (Barletta et al., 2009; Ling et al., 2011). In this study, the mixing ratios of chloromethane sat three sites were much higher in winter than those in summer (Fig. 6). The high winter chloromethane mixing ratio observed at Mt. Wuyi indicates a strong biomass/coal burning influence from long-range transport. Comparison with literature shows the chloromethane concentrations at three sites were similar as the rural site Mt. Waliguan and urban Shanghai in China (Table 2).

3.4. VOCs characteristic ratios

Ratios of some specific compounds are frequently used to identify their sources and transport pathways (e.g. Yurdakul et al., 2013). The ratios among BTEX, propane/benzene and isomeric pentanes are discussed in the following section.

3.4.1. BTEX ratios

Benzene is a tracer of vehicle exhaust and biomass burning, while toluene is mainly emitted from evaporation of solvents used in painting, printing and coating, in additional to its use in fossil fuel (Yuan et al., 2010). Therefore the ratios of toluene to benzene (T/B) can be used as indicator of the non-traffic sources contributions to measured VOC concentrations (Elbir et al., 2007). Low T/B ratios (<2) indicates strong influences from vehicle emissions and biomass burning, whereas ratios >2 indicates contributions from non-traffic sources (especially solvent evaporation) (Gelencsér et al., 1997; Elbir et al., 2007).

Average T/B ratios (Table 3) showed significant difference between the mountainous forest site Mt. Wuyi and two urban sites FZ and XM. The ratio of T/B at Mt. Wuyi was 0.55 and 0.76 in summer and winter, respectively. Such low T/B ratios indicate that vehicle emission and biomass burning is the main source for those aromatics at Mt. Wuyi. High average T/B ratios in the two urban sites indicate stronger influence from solvent usage.

The ratios of *m*,*p*-Xylene to ethylbenzene (X/E) and to benzene (X/B) have been applied as indicators of photochemical age of samples (Zalel et al., 2008). Since *m*,*p*-Xylene has a shorter lifetime than ethylbenzene and benzene (Table 2), aged air mass containing VOCs travels long distance from sources would be expected to have low X/E and X/B ratios, whereas fresh air from local emissions should have higher ratios. In this study, the X/E and X/B ratios (Table 3) were relatively low in winter Mt. Wuyi and reached the highest in FZ and XM in summer, indicating long-range transport of sampled air in winter Mt. Wuyi and strong influence from local sources in FZ and XM in summer.

3.4.2. Propane/benzene ratio

Propane and benzene have similar atmospheric lifetimes due to similar reaction rates with OH radical, thus propane/benzene (P/B) ratio represents approximately the emission ratio regardless of transport mixing and dilution. The ratio indicates influence from gasoline emission (ratio < 1), or from natural gases or LPG (ratio > 1) (Russo et al., 2010). At all three sites in two seasons, the P/B ratios (Table 3) were larger than 1 and in the range of 3.4–5.5 (FZ > XM > Mt. Wuyi). The ratios were nearly the same in summer and winter at the mountainous site, whereas in urban sites, the summer ratios were always higher than winter ratios, demonstrating stronger influence/sources from natural gases or LPG in FZ and XM.

3.4.3. Pentanes ratio

The two pentane isomers (*i*-pentane and *n*-pentane) have similar reactivity (Jobson et al., 1998), thus the ratio of *i*-pentane/*n*-pentane (I/N) can be used in differentiating the potential sources. High I/N ratios were reported for vehicle emissions within the range of 2.2-3.8, lower ratios between 0.56 and 0.80 can be used as the diagnostic ratios of coal combustion (Russo et al., 2010). The ratio of I/N (Table 3) at Mt. Wuyi with the higher ratios in summer (average 1.72) than that in winter (average 1.33), indicated that vehicle emissions were the important sources for VOCs at Mt. Wuyi during the summer time, while coal combustion contributed more VOCs additional to vehicle emission in winter. As mentioned in backwards trajectory analysis (Section 3.1), the pollution sources at Mt. Wuyi were mainly coming from surrounding areas in summer and long-range transport form polluted area in winter. The average ratios in FZ and XM were 2.08, 2.13 in summer and 2.05, 2.19 in winter, respectively. The relative high ratio indicated that vehicle emission were the important sources for VOCs in FZ and XM. High R² values (>0.86, no shown) of linearity regression fitting for the pentane isomers ratios in FZ and XM in summer and winter suggested that these two cities were mostly influenced by local pollution sources during the two campaign periods.

3.5. Ozone formation potentials (OFPs) for VOCs

The OFPs for individual VOC species of Mt. Wuyi, FZ and XM during summer and winter were calculated. As shown in Fig. 7, the top 10 VOC species with the highest OFP were mainly from aromatics and alkenes. In summer, isoprene and propylene were the OFP dominators at all three sites, whilst in winter, propylene became the predominant VOC species with the highest OFP at all three sites. Similar results namely that propylene had the highest OFP was also observed in an urban city Xi'an in China, and Tokyo in Japan (Hoshi et al., 2008; Li et al., 2017). Fig. 8 shows the contributions of VOCs groups to the total OFP (tOFP). Among the three sites, XM exhibited the highest tOFP, followed by FZ and Mt. Wuyi. The OFPs of alkenes accounted for more than half of the tOFP at Mt. Wuyi. More than 45% of the tOFP at FZ and XM were from the aromatics in summer, while the OFPs of alkenes were much increased and accounted for about 42-48% of tOFP in winter. The results indicate the apparent difference of chemical reactivities of VOCs in FZ and XM: the ozone formation was mainly influenced by aromatic VOCs in summer, while alkenes could also make much more contribution to ozone formation in winter. Unlike FZ and XM, The OFPs of Mt. Wuyi were significantly influenced by alkenes VOCs in both summer and winter. The results can be helpful for policy makers on preventing local ozone formation in different seasons in both remote and city locations.

3.6. Lifetime-variability analysis

In this study, data of six NMHCs (xylene, ethylbenzene, toluene, pentane, *n*-butane and benzene) is used for variability analysis among three sites in two seasons. Since the major removal process of the abovementioned NMHCs is the OH oxidation, the OH lifetime is chosen to represent trace gas lifetime. OH concentration is set to be 5×10^5 molecules cm⁻³ for all samples from three sites, but the choice of OH concentration does not affect the b-value because the points would shift to the same extent along x-axis (lifetime) (Williams et al., 2001).

The variability-lifetime plots for three sites are shown in Fig. 9. As mentioned in the former section, a high b-value indicates the remoteness of emission sources, whereas lower b-values demonstrate strong emission (Pollmann et al., 2016). The b-values in this study indicated much stronger emission in FZ and XM than at Mt. Wuyi. By checking the outliers on the plots, Mt. Wuyi suffered more benzene emission in winter and more pentenes in summer, FZ and XM had more pentenes in both seasons, which are consistent with the conclusions of former sections. It has to be noted that the correlation for summer XM is too

poor, probably because of 1) high emissions of most NMHCs; 2) more Cl radical from ocean in summer (Fig. 6). Some NMHCs (e.g. *n*-butane and toluene) react very fast with Cl (Li et al., 2018), and Cl can be activated by sea salt aerosol (Keene et al., 2007) or the presence of nitryl chloride (ClNO₂) especially in polluted regions (high-NO_x) during summer time due to high photolysis (Simpson et al., 2015). Thus under high Cl condition, the removal from Cl for some NMHCs (e.g. *n*-butane and toluene) is even comparable with the OH removal, this causes larger variabilities in summer XM.

4. Conclusions

This study provided comprehensive VOCs measurement during two seasons (summer and winter of 2016) at three sites (one mountainous forest site, two urban sites) where only little data of VOCs exists. The major findings and conclusions of this study are:

- (1) Most VOCs, especially alkanes, alkenes and aromatics, which react primarily with OH radical, exhibit seasonal and diurnal patterns driven by the variation of OH radicals.
- (2) Anthropogenic emissions, e.g. vehicular exhaust, solvent usage, LPG evaporation, are apparent in urban sites FZ and XM. In many cases, the emissions in XM are larger than that in FZ, which is supported by lifetime-variability analysis (poor correlation in XM).
- (3) At the mountainous forest site Mt. Wuyi, VOCs were affected by air from long-range transport in winter and local emission in summer.
- (4) Aromatics contribute the most for ozone formation in summer and winter, the contribution of alkenes increases in winter. Isoprene and propylene are the major contributors in summer and propylene dominates in winter.

Long-term observations at the three sites would be beneficial to understand the changes of source profiles of VOCs and transport of air and how does the urbanization affect natural reserves. This study provides important data for future researches.

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