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Characteristics of ambient volatile organic compounds and the influence of biomass burning at a rural site in Northern China during summer 2013



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HIGHLIGHTS

- Characteristics of VOCs and effect of biomass burning at a rural site were studied.
- More detailed VOC temporal and diurnal variation characteristics were identified.
- E/X ratio and relation with O₃ showed that studied site received an aged air parcel.
- Air transport from biomass burning area had an important effect on VOCs.

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ABSTRACT

Volatile organic compounds (VOCs) were measured at a rural site in the North China Plain during summer 2013, which focused on VOCs characteristics and impact of biomass burning. Alkanes and halocarbons made the largest contribution to the sum of the mixing ratio of each VOC compound (total VOCs). Most VOC species mixing ratios had similar day-to-day variability, indicating that the air mass at the sampling site had small local perturbation. Accumulation of pollutants due to biomass burning and advection of plumes from urbanized areas upwind had important impact on diurnal variation patterns of the VOC group. Ethylbenzene/m,p-xylene ratio and its relationship with O₃ indicated that sampling site received an aged air parcel. The aromatics and alkenes were the dominant contributors to total ozone formation potential (OFP). The top 5 VOC species based on OFP were toluene, isoprene, ethene, propene and n-Hexane. During the biomass burning period, VOCs had higher OFP values, especially the aromatics and alkynes. The backward trajectories indicated that extensive transport of biomass burning from the Shandong and Hebei provinces had an important effect on VOCs pollution levels.

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1. Introduction

Volatile organic compounds (VOCs) along with nitrogen oxides under sunlight can lead to the production of secondary air

pollutants through complex photochemical cycles, resulting in tropospheric ozone and secondary organic aerosols (SOAs). Furthermore, exposure to VOCs can induce a wide range of acute and chronic health effects, such as sensory irritation, nervous system impairment, asthma and cancer (Mølhav, 1991; USEPA, 1990). For example, benzene, 1,2-dichloroethane and 1,3-butadiene have been identified as known carcinogens by the USEPA (Calabrese and Kenyon, 1991; USEPA, 2009). Moreover, in China, study on the

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national emission inventory of anthropogenic VOCs in China by Wei et al. (2011) found that they are on track to increase from 19.4 Tg in 2005 to 25.9 Tg in 2020, even if China's legislative standards for VOC emissions are implemented effectively in the future. Thus, understanding the pollution characteristics of VOCs is necessary to improve air quality and develop environmental management strategies in China.

In recent years, a number of studies on VOC mixing ratios have been conducted in China (Lee et al., 2002; Duan et al., 2008; Liu et al., 2008a; Cai et al., 2010; Huang et al., 2011; Li et al., 2014). These studies suggest that industrial emissions, vehicular emissions and combustion processes are main anthropogenic VOC sources. However, the previous studies on the VOC mixing ratios in China were mostly conducted in several megacities, such as Beijing, Tianjin, Shanghai, the Pearl River Delta and the Yangtze River Delta (Wang et al., 2012a; Zhou et al., 2011; Geng et al., 2008, 2009; Louie et al., 2013); such studies were rarely conducted in rural sites, where 46.27% of the population lives in 2013 (China Statistical Yearbook, 2014). Due to lack of suitable disposal methods, open biomass burning is a common activity in rural areas particularly during harvest seasons. Lü et al. (2006) recently reported China contributing 25% of the total annual amount of biomass burned in Asia. Some studies have indicated biomass burning is an important source of VOCs in rural site (Wang et al., 2004; Guo et al., 2007). The emitted active trace gases from biomass burning (VOCs and NO_x) could pose a threat to human and ecosystem health (Bo et al., 2008). Furthermore, severe air pollution events have also frequently occurred in rural areas (Tanimoto, 2009; Sharma et al., 2013), especially in the downwind of urban areas receive air masses containing anthropogenic emissions (Wang et al., 2012b). Thus, the study of VOCs in the rural regions is very important to reduce VOC pollution in China.

The North China Plain has been among the most concerned area in China, with high density of population (van Donkelaar et al., 2010) and the greatest emissions of anthropogenic aerosols in the country (Zhang et al., 2009). Moreover, model simulation coupled with precursor mixing ratios identified that the O₃ production in this region was a VOC-limited regime (Luo et al., 2000; Carmichael et al., 2003). The Chinese Academy of Sciences-Yucheng site is downwind of urban Jinan in summer, and within a rural-scale zone surrounded by farmlands. The location of the Yucheng site makes it an ideal site to investigate the pollution characteristics of VOCs and the influence of biomass burning on the rural site, and to characterize the long-range transport of air pollution from an upwind urban area to the rural background monitoring site. The objectives of this study are as follows, (1) to analyze the general characteristic of observed VOCs, including mixing ratios and temporal variations during the different sampling periods in rural site; (2) to study diurnal variation patterns of the VOC group, to examine photochemical process and solvent evaporation contributions to VOCs; (3) to calculate the reactivities of VOCs in terms of ozone formation potential (OFP), to identify the major VOC species producing ozone and the effect of biomass burning and (4) to estimate the effects of long-range transport on the VOC levels during biomass burning by back-trajectory analysis.

2. Experimental methods

2.1. Site description

VOC samples were collected on the top of a container (2.4 m above ground level) inside the experimental field of Chinese Academy of Sciences-Yucheng site, which is located in the Dezhou city of Shandong province (36.87°N, 116.57°E) (Fig. 1). The Yucheng site is located 50 km northwest of Jinan, which is the heavily

polluted capital city of the Shandong province. The Yucheng site is within a rural-scale zone surrounded by vast agricultural fields. And southerly wind prevailed at the sampling site in summer, which means that Yucheng site was downwind of Jinan and is considered as a receptor monitoring site. Wind speed, wind direction, temperature, relative humidity (RH) and UV radiation were measured by an automatic meteorological station (MILOS520, Vaisala, Finland). O₃ was measured by a UV photometric analyzer (Thermo Environment Instruments Inc., Model 49C). During our observations, the prevailing winds came from the south, with an average speed of 2.4 m/s. The weather was hot and wet in summer, with an average ambient temperature of 25.3 °C and RH of 71.5%. O₃ data were averaged over 1 h.

2.2. VOC sampling and analysis

Ambient air samples were collected using 3.2 L stainless steel canisters. The canisters were evacuated to <100 mtorr and then pressurised to 20 psi with high purity nitrogen. After three cycles of evacuation and refilling, the canisters were evacuated to <20 mtorr for use. The stability of the canister samples was tested (Liu et al., 2008b). A passive capillary was connected to the canister to keep the sampling airflow rate constant. The filling time for each canister was about 1 min.

Canister samples were collected from 28 June to 17 July, 2013, only on sunny/cloudy days. To examine the diurnal variations, VOC samples were intensively collected on 28, 29 June and 6 July (8 samples a day with a 2 h interval from 6:00–20:00 in these three days), 15 July (raining in the morning, only 3 samples with a 2 h interval from 14:00–18:00), 16 July (5 samples with a 2 h interval from 8:00–18:00, except 12:00) and 17 July (raining in the afternoon, only 3 samples with a 2 h interval from 8:00–12:00). VOC samples were collected twice a day at 6:00 and 14:00 h in other sampling time (30 June, 3 July, 5 July, 7 July and 8 July). Altogether 45 samples were collected during this campaign. The sampling height was about 4.1 m (container height added to sampling personnel height) above the ground. After sampling, the samples were delivered to Peking University for chemical analysis within two weeks after collection.

The VOC samples were quantified using a cryogenic pre-concentrator (Model 7100, Entech Instruments, Inc., Simi Valley, CA, USA) and a gas chromatograph (GC, HP-7890A, Hewlett Packard Co., Palo Alto, CA, USA) equipped with two columns and two detectors. High-purity helium (He) was used as the carrier gas at a constant flow rate of 1.2 ml min⁻¹. Each aliquot of 300 ml from a canister was drawn into the cryogenic trap and cooled to -180 °C for pre-concentration. During injection, the trap was resistively heated to 60 °C within seconds, and a stream of high purity He flushed the trapped VOCs onto the columns. The C₂–C₃ hydrocarbons were separated on an Al₂O₃ PLOT column (30 m × 0.25 mm × 3.0 μm, J&W Scientific, Folsom, CA, USA) and quantified with a flame ionisation detector (FID). The other species were separated on a semi-polar column (60 m × 0.25 mm × 1.8 μm, J&W Scientific) and quantified using a quadrupole mass spectrometer (MS, Hewlett Packard 5973), which was operated in Selected Ion Mode (SIM) with a maximum of six ions being monitored for each time window. The GC oven was initially held at 30 °C for 7 min and was raised to 120 °C at 5 °C min⁻¹. After 5 min the temperature was raised to 180 °C at 6 °C min⁻¹ and held for 7 min.

Gas standards were used as a calibration standard for the GC-MSD/FID system (Wang et al., 2010). Three VOCs with known concentrations, including bromochloromethane, 1,4-difluorobenzene and 1-bromo-3-fluorobenzene were used as internal standards for GC/MSD quantification. Each day calibrations

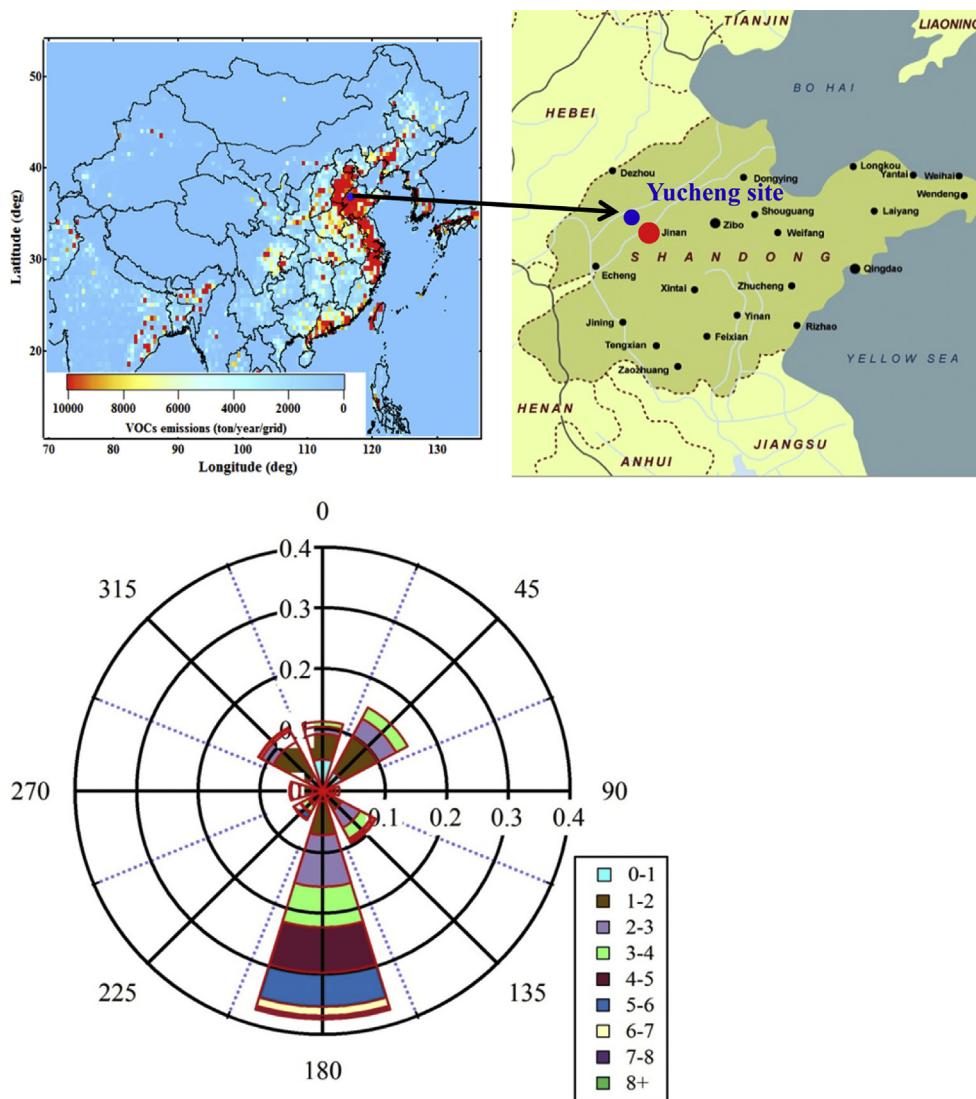


Fig. 1. The site of the Chinese Academy of Sciences-Yucheng site (marked with a blue circle) and the Asian emission inventory of VOCs in 2006 (Zhang et al., 2009), top left panel. Yucheng site (marked with a blue circle) and Jinan city (marked with a red circle), top right panel. The wind rose plot (m/s), bottom left panel. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

were conducted before analysis of the canister samples. The deviation between the analytical results of the daily calibration and the theoretical concentrations was within 10%. The standard deviations of a group of parallel ambient samples were within 15%. The method detection limits (MDLs) of various VOC species ranged from 9 to 57 pptv. The response of the instrument to VOCs was calibrated after every eight samples using standard runs of a calibration gas with ambient concentrations.

3. Results and discussion

3.1. General characteristics of observed VOCs

Fifty-eight VOC species including alkanes, alkenes, alkynes, aromatics and halocarbons were measured at the Yucheng site on sunny/cloudy days from 28 June to 17 July, 2013. The average mixing ratios of these 58 species are summarized in Table 1. The average mixing ratio for the sum of the mixing ratio of each VOC compound (total VOCs) and total non-methane hydrocarbons (NMHCs) were $16,134 \pm 8284$ pptv and $11,396 \pm 436$ pptv,

respectively. Alkanes (40.28%) provided the largest contribution to the total VOCs, followed by halocarbons (29.12%), aromatics (13.56%), alkenes (11.16%) and alkynes (5.88%). Compared with the results obtained from other rural sites in China, the total NMHC mixing ratio reported here was lower than that in Changdao Island (Yuan et al., 2013) and Lin'an in the Zhejiang province (Wang et al., 2004). The total NMHC mixing ratio at Dinghu Mountain in the Guangdong province in 2006 (Tang et al., 2007) was more than two times higher than that at the Yucheng site, but the total NMHC mixing ratio in Mountain Tai in 2006 (Suthawaree et al., 2010) was lower than that at the Yucheng site.

Hotspots for the region during the sampling period were investigated. As shown in Fig. 2(a) and (b), a highly active hotspots disturbance near the site was obvious in 28 June to 07 July, while in 08 July to 17 July, the hotspots noticeably moved south and the active fire spot almost disappeared at the sampling site (<https://firms.modaps.eosdis.nasa.gov/firemap/>). Therefore, the entire sampling period was separated into biomass burning period (28 June–07 July) and non-biomass burning period (08 July–17 July).

The average mixing ratios of the VOC species in the biomass

Table 1

The average mixing ratio and standard deviation (SD) of detected VOC species at the Yucheng site during different sampling periods (unit: pptv).

Name	The whole sampling period		Biomass burning episode		Non-biomass burning episode	
	Mixing ratio	SD	Mixing ratio	SD	Mixing ratio	SD
Ethane	2655	1076	2965	1289	2344	781
n-Butane	506	382	732	429	362	220
Propane	1139	770	1825	1234	752	278
i-Butane	378	225	590	463	238	136
i-Pentane	414	402	507	390	339	224
n-Pentane	160	122	200	169	125	80
2,2-Dimethylbutane	42	18	78	16	23	19
2,3-Dimethylbutane	29	12	51	21	18	10
2-Methylpentane	102	91	147	78	58	67
Cyclopentane	31	12	53	21	16	11
3-Methylpentane	61	38	96	19	36	24
n-Hexane	737	597	1107	609	468	335
2,4-Dimethylpentane	50	12	74	21	35	26
Methylcyclopentane	52	40	80	10	31	25
2-Methylhexane	26	9	46	15	9	16
2,3-DimethylPentane	22	8	39	16	10	4
Cyclohexane	32	13	50	24	15	8
3-Methylhexane	39	10	63	12	13	8
n-Heptane	46	18	71	19	21	12
Methylcyclohexane	37	15	56	36	20	8
n-Octane	48	21	64	35	26	20
n-Nonane	40	6	72	7	11	5
n-Decane	34	12	48	17	10	9
n-Undecane	40	18	56	29	12	16
Ethene	896	707	1351	1004	557	527
1-Butene	38	22	67	36	17	14
Propene	417	354	666	525	214	132
cis-2-Butene	34	10	67	26	10	6
1-Pentene	9	7	11	7	10	6
Isoprene	386	304	464	417	238	159
1-Hexene	55	37	83	14	11	11
Ethyne	937	448	1654	186	395	352
Styrene	23	11	45	17	9	13
Benzene	561	294	858	334	273	241
Toluene	913	575	1376	1053	461	376
Ethylbenzene	94	67	183	96	22	14
m/p-Xylene	79	55	151	136	20	7
o-Xylene	66	50	124	32	15	9
n-Propylbenzene	80	56	132	39	38	23
m-Ethyltoluene	93	37	155	44	34	29
p-Ethyltoluene	98	55	167	39	19	12
o-Ethyltoluene	90	73	131	93	50	45
1,2,4-Trimethylbenzene	99	55	149	39	43	12
o-Diethylbenzene	88	56	144	39	36	13
CCl ₂ F ₂	604	144	791	115	507	117
CHClF ₂	577	329	698	281	357	246
CH ₃ Cl	1371	496	1541	556	927	372
CH ₃ Br	25	4	37	23	10	4
CH ₃ CH ₂ Cl	45	33	81	41	23	18
CCl ₃ F	311	77	338	57	298	61
C ₂ Cl ₃ F ₃	84	21	115	20	65	17
CH ₂ Cl ₂	909	816	1059	370	744	61
1,1-Dichloroethane	34	14	56	20	12	7
CHCl ₃	122	73	178	58	75	48
CCl ₄	97	24	129	94	80	30
1,2-Dichloroethane	282	134	367	36	158	64
1,2-Dichloropropane	141	81	221	42	73	65
Chlorobenzene	56	22	88	16	25	16
Total (VOCs)	16,134	8284	22,736	14,980	10,952	5021

burning and non-biomass burning periods at the sampling site are shown in Table 1. Total VOC mixing ratios were higher in the biomass burning period ($22,736 \pm 14,980$ pptv) than that in the non-biomass burning period ($10,952 \pm 5021$ pptv). The sequence of contributions of the 5 VOC groups to the total VOC mixing ratio was the same during the two periods, and the order, from high to low, was alkanes, halocarbons, aromatics, alkenes and alkynes. In addition, most VOC species had a higher mixing ratio in the biomass burning period. Although certain differences existed in the distribution patterns during the two periods, the main VOC species

in the two periods were alkanes, such as propane, n-Butane and n-Hexane, C₂–C₅ alkenes, such as ethene, propene and isoprene, and aromatics, such as toluene, m/p-xylene and m-Ethyltoluene. CH₃Cl is a good indicator of biomass burning due to its high emissions.

3.2. Day-to-day variability of the major VOC species during the entire sampling period

To better study the day-to-day variability of the selected VOC species, we used log scales to show their mixing ratio. As shown in

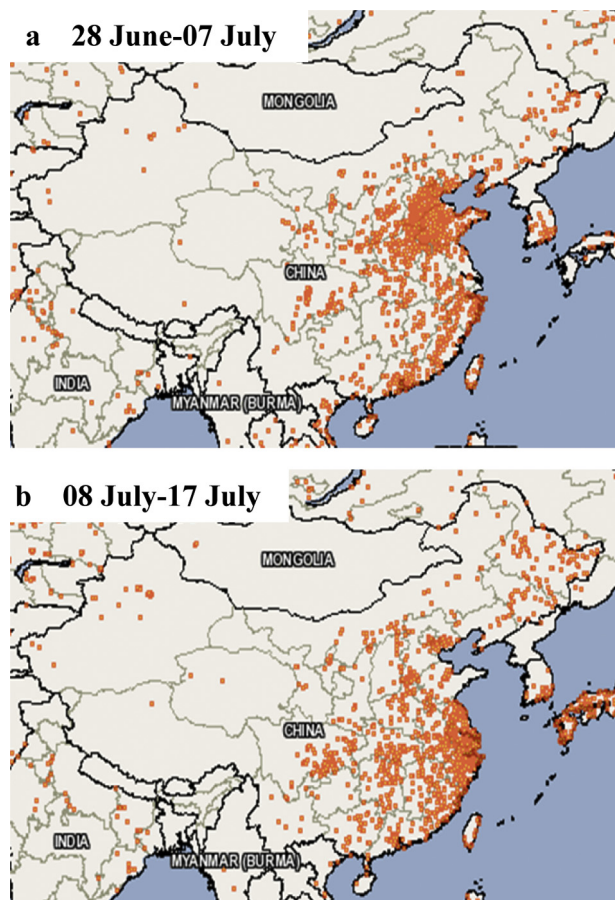


Fig. 2. Hotspots diagram (<https://firms.modaps.eosdis.nasa.gov/firemap/>), (a) the biomass burning episode (28 June to 07 July) and (b) the non-biomass burning episode (08 July to 17 July).

Fig. 3a and b, most VOC species mixing ratios had similar day-to-day variability, indicating that the air mass at the Yucheng site had small local perturbation (Sharma et al., 2000; Kato et al., 2004). Fig. 3a and b also illustrated that the higher carbon number VOC species had lower mixing ratios, whereas lower carbon numbers had higher mixing ratios.

It was noted that the n-Hexane mixing ratio had a dissimilar day-to-day variability to other VOC species. According to Chan et al. (2006), n-Hexane is mostly used in construction coating solvents and paint thinners. Owing to the day-to-day variability of n-Hexane, it can be concluded that solvent usage affected the air masses at the sampling site. Toluene is primarily emitted by mobile sources and solvent usage (Liu et al., 2008b) and also shows a different variation with other species, indicating that mobile sources and solvent usage were important sources of VOCs.

Fig. 3c shows the peaks of CH_3Cl appear approximately at the same time as those of CH_3Br . The mixing ratios of CH_3Cl and CH_3Br were all above the earth's atmospheric background mixing ratios (CH_3Cl : 530–560 pptv, CH_3Br : 8–9 pptv) (World Data Centre for Greenhouse Gases, 2008). These species are tracers of biomass burning emissions (Andreae and Merlet, 2001), suggesting that the Yucheng site was affected by biomass burning during the sampling period.

3.3. Diurnal variation patterns of VOC mixing ratios

Fig. 4 shows that the total VOCs, alkanes, alkenes, alkynes and aromatics at the Yucheng site had peaks in the early morning (6:00

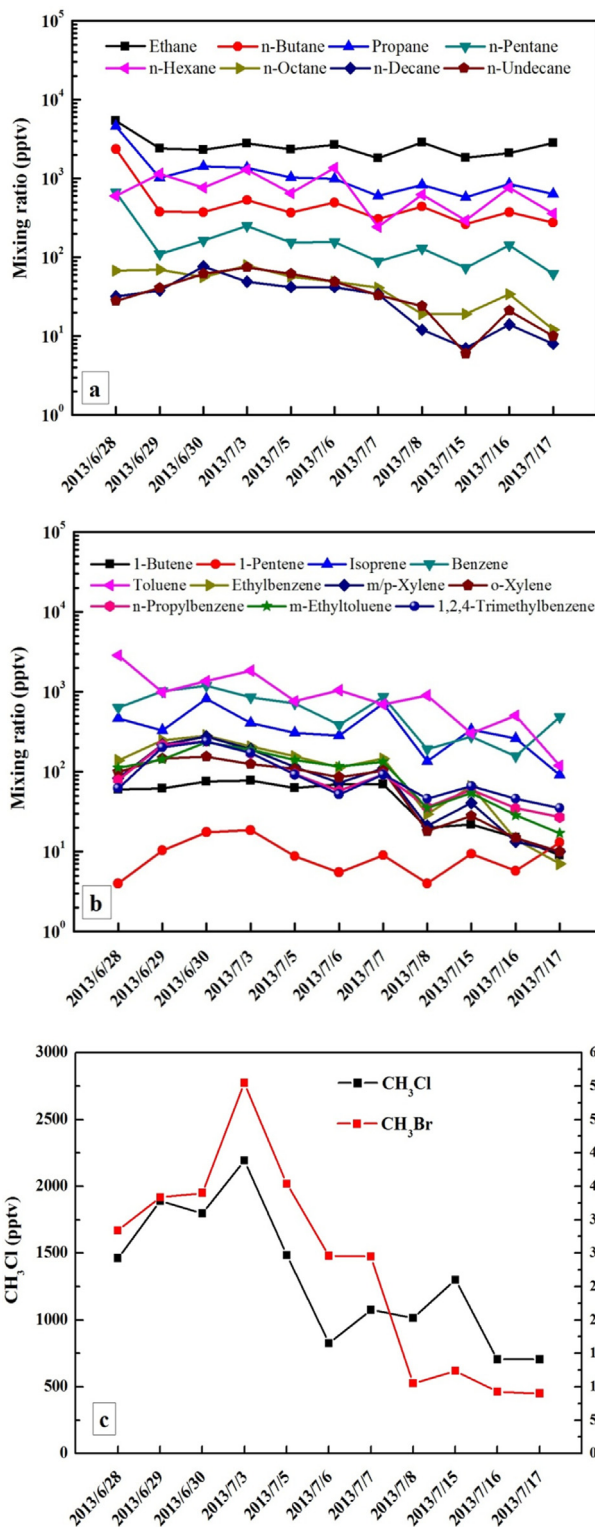


Fig. 3. Mixing ratios of selected hydrocarbons from measured VOC species.

then decreased, and began to increase until 16:00. The early morning peaks may be as a result of biomass burning and accumulation of pollutants due to advection of plumes from urbanized areas upwind (67.43% of the wind direction was south) coupled by stagnant meteorological conditions (such as low mixing height and wind speed, with the average wind speed 1.2 m/s between

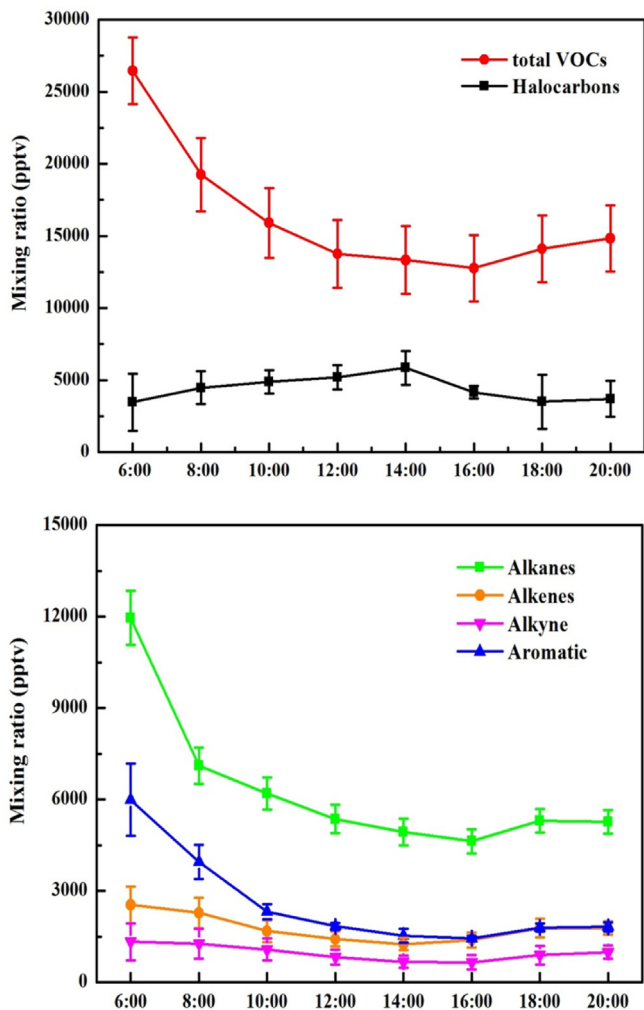


Fig. 4. Diurnal variation patterns of measured total VOCs, halocarbons, alkanes, alkenes, alkynes and aromatics at the sampling site (28, 29 June and 6, 15, 16, 17 July, 2013).

20:00–6:00). In the afternoon (16:00), the weak photochemical removal processes and low mixing height are the likely reasons for the elevated mixing ratio of VOCs.

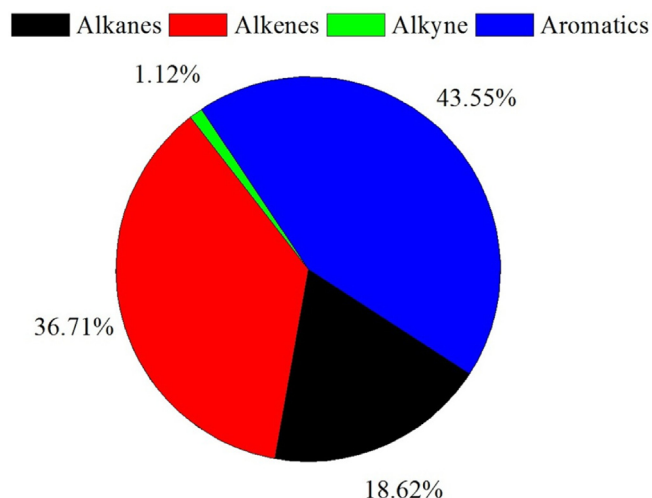


Fig. 6. Ozone formation potential distributions (%) of four VOC groups to the total ozone formation potential at the Yucheng site.

The photochemical process can be examined using the ratio of ethylbenzene/m,p-xylene (E/X), which have a common origin but are considerably different in reactivity (Atkinson, 1995). The calculated lifetimes of ethylbenzene, m-xylene and p-xylene are 1.6 days, 11.8 h and 19.4 h (Atkinson, 1994; Monod et al., 2001) (assuming $[OH] = 10^6 \text{ rad cm}^{-3}$). Ethylbenzene is considered a less reactive species while xylenes are considered a more-reactive species. A higher E/X ratio implies an aged air parcel (Hsieh and Tsai, 2003). As shown in Fig. 5, about 60% of E/X ratios were higher than 1.0, which indicated that the sampling site receives aged air mass. Fig. 5 also shows that the peaks of ethylbenzene/m,p-xylene and O_3 approximately appeared at the same time and ethylbenzene/m,p-xylene and O_3 had high correlation ($r = 0.51$, $P < 0.01$). Consequently, the Yucheng site can be characterized as a downwind environment receiving older air.

The mixing ratios of halocarbons reached peaks at 14:00 and then slowly decrease, which may be related to the evaporative emissions of some halocarbon species. For example, CH_2Cl_2 , $CHCl_3$, CCl_4 and 1,1-dichloroethane, which are important organic solvents,

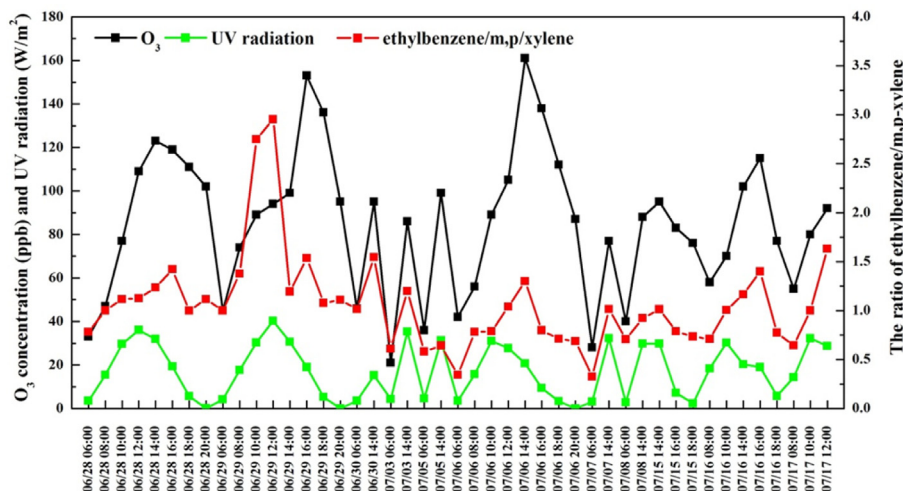


Fig. 5. The time-series of O_3 concentrations (ppb), UV radiations (W/m^2) and ratios of ethylbenzene/m,p-xylene at the Yucheng site.

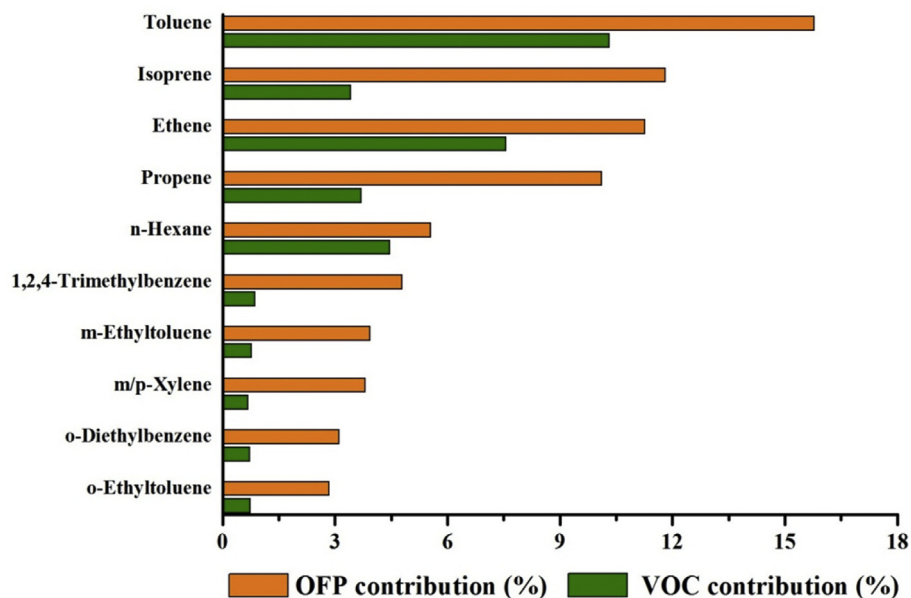


Fig. 7. Top 10 VOC species contributing to total ozone formation potential (%) and the corresponding contributions to the total VOCs mixing ratio (%) at the Yucheng site in 2013.

increase in the evaporative emissions due to elevated temperatures (Abrahamsson et al., 2004).

3.4. Variations in ozone formation potential

Ozone formation potential (OFP) was used to evaluate the photochemical reactivity of different VOC species (Carter, 1994). The OFP of an individual VOC species can be calculated as the product of ambient concentrations of VOC species and the

corresponding values of maximum incremental reactivity (MIR). MIR values derived from study by Carter (2009) were used. Using the following equation, OFP can be calculated as

$$\text{OFP}_i = \text{VOC}_i \times \text{MIR}_i$$

where OFP_i and VOC_i are the ozone formation potential and the mixing ratio of VOC species i , both in units of $\mu\text{g}/\text{m}^3$. MIR_i is the maximum increment reactivity for individual VOC species i to

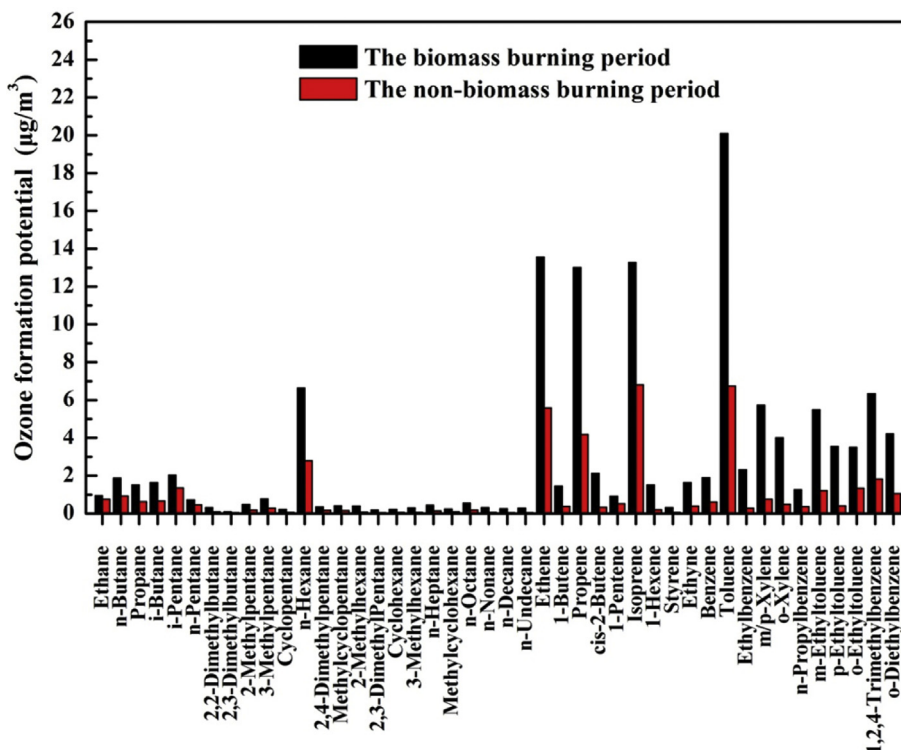


Fig. 8. The ozone formation potential values ($\mu\text{g}/\text{m}^3$) of VOC species in the biomass burning and non-biomass burning periods.

indicate its contribution to local ozone formation.

Although important species in climate change, halocarbons have very low photochemical reactivity and were not included in the calculation, as MIR values were not available (Carter, 2009). The total OFP value at the Yucheng site was $82.76 \pm 14.39 \mu\text{g}/\text{m}^3$ during the 2013 campaign. The contribution of the VOC group to the total OFP is illustrated in Fig. 6. The aromatics and alkenes were the dominant contributors to total OFP. Aromatics and alkenes together consisted of around 80.26% of the total OFP of VOCs, while alkanes and alkynes contributed around 19.74%.

Fig. 7 shows the top 10 VOC species based on OFP, along with their corresponding contributions to the total VOC mixing ratios. These 10 species accounted for 71.84% of the total ozone formation and 29.82% of the total VOC mixing ratio. As shown in Fig. 7, toluene had the highest OFP, followed by isoprene, ethene, propene, n-Hexane, 1,2,4-Trimethylbenzene, m-Ethyltoluene, m/p-xylene, o-Diethylbenzene and o-Ethyltoluene. Toluene was ranked fifth in terms of total VOC mixing ratio contribution and it was the most activated VOC species for ozone formation, making up 15.94% of the total OFP at the Yucheng site. This result indicates that a species with large OFP contributions does not necessarily have a large mixing ratio. Isoprene was the second most abundant species, accounting for 11.93% of the total OFP contribution, yet it only had 2.86% of the total VOC mixing ratio. Note that the highly ranked species obtained using the OFP method were toluene, 1,2,4-Trimethylbenzene, m/p-xylene, all closely associated with the use of solvents. This suggests that evaporative emissions from solvent use are important in ozone formation at the Yucheng site.

As shown in Fig. 8, the highest total OFP value ($121.78 \mu\text{g}/\text{m}^3$) was found in the biomass burning period, and was 3.69 times higher than that in the non-biomass burning period ($45.12 \mu\text{g}/\text{m}^3$). This result revealed that products of biomass burning are important ozone precursors in the atmosphere. Previous studies have shown that biomass burning emissions can contribute to elevated ozone concentrations at the source origin (Jaffe et al., 2004; Boian and Kirchhoff, 2005; Shan et al., 2009) and downwind of significant biomass burning source regions (Boian and Kirchhoff, 2005).

The aromatics (45.87%) and alkynes (1.29%) in the biomass burning period had higher OFP contributions than in the non-biomass burning period (aromatics, 35.24% and alkynes, 0.95%), while the contribution of alkanes and alkenes to OFP was higher in the non-biomass burning period (alkanes, 20.70% and alkenes, 43.11%) compared with those in the biomass burning period (alkanes, 16.56% and alkenes, 36.28%).

3.5. Effect of air mass transport on the VOC levels during the biomass burning periods

To investigate the influence of regional transport, back trajectories of the Yucheng site during the campaign were performed using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model (Draxler and Rolph, 2003). We calculated three-dimensional, three-day back trajectories and classified the trajectories into four different groups during the biomass burning and non-biomass burning periods (Fig. 9), based on transport directions and speeds in both the horizontal and vertical scales.

Fig. 9a shows the route of air masses during the biomass burning period. The highest VOC concentrations were observed in Cluster 3, which contained the shortest trajectories and moved slowly. Cluster 3, which was also the most frequent trajectory cluster (45%), originated from the northeast of the Hebei province, turned to the northwest, flowed over the Shandong province and then to the sampling site. The areas that the trajectory passed over had a larger biomass burning disturbance relative to other provinces in China. Moreover, the Hebei and Shandong provinces are well populated,

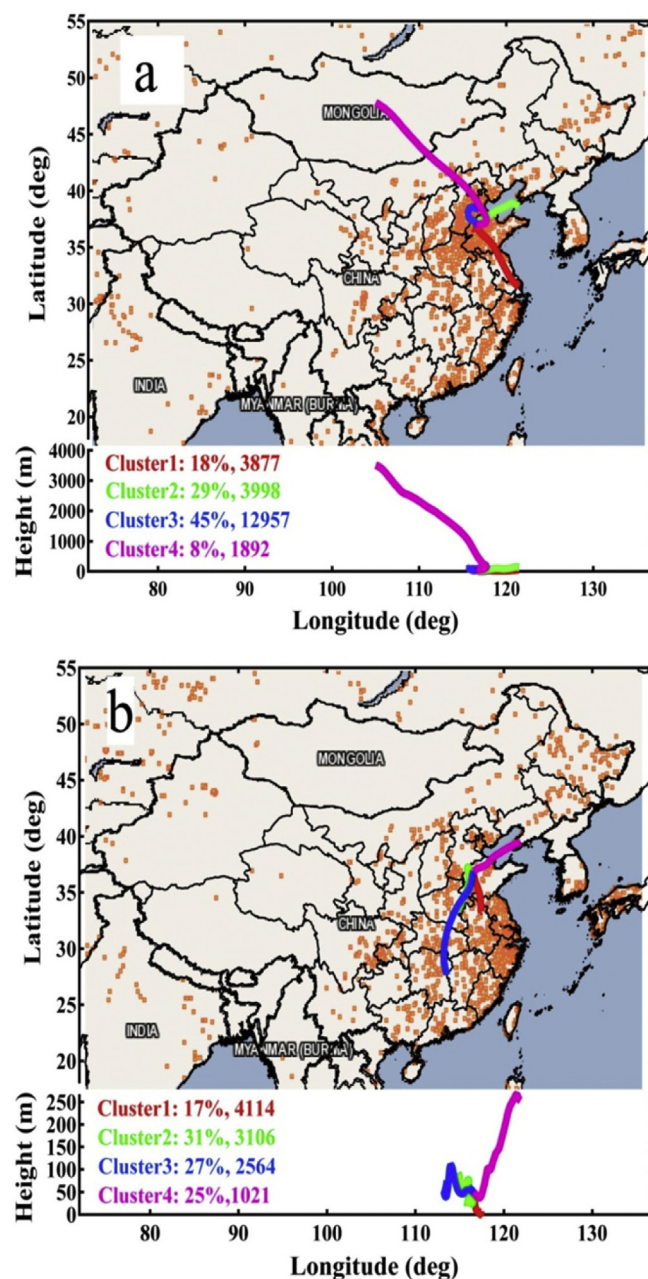


Fig. 9. Mean three-day backward trajectory clusters during biomass burning (a) and non-biomass burning (b) periods. The orange dots are hotspots during the campaign. The numbers in the legend show the percentage of each air mass category identified and the average VOC mixing ratio (pptv) in each cluster. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

industrial zones of China, with high emission levels of VOCs (Zhang et al., 2009). Cluster 1 and Cluster 2 had similar VOCs mixing ratios. Both of them passed over VOCs polluted (Zhang et al., 2009) and biomass burning area, but had low frequent and long trajectories compared with Cluster 1. Cluster 4 originated in the northwest of sampling site and contained the longest trajectories and the highest altitudes in this study. It moved rapidly and impacted few on VOCs at sampling site.

During the non-biomass burning period, Cluster 1 had the highest VOC concentration, was associated with trajectories having the shortest transport patterns and moved very slowly at altitudes between 0 m and 100 m (Fig. 9b). And Cluster 1 passed over high

VOCs polluted area, such as Shandong and Anhui provinces (Zhang et al., 2009). These results indicated that air pollutants in Cluster 1 were influenced by anthropogenic sources in the southeast of the Shandong province. Cluster 2 and Cluster 3 arrived from the southwest, including the Henan, Hubei and Hunan provinces, which had low VOC emission quantities relative to Cluster 1 passed over areas (Zhang et al., 2009). Moreover, Cluster 2 and Cluster 3 trajectories were long and moved quickly compared with Cluster 1. Clusters 4 derived from the Bohai Sea and were relatively clean and could effectively diffuse and dilute the VOC pollution at the sampling site. Thus, it had lowest VOC mixing ratios.

4. Summary

In this study, field measurements of VOCs were conducted at the Yucheng site, a rural site downwind of Jinan, in the Shandong province, from 28 June to 17 July, 2013. The average mixing ratios for the total VOCs and total NMHCs were $16,134 \pm 8284$ pptv and $11,396 \pm 436$ pptv, respectively. The hotspots data indicated that biomass burning period was between 28 June and 07 July. Over the entire sampling period, the dominant contributors to total VOC mixing ratios were alkanes and halocarbons. Most VOC species mixing ratios had similar day-to-day variability, and the higher carbon number VOC species having lower mixing ratios, showing that air mass at the Yucheng site had small local perturbation. The early morning peaks of the VOC species at the Yucheng site were thought to be the result of biomass burning and advection of plumes from more urbanized areas upwind. The peak of halocarbons at 14:00 may be related to the evaporative emissions of some halocarbon species. Ethylbenzene/m,p-xylene ratio and its relation with O_3 indicated that sampling site received an aged air parcel. The aromatics and alkenes were the dominant contributors to total OFP. The top 5 VOC species based on OFP were toluene, isoprene, ethene, propene and n-Hexane. Aromatics and alkynes in the biomass burning period had higher OFP contributions, while the contribution of alkanes and alkenes to OFP was higher in the non-biomass burning period. Back-trajectory calculations demonstrated that the effect of biomass burning on air masses arriving to the site had an important role in atmospheric VOCs.

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