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Influence of Cloud/Fog on Atmospheric VOCs in the Free Troposphere: A Case Study at Mount Tai in Eastern China

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ABSTRACT

Field measurements of volatile organic compounds (VOCs) were conducted in July of 2015 at Mount Tai, where 63 species of VOCs were measured using GC-MS. In this study, air samples were collected in two different weather conditions: cloud/fog and non-cloud/fog respectively and influences of the cloud/fog on VOCs species were analyzed. The sources of air masses were calculated by back trajectories with HYSPLIT model. Five main kinds of VOCs were analyzed and oxy-VOCs (OVOCs) had the largest contribution (67% on the cloudy/foggy days and 72% on the non-cloudy/foggy days) to total measured VOCs among all of the samples collected at Mount Tai. Acetone was the most abundant compound (18 ppb on the cloudy/foggy days and 15 ppb on the non-cloudy/foggy days) among the VOCs. The concentrations of VOCs collected in cloudy/foggy days were higher than those measured in non-cloudy/foggy days and indicated that cloudy/foggy days favoured the accumulation of atmospheric VOCs. However, the concentrations of most OVOCs in non-cloud/fog conditions were higher than those in cloud/fog conditions. Atmospheric photochemical reactions may partly account for this result. Air mass trajectory analysis shows that most air masses from heavily polluted areas results in the increase of atmospheric VOCs. OVOCs and aromatics provided the main contribution to ozone formation potential. Besides cloud and fog, VOC concentration is concerned with integrated factors including temperature, relative humidity, wind speed and direction.

Keywords: Atmospheric VOCs; Mount Tai; Cloud; Fog; Photochemical reactions.

INTRODUCTION

Meteorological conditions, such as cloud and fog, have a significant effect on the dispersion, chemical/physical transformation and removal of atmospheric pollutants (David and Nair, 2011; Sahu *et al.*, 2016). Clouds have an important effect on tropospheric photochemistry, and further influence the concentrations of tropospheric compounds (Tie *et al.*, 2003). Prather and Jacob (1997) found that the upper troposphere is more active in producing ozone (O_3) by convective injection of peroxides, aldehydes and ketones. Barth *et al.* (2002) found that the aqueous phase chemistry in clouds plays an important role in the variation of O_3 concentrations in the troposphere. Moreover, clouds alter the actinic flux by scattering solar radiation, which consequently impact the photolysis rates of several key oxidant species (Tie *et al.*, 2003).

Fog is an aerosol system composed of liquid or solid hydrometeor particles that are suspended in the air near the ground (Taylor, 1917; Yang *et al.*, 2012). Fog, which usually forms under circumstances of stable stratification, weak winds and a shallow mixing layer, will result in the increase of the concentration of pollutants in the atmosphere by the accumulations in the surface layer. In addition, the droplets in fog work as the "micro-reactors" in the air because of their small size, high humidity, large specific surface area and long residence time. Therefore, they are conducive to producing secondary pollutants by transforming some primary pollutants (Yang *et al.*, 2012).

VOCs, one of the principal trace constituents in the atmosphere, play an important role in atmospheric chemistry (Barletta *et al.*, 2002; Guo *et al.*, 2004a, b). They contain a wide range of organic compounds with many different functional groups (Yu and Crump, 1998; Sahu, 2012). Some

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of the VOCs and their photochemical products, such as benzene, toluene, formaldehyde and acraldehyde, have adverse effects on human health. By entering through the respiratory tract or skin into the human body, they may lead to acute or chronic health problems, such as inflammation, heart and lung diseases and even cancer (Ras *et al.*, 2010; Chen *et al.*, 2016). VOCs also have negative impacts on natural environment in a large extent. They have a significant contribution to forming atmospheric fine particles and influencing the oxidizing capacity of the atmosphere by reacting with OH radicals. In addition, atmospheric chemical reaction cycles consisting of VOCs and NO_x (NO_x = NO + NO_2) in the presence of solar radiation lead to the formation of ozone and secondary organic aerosols (SOA) (Liu *et al.*, 2008; Sahu *et al.*, 2016), indirectly influencing the radiation balance of the earth's surface and consequently contributing to climate change (Pandis *et al.*, 1992; Kroll and Seinfeld, 2008; Derwent *et al.*, 2010; Wang *et al.*, 2012).

In addition to anthropogenic and biogenic sources, VOCs may also be formed by atmospheric transformations of other kinds of VOCs in the atmosphere (Atkinson and Arey, 2003), e.g., the oxidation of hydrocarbons in the atmosphere is an important source of OVOCs (Mellouki *et al.*, 2015). Anthropogenic sources dominate as urban sources of VOCs, such as emissions from vehicles, landfills, refineries, petrochemical sources, solvent usage and industrial facilities (Atkinson and Arey, 2003).

Researches on VOCs in China are mainly focused on metropolises and urban agglomeration, such as Beijing, the Pearl River Delta and the Yangtze River Delta (Zhang *et al.*, 2014). And there is relatively little information about VOCs in remote areas, especially in the high mountains. Research on VOCs in the high mountains is of great significance to the study of global temporal and spatial variation of VOCs. Studies now have been performed on the concentration characteristics, seasonal and diurnal variations and source identification of VOCs at the summit of some mountains in China (Tang *et al.*, 2007; Tang *et al.*, 2008; Zhang *et al.*, 2014; Yang *et al.*, 2016).

Many studies have concentrated on characterizing the deposition of pollutants in cloud/fog water. However, relatively fewer researches were focused on variations in gaseous pollutants during cloud/fog events, especially in the high mountains. Yang *et al.* (2012) found VOCs concentration had significantly negative correlation with visibility during winter fog events in Nanjing. Sahu *et al.* (2016) found that the stagnant weather conditions, such as fog and drizzle, favoured the accumulation of VOCs. It was also stated in some papers that the existence of clouds has an impact on photolysis and oxidants in the troposphere (Barth *et al.*, 2002; Tie *et al.*, 2003), and then it will affect the atmospheric pollutants. In addition, field investigations of VOCs have been conducted at Mount Tai in June 2006 (Ting *et al.*, 2009). Based on earlier research studies about VOCs in the high mountains or cloud/fog events, targeted sampling in foggy (cloudy/foggy condition) and sunny (non-cloudy/foggy condition) days at Mount Tai in July 2015 was conducted to mainly study the influence of cloud and fog on the characteristics of atmospheric VOCs in the free troposphere.

EXPERIMENT AND METHODS

Sample Collection

The sampling campaign was carried out in the meteorological observation station (36.25°N, 117.10°E) at an elevation of 1,534 m a.s.l on Mount Tai, which is the highest mountain in the North China (Huabei) Plain. Mount Tai is located in the eastern part of the North China Plain, one of the major agricultural areas in China, in the middle of the Shandong province. Industrial cities and coal-producing areas, such as Jinan, Weifang, Laiwu and Yanzhou, are within 200 kilometres of Mount Tai. Located in a warm temperature zone and characterized by a continental monsoon climate, summers in Mount Tai are hot and rainy. Because of high altitude, the temperature at the mountaintop is generally much lower than that at the foot of Mount Tai. Rising from the ground, Mount Tai obstructs the warm and moist air masses from plain areas during their horizon transmission. And then the air masses forced to rise in the windward slope cool easily and condense into cloud/fog. Cloud and fog are important weather phenomena in the atmosphere, and they are thought to have similar physical/chemical mechanism. With low water content, pollutant levels in cloud/fog are generally much higher than precipitation. Enveloped cloud/fog is the noted natural splendor at Mount Tai and attracts millions of tourists each year. Therefore, Mount Tai is a representative mountain site for cloud/fog observation in summer.

Targeted air samples on cloudy/foggy days and non-cloudy/foggy days were collected into SUMMA canisters with a capacity of 3.2 litres from July 10–25, 2015. The sampling time of the collected samples ranged from 0.5 h to 4 h. The flow rate was controlled by a CS1200 flow-limiting valve. The sampling process and analysis were conducted according to the US EPA Methods TO-14 and TO-15. The concentrations of O_3, NO and NO_2 as well as meteorological data, such as the atmospheric pressure, wind speed, relative humidity (RH) and temperature (T), were continuously recorded. The SUMMA canisters were cleaned and evacuated three times by Entech 3100A Canister Cleaner before sampling. In addition, field blanks of pure nitrogen were collected periodically and processed by the same analytical procedures as the samples.

Sample Analysis

Analyses of all of the samples were performed by a preconcentrator instrument (Entech7100A) and then followed by a GC-MS system (GC/MS QP 2010). The details of the analytical procedures of VOCs have been described previously by Yang *et al.* (2016) and will be described here briefly.

A 400-mL sample was concentrated in an Entech7100A preconcentrator, where nitrogen, oxygen, argon, water and carbon dioxide were removed by a three-stage preconcentration. Finally, the highly concentrated compounds were rapidly desorbed and then swept into the column of the GC for separation and analysis.

Each target VOC was identified by its retention time and m/z (mass to charge ratio) based on USEPA standard gases, and analysis was conducted under the SIM mode.

Quantification of the target VOCs was performed using the internal standard curves method with four internal standards (bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5 and 3-bromofluorobenzene), and the corresponding VOCs of each internal standard see Yang *et al.* (2016). The correlation coefficients of the curves ranged from 0.900 to 1.000. In this study, 63 VOCs were measured in atmospheric samples from Mount Tai in July 2015, including alkanes, alkenes, aromatics, halocarbons and OVOCs, as shown in Table 1.

HYSPLIT Model

Long-range transport can carry air pollutants including VOCs emitted from source regions to the study site (Gao *et al.*, 2005; Zhang *et al.*, 2014). The pollutants emitted in the planetary boundary layer (PBL) are transported from PBL to free troposphere by strong convections in summer. Pollutants transported within the free troposphere can travel long distances and strongly influence the concentrations of trace gases (Gao *et al.*, 2005; Ting *et al.*, 2009). To study the impact of back trajectories on the VOC concentrations of the samples in this study, an online version of the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, whose website is http://ready.arl.noaa.gov/HYSPLIT.php, was used to study the influence of the long-range transport of air masses. Back trajectories with 48 h duration were calculated for each day during sampling.

Table 1. The average mixing ratios of VOCs under cloud/fog and non-cloud/fog conditions on Mount Tai.

Compound	mixing ratio (ppb)		Compound	mixing ratio (ppb)	
	cloud/fog	non-cloud/fog		cloud/fog	non-cloud/fog
Alkanes			Chloroethane	0.057 ± 0.04	0.090 ± 0.01
Hexane	0.069 ± 0.08	0.088 ± 0.01	DCM	0.230 ± 0.06	0.163 ± 0.02
Cyclohexane	0.064 ± 0.03	0.012 ± 0.02	Chloroform	0.575 ± 0.34	0.303 ± 0.12
Heptane	0.038 ± 0.03	0.016 ± 0.03	CTC	0.063 ± 0.07	0.002 ± 0.00
Alkenes			1,1-DCA	0.041 ± 0.01	0.021 ± 0.02
Propene	0.337 ± 0.32	0.322 ± 0.06	1,2-DCA	0.396 ± 0.16	0.329 ± 0.14
Chloroethylene	0.077 ± 0.02	0.074 ± 0.01	1,2-DCP	0.130 ± 0.11	0.091 ± 0.08
1,3-Butadiene	0.066 ± 0.00	0.045 ± 0.04	1,1,1-TCA	0.022 ± 0.02	0.015 ± 0.01
1,1-DCE	0.035 ± 0.02	0.014 ± 0.02	1,1,2-TCA	0.051 ± 0.05	0.034 ± 0.02
(E)-1,2-DCE	0.027 ± 0.02	0.012 ± 0.01	1,1,2,2-TeCA	0.213 ± 0.03	0.063 ± 0.10
(Z)-1,2-DCE	0.079 ± 0.09	0.062 ± 0.02	1,2-EDB	0.015 ± 0.03	0.018 ± 0.03
(E)-1,3-DCp	0.038 ± 0.05	0.024 ± 0.02	BDCM	0.019 ± 0.02	0.033 ± 0.01
(Z)-1,3-DCp	0.101 ± 0.15	0.032 ± 0.03	DBCM	0.058 ± 0.01	0.021 ± 0.03
TCE	0.032 ± 0.04	0.009 ± 0.01	Bromoform	0.066 ± 0.05	0.071 ± 0.06
PCE	0.001 ± 0.00	0.024 ± 0.02	Chlorobenzene	0.107 ± 0.13	0.002 ± 0.00
HCBD	0.450 ± 0.30	0.342 ± 0.30	1,2-DCB	0.239 ± 0.20	0.214 ± 0.02
Aromatics			1,3-DCB	0.262 ± 0.21	0.154 ± 0.02
Benzene	0.406 ± 0.33	0.465 ± 0.23	1,4-DCB	0.237 ± 0.26	0.198 ± 0.11
Toluene	0.356 ± 0.14	0.197 ± 0.22	1,2,4-TCB	0.286 ± 0.53	0.025 ± 0.01
Ethylbenzene	0.148 ± 0.10	0.130 ± 0.02	Benzyl chloride	0.366 ± 0.24	0.501 ± 0.08
m/p-Xylene	0.167 ± 0.12	0.059 ± 0.10	**OVOCs**		
o-Xylene	0.005 ± 0.01	0.003 ± 0.00	Ethanol	0.114 ± 0.08	0.311 ± 0.54
p-Ethyltoluene	0.135 ± 0.09	0.146 ± 0.01	Isopropanol	0.049 ± 0.10	1.828 ± 1.77
1,3,5-TMB	0.158 ± 0.02	0.099 ± 0.08	Acrolein	0.046 ± 0.03	0.031 ± 0.01
1,2,4-TMB	0.200 ± 0.13	0.187 ± 0.15	Acetone	18.064 ± 13.96	15.216 ± 8.39
Styrene	0.134 ± 0.08	0.073 ± 0.06	2-Butanone	0.141 ± 0.16	0.203 ± 0.17
Naphthalene	0.502 ± 0.68	0.369 ± 0.46	MTBE	0.001 ± 0.00	0.028 ± 0.02
Halocarbons			Vinyl acetate	0.002 ± 0.00	0.029 ± 0.02
CFC-11	0.311 ± 0.03	0.307 ± 0.02	Ethyl acetate	0.262 ± 0.18	0.334 ± 0.15
CFC-12	0.594 ± 0.02	0.559 ± 0.00	THF	0.031 ± 0.03	0.052 ± 0.02
CFC-113	0.112 ± 0.00	0.110 ± 0.00	MMA	0.044 ± 0.03	0.005 ± 0.00
CFC-114	0.068 ± 0.00	0.057 ± 0.00	p-Dioxane	0.031 ± 0.05	0.027 ± 0.03
Chloromethane	1.214 ± 0.40	0.939 ± 0.19	MNBK	0.126 ± 0.09	0.173 ± 0.15
Bromomethane	0.035 ± 0.04	0.059 ± 0.01	MIBK	0.058 ± 0.03	0.060 ± 0.02

DCE: Dichloroethene; DCp: Dichloropropene; TCE: Trichloroethylene; PCE: Perchloroethylene;
HCBD: Hexachlorobutadiene; TMB: Trimethylbenzene; CFC-11: Trichlorofluoromethane;
CFC-12: Dichlorodifluoromethane; CFC-113: Trichlorotrifluoroethane; CFC-114: Dichlorotetrafluoroethane;
DCM: Dichloromethane; CTC: Carbon tetrachloride; DCA: Dichloroethane; TCP: Dichloropropane;
TCA: Trichloroethane; TeCA: Tetrachloroethane; EDB: Ethylene dibromide; BDCM: Bromodichloromethane;
DBCM: Dibromochloromethane; DCB: Dichlorobenzene; TCB: Trichlorobenzene; MTBE: Tert-butyl methyl ether;
THF: Tetrahydrofuran; MMA: Methyl methacrylate; MNBK: Methyl n-butyl ketone; MIBK: Methyl isobutyl ketone.

RESULTS AND DISCUSSION

Impact of Fog on the General Characteristics of Atmospheric VOCs

In this study, 63 VOCs were measured in atmospheric samples from Mount Tai in July 2015 as shown in Table 1. Some samples were collected on cloudy/foggy days and others on non-cloudy/foggy days during our sampling period. The distributions of the 5 types of VOCs measured on cloudy/foggy and non-cloudy/foggy days are shown in Fig. 1. The measurements indicated that the dominant VOC species are primarily OVOCs (67% on the cloudy/foggy days and 72% on the non-cloudy/foggy days) and halocarbons (20% on the cloudy/foggy days and 17% on the non-cloudy/foggy days) among all of the samples collected at Mount Tai. OVOCs also had the largest contribution (67–85%) in the previous study (Sahu *et al.*, 2016). OVOCs, which had the largest contribution to total measured VOCs in this study, may mainly originate from both photochemical oxidation of non-methane hydrocarbons (NMHCs) and direct emissions by biogenic and anthropogenic sources (Legreid *et al.*, 2008; Tanimoto *et al.*, 2013; Sahu *et al.*, 2016).

As shown in Fig. 1(b), all of the VOC concentrations on the cloudy/foggy days were higher than those on the non-cloudy/foggy days. The result agrees with Sun *et al.* (2006). Poor dispersion of VOCs and weak photochemical reactions on the cloudy/foggy days is the most likely explanation for this result. Alkanes had the greatest contribution to this difference, and their concentration under cloudy/foggy conditions was 46% higher than that under non-cloudy/foggy conditions.

Tiny droplets or ice crystals from heavy cloud/fog can reflect or scatter sunlight, which reduces the amount of solar radiation that reaches the earth's surface as well as the ground temperature. Under this circumstance, the change in temperature is negligible along the vertical gradient, which is conducive to generating an inversion layer and static weather conditions (Zhou, 2015). Consequently, stagnant weather condition discourages further diffusion of air pollutants and favours the accumulation of VOCs. In addition, heavy cloud/fog days tend to be paired with stable stratification and weak winds, leading to greater difficulty in further atmospheric pollutant dispersion (Yang *et al.*, 2012). And since solar radiation has been weakened from the cloud/fog, the photochemical reactions consuming VOCs could not take place effectively (Yang *et al.*, 2012).

On non-cloudy/foggy days, such as sunny days, strong solar radiation can cause the mixing height of the PBL to increase. Therefore, the measurements of VOCs under non-cloud/fog conditions were generally lower due to efficient dispersion and photochemical reactions. Consequently, the VOC concentrations were generally higher on cloudy/foggy days.

However, there was an exception on July 14 during our sampling campaign. The total concentration of VOCs on July 14, which experienced non-cloud/fog conditions, was 33 ppb, higher than some of the levels found on cloudy/foggy days. The back trajectories of July 14 (red line), as shown in Fig. 2(a), may explain this phenomenon.

On July 14, mixed air masses arrived at the peak of Mount Tai from some industrial cities in Shanxi and Henan Province, such as Taiyuan, Yangquan, Changzhi and Jiaozuo

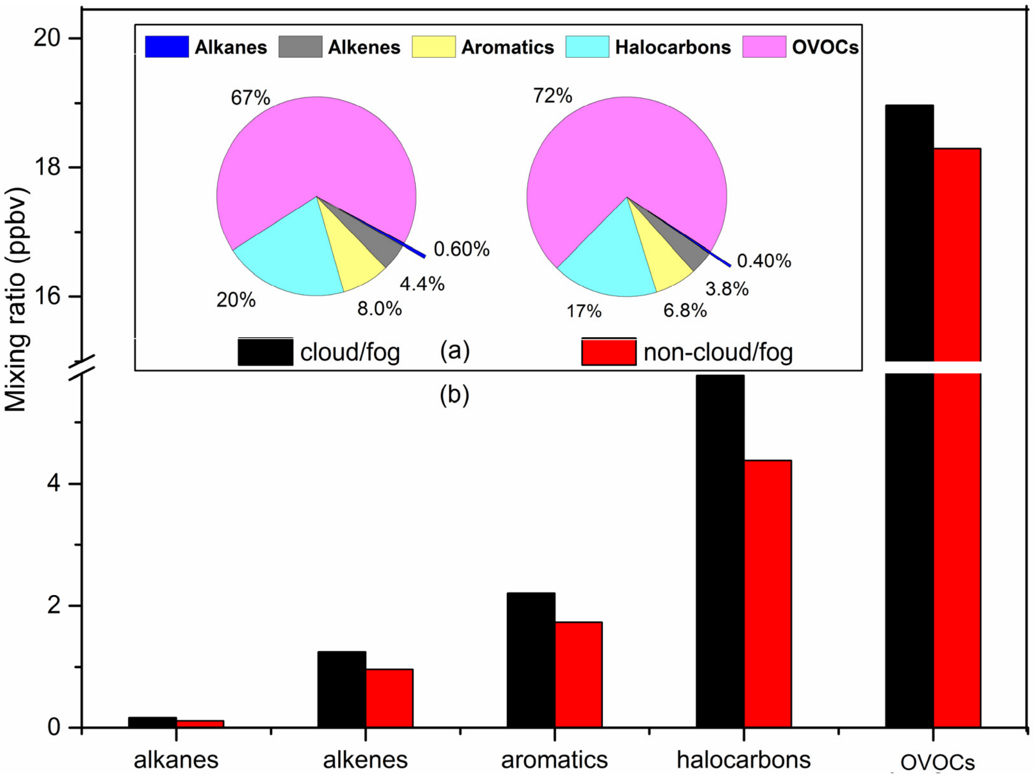

Fig. 1. Contributions and comparison of VOCs concentrations on cloudy/foggy and non-cloudy/foggy days at Mount Tai.

in Fig. 2(b). These industrial cities are the most heavily polluted areas. Apart from this, the vertical components of the trajectories revealed an upward transport of pollutants from heavy polluted areas, as indicated by the blue air masses in Fig. 2(b), and thus, the concentration of pollutants at the sampling site will increase accordingly. Hence, higher levels of VOCs during the period of sampling were observed on that day, which is related to the transport of mixed air masses from polluted areas as well as the rising of tropospheric air masses.

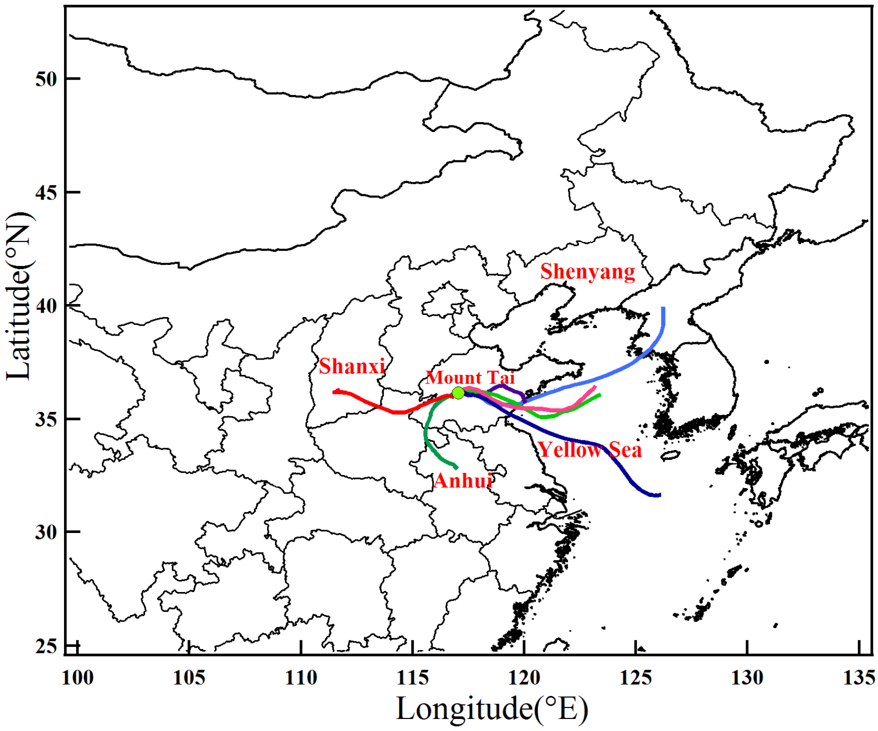

Fig. 2(a). The results of the backward trajectory model during the measurement.

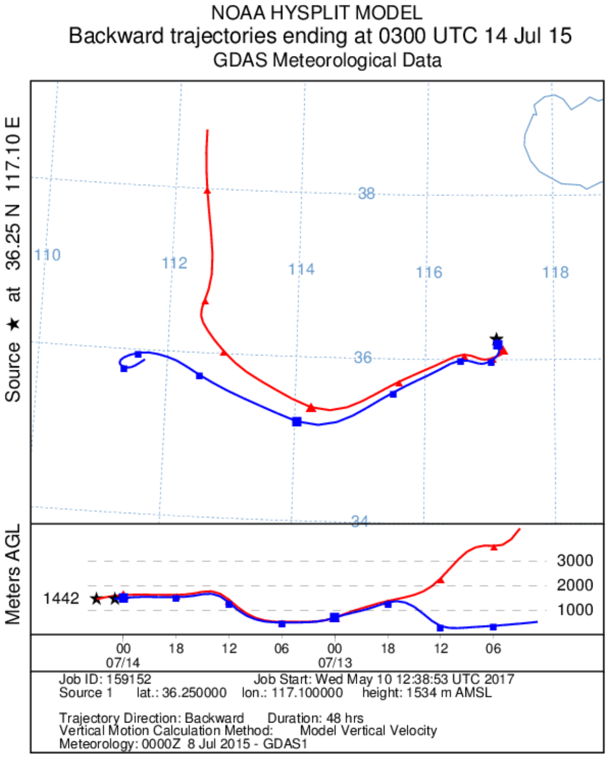

Fig. 2(b). The results of the backward trajectory model on July 14.

The relationship between VOCs and other meteorological parameters (e.g., T, RH, wind speed and direction) was also discussed as shown in Fig. 3. The relative humidity was above 60% and the temperature was between 15 and 25°C during the sampling period. Fig. 3 also shows the south wind and wind speed (> 2 m s^{-1}) played a dominant role during the measurements. In our study, a single meteorological parameter doesn't have a definite impact on the characteristics of VOCs. The measured VOC concentration is a consequence of interactions among all the meteorological factors and chemical reactions.

Impact of Cloud and Fog on OVOCs

As described above, OVOCs had the largest contribution to the total measured VOCs; thus, the impact of cloud/fog on OVOCs formed the main discussion. Sahu *et al.* (2016) compared the mixing ratios of VOCs measured under 7 different kinds of different weather conditions, such as clear sky, fog, drizzle and so on and found that OVOCs showed strong dependence on weather conditions. In our study, the difference in the concentration of OVOCs seems to show a more significant variation due to different weather conditions than other types of VOCs as shown in Fig. 1(a). This result shows that cloudy and foggy conditions may have a significant impact on the characteristics of OVOCs.

Although nearly all of the VOC concentrations were generally higher on cloudy/foggy days, most of the OVOC concentrations except for MMA, acrolein and acetone were higher on non-cloudy/foggy days, as shown in Fig. 4. On non-cloudy/foggy days, such as sunny days with stronger solar radiation, VOCs may react with OH radicals, NO_3 radicals and O_3 to produce a series of complicated photochemical reactions. Some OVOCs may also be formed in the atmosphere as products of atmospheric transformations of other VOCs. For example, alcohols and aldehydes are produced by photochemical reactions of alkanes, and part of its reaction mechanism is shown below (Eqs. (1)–(5)). In the equations, hv is the photon energy with a wavelength between 280 and 430 nm (Seinfeld, 1989), R is an organic moiety (e.g., CH_3, C_2H_5). In addition, a comparison of the concentrations between alkanes and alcohols on cloudy/foggy and non-cloudy/foggy days, as presented in Table 1, shows that the data agree with the reactions. Generally speaking, the concentration of alkanes was relatively higher on cloudy/foggy days, while most of OVOCs mainly except for acetone was higher on non-cloudy/foggy days.

$$NO_2 + hv \rightarrow NO + O \tag{1}$$

$$RH + NO \xrightarrow{O_2} RO_2 + H_2O \tag{2}$$

$$RO_2 + NO \rightarrow RO + NO_2 \tag{3}$$

$$RO \xrightarrow{O_2} RCHO + HO_2 \tag{4}$$

$$RCH_2O_2\text{-} + RCH_2O_2\text{-} \rightarrow RCHO + RCH_2OH + O_2 \tag{5}$$

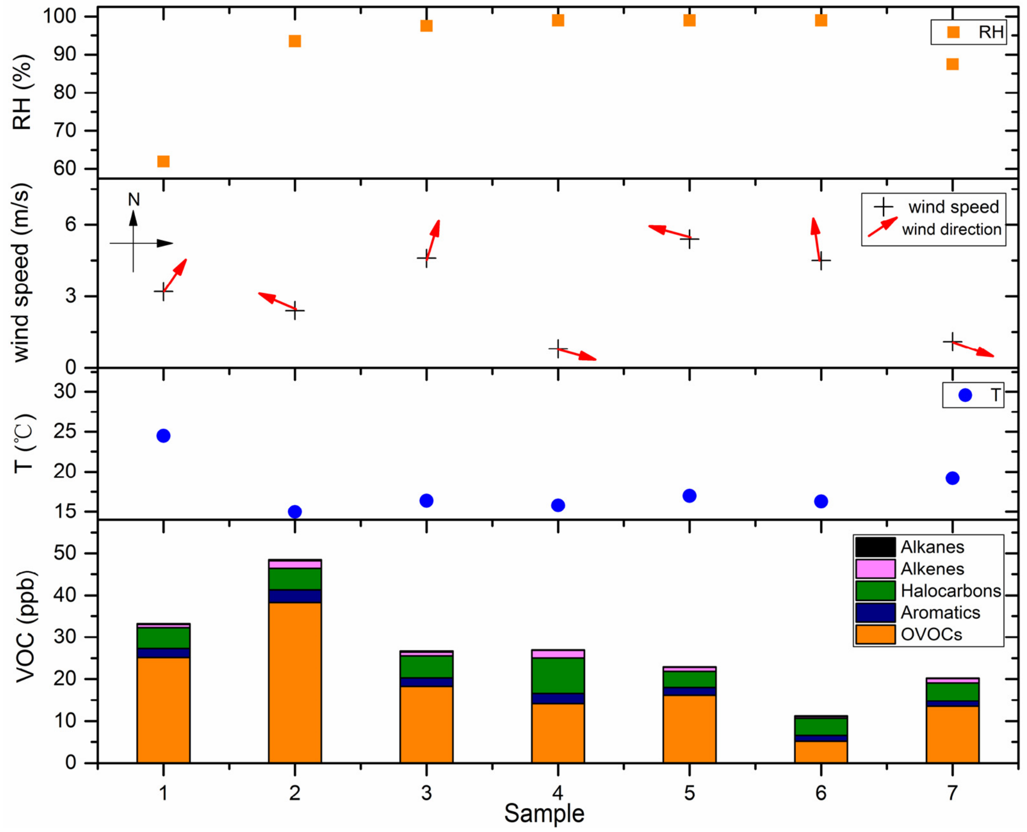

Fig. 3. Diurnal variation of mean values of RH, T, wind speed and direction and VOC concentration.

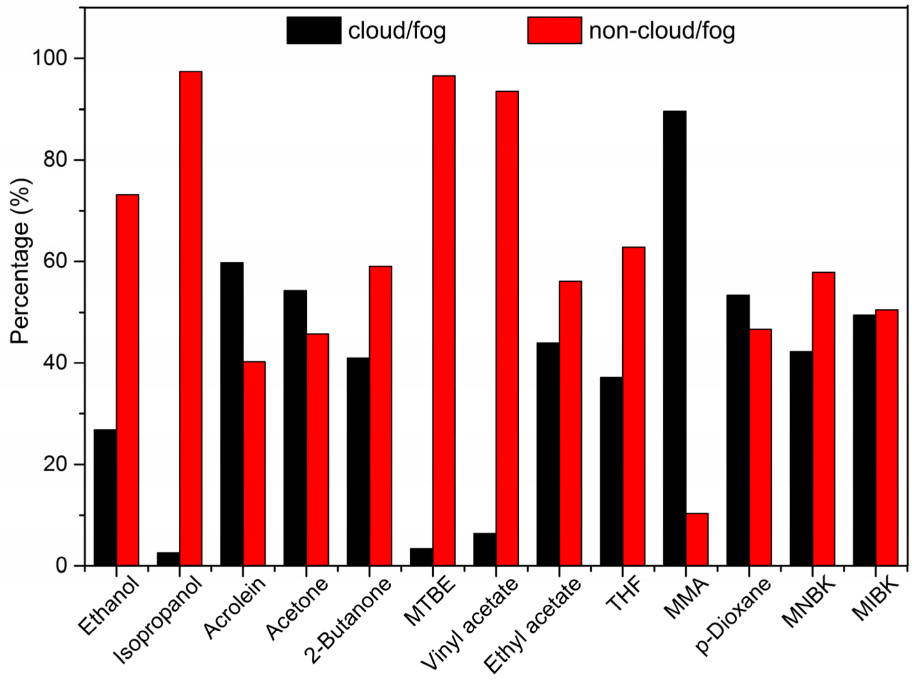

Fig. 4. Contributions of the concentrations of OVOCs under cloud/fog and non-cloud/fog conditions.

In the presence of cloud/fog, VOCs may partially dissolve into the aqueous phase according to their solubility. Dissolved organic compounds can take part in various isomerization, oligomerization and hydrolysis reactions in fog droplets. In addition, microbial activity may also contribute to the oxidation of dissolved organics in cloud droplets during periods with low free radical load (Vaïtilingom *et al.*, 2010). However, most importantly, aqueous photolysis and its reaction with dissolved OH radicals are significant chemical sinks of VOCs in cloud and fog droplets (Epstein and Nizkorodov, 2012). Saxena and Hildemann (1996) found that highly water-soluble organics could be produced by the photo-oxidation of VOCs in the atmosphere. The functional groups of water-soluble fraction contain carboxyls, carbonyls, hydroxyls, etc. (Epstein *et al.*, 2013). Therefore, OVOCs dissolved in atmospheric water droplets may react with dissolved OH radicals or undergo direct photolysis by actinic radiation. Epstein and Nizkorodov (2012) found aqueous photolysis and aqueous phase OH oxidation are significant sinks for some organic compounds, including organic acids, aldehydes, ketones and ethers. Tie *et al.* (2003) used FTUV and MOZART-2 models to estimate the impacts of clouds on photolysis and tropospheric chemistry. The results suggested that clouds have an important impact on the tropospheric oxidation capacity and increase global mean OH concentration. In addition, wet and/or dry deposition of OVOCs in the troposphere is also an important loss mechanism (Mellouki *et al.*, 2015). Consequently, OVOCs concentration was generally lower in cloudy/foggy days.

As shown in Table 1, it is significant that acetone (18 ppb on the cloudy/foggy days; 15 ppb on the non-cloudy/foggy days) was the most abundant compound among the 63 VOCs on the cloudy/foggy as well as non-cloudy/foggy samples, which was then followed by chloromethane (1.2 ppb) on cloudy/foggy days and isopropanol (1.8 ppb) on non-cloudy/foggy days. Similar results were found in a previous study (Garzón *et al.*, 2015). Atmospheric acetone plays an important role in atmospheric chemistry, acting as a principal source of hydrogen oxide radicals ($HO_x = OH + HO_2$) (Jaeglé *et al.*, 2001; Fischer *et al.*, 2012; Hu *et al.*, 2013), and is thought to originate from the photochemical oxidation reaction of VOCs (Chatfield *et al.*, 1987; Reissell *et al.*, 1999; Garzón *et al.*, 2015). Acetone can also be emitted by the metabolic process and plant decay of terrestrial vegetation (Warneke *et al.*, 1999; Fall, 2003). This may account for the high acetone levels at Mount Tai, which is rich with vegetation. In addition, acetone has relatively stable chemical properties and a longer mean tropospheric lifetime, which is estimated to be between 14 and 35 days, and its photolysis rate and reaction rate with OH radicals are 60 and 53 days (Atkinson, 2000; Fischer *et al.*, 2012; Hu *et al.*, 2013), respectively. Therefore, emissions of acetone have a cumulative effect in the atmosphere among various sources, which also results in a higher concentration of acetone. Lastly, there is a local source of ketone compounds from incense burning at temples on Mount Tai (Chen *et al.*, 2012), which may also contribute to the high concentration of acetone at Mount Tai.

Comparison of Ozone Formation Potential (OFP) in the Conditions of Cloud/Fog and Non-Cloud/Fog

OFP is used as an index to quantify the potential of a VOC compound in ozone production (Carter, 1994; Yang *et al.*, 2016). The actual production of ozone is eventually produced by a specific hydrocarbon and dependent on its particular oxidation mechanism, the amount of VOCs and NO_x concentrations (Carter, 1994, 1998; Goldan *et al.*, 2004). Therefore, OFP does not fully account for the entire atmospheric chemistry of the related compounds, but it does provide a simple way to measure the relative contribution assessment of individual VOCs to photochemistry (Goldan *et al.*, 2004).

The OFP is used to quantify the contribution of each type of VOC to ozone formation. The formula used to calculate OFP for each type of VOC is as follows:

$$\mathrm{OFP_i} = \mathrm{c_i} \times \mathrm{MIR_i} \quad (6)$$

In the formula, c_i denotes the environmental concentration of each type of VOC and the constant MIR_i denotes the maximum ozone incremental reaction coefficient for each type of VOCs (Carter, 2009). Not every VOC has a constant MIR, so only VOCs that have a constant MIR were selected for comparison. Fig. 5 shows the OFP for each species of VOCs measured in the air. Acetone and propene contributed more to the total calculated OFP, with contributions of 26% and 16%, respectively. Based on the results, VOCs with higher concentrations will not necessarily contribute more to the total calculated OFP. For example, the concentration of chloromethane is the second highest, accounting for 4.0% of the VOCs; however, it only contributes 0.17% of the total calculated OFP. While propene only accounts for 1.2% of the total measured VOC concentration, it contributes to 16% of the total calculated OFP.

For all five types of VOCs, the concentrations and photochemical reactivities of OVOCs and aromatics are comparatively higher; thus, they have the largest contributions to ozone production. On the contrary, the concentrations and photochemical reactivity of alkanes and halocarbons are comparatively lower; thus, they have little contribution to ozone production. Moreover, the concentrations of each type of alkenes are generally lower, but the OFP of alkenes (5.3 ppb) was higher than those of alkanes (0.17 ppb) and halocarbons (0.33 ppb). The results for aromatics, alkenes and alkanes agree with the findings of Zhou *et al.* (2014) whose contributions of aromatics, alkenes and alkanes to OFP are 42%, 39% and 17%, respectively. The C=C double bonds of alkenes enable them to be more reactive in photochemical reactions and have higher values of the constant MIR and therefore contribute more to the total OFP than alkanes and halocarbons.

The OFP are calculated on the cloudy/foggy and non-cloudy/foggy days, and the contributions of VOCs to OFP are shown in Fig. 6. The OFP of cloudy/foggy days is generally higher than that of non-cloudy/foggy days, which shows that cloudy/foggy days have the potential to form more ozone. This result is also in accordance with the findings in section 3.1. Tie *et al.* (2003) also found that tropospheric O_3 concentrations increased by 8% because of the impact of clouds in their study.

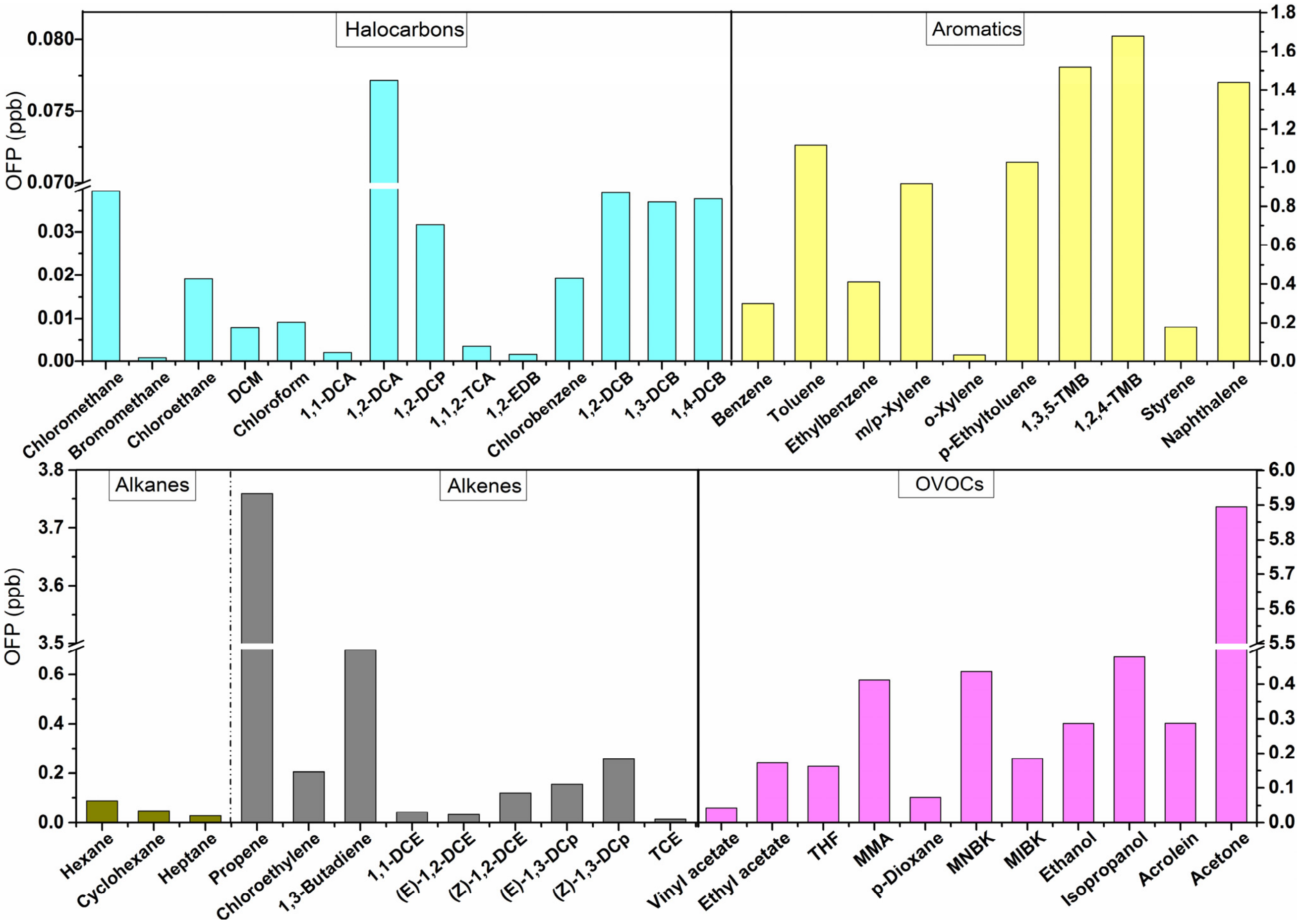

Fig. 5. OFP distributions of each type of VOC measured in the air at Mount Tai.

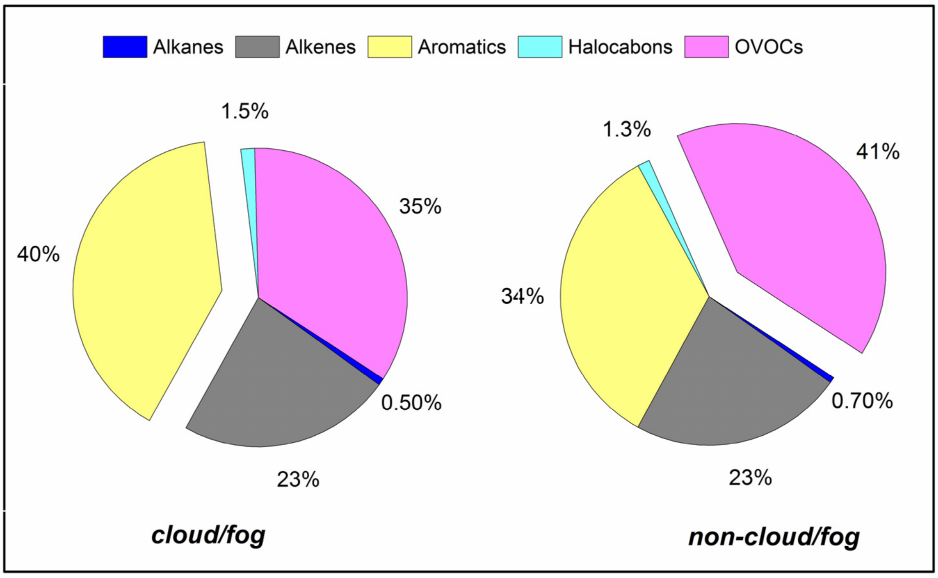

Fig. 6. Contributions of five species of VOCs to OFP in the air on the cloudy/foggy and non-cloudy/foggy days at Mount Tai.

For the samples collected on cloudy/foggy days, aromatic hydrocarbons (40%) had the largest contribution to the total OFP, while OVOCs had the largest contribution (41%) on non-cloudy/foggy days. The results obtained also coincide with the findings in section 3.2. OVOCs, which had the largest contribution to ozone formation on non-cloudy/foggy days, may be related to the photochemical reactions that produce OVOCs. Since the photochemical reactions were weakened on cloudy/foggy days due to the lack of solar radiation, the OFP of OVOCs was relatively low.

On cloudy/foggy days, the main ozone precursor was aromatics, while OVOCs were the main ozone precursor on non-cloudy/foggy days. The value of total calculated OFP increased from 21 ppb on non-cloudy/foggy days to 24 ppb on cloudy/foggy days. Therefore, cloud/fog has an impact on the dispersion and removal of atmospheric VOCs.

As we mentioned before, O_3 and NO_x are also measured at Mount Tai. VOC and NO_x are two main precursors of O_3, and O_3-NO_x-VOC chemistry has an impact on the evaluation of ozone formation (Sillman and He, 2002). These measurements provide more detailed information to analyze the O_3 formation (Geng *et al.*, 2008). Numerical simulations of ozone pollution in Los Angeles in the 1980s (Seinfeld, 1989) provided an indicator (VOC/NO_x ratio) to evaluate VOC- or NO_x-limited regimes leading to ozone formation. At VOC/NO_x ratios of about 8 or less, VOC control is generally more effective, otherwise NO_x control is generally more effective. In our study, we just use this ratio to determine whether ozone formation was VOC-limited or NO_x-limited. Fig. 7 shows the diurnal variations of five kinds of VOC concentration, VOC/NO_x ratio, O_3 concentration measured and OFP calculated during the sampling period. It's clearly shown that each kind of VOC concentration, NO_x concentration and total OFP all had an anti-correlation with O_3 concentration before Day 4 and then had the same trend. VOC/NO_x ratios were lower than 8 between Day 4 and Day 7, which suggested that ozone formation was mainly VOC-limited during these days. It should be noted that the VOC/NO_x ratio is an approximate not accurate value in Los Angeles, and there may be different situations in different regions. A photochemical model and more measurements are needed to get a more accurate analysis.

CONCLUSIONS

VOCs measurements were conducted at the peak of Mount Tai (1534 m a.s.l) in July 2015 to study the influence of cloud/fog on atmospheric VOCs in the free troposphere. Sixty-three species of VOCs were measured, including alkanes, alkenes, aromatics, halocarbons and OVOCs.

In this study, samples were collected on cloudy/foggy and non-cloudy/foggy days. Acetone was the most abundant pollutant among all of the VOCs. OVOCs had the largest contribution to total measured VOCs among all of the samples, which may be due to the photochemical oxidation of NMHCs as well as biogenic or anthropogenic source emissions.

In the presence of cloud/fog, the weather is generally stable and conducive to the accumulation of atmospheric pollutants. Moreover, cloud/fog reduces the photochemical oxidation of VOCs because of the reduction of solar radiation. Therefore, the VOCs concentrations on cloudy/foggy days were higher than those on the non-cloudy/foggy days. However, the concentrations of most OVOCs on non-cloudy/foggy days are substantially higher, which may be due to the gas phase reactions on non-cloudy/foggy days as well as the aqueous phase reactions in the presence of cloud/fog.

OFP was calculated to assess the contribution of VOCs to potential ozone production. The OFP on cloudy/foggy days is generally higher than that on non-cloudy/foggy days, which is in accordance with the higher VOC concentrations

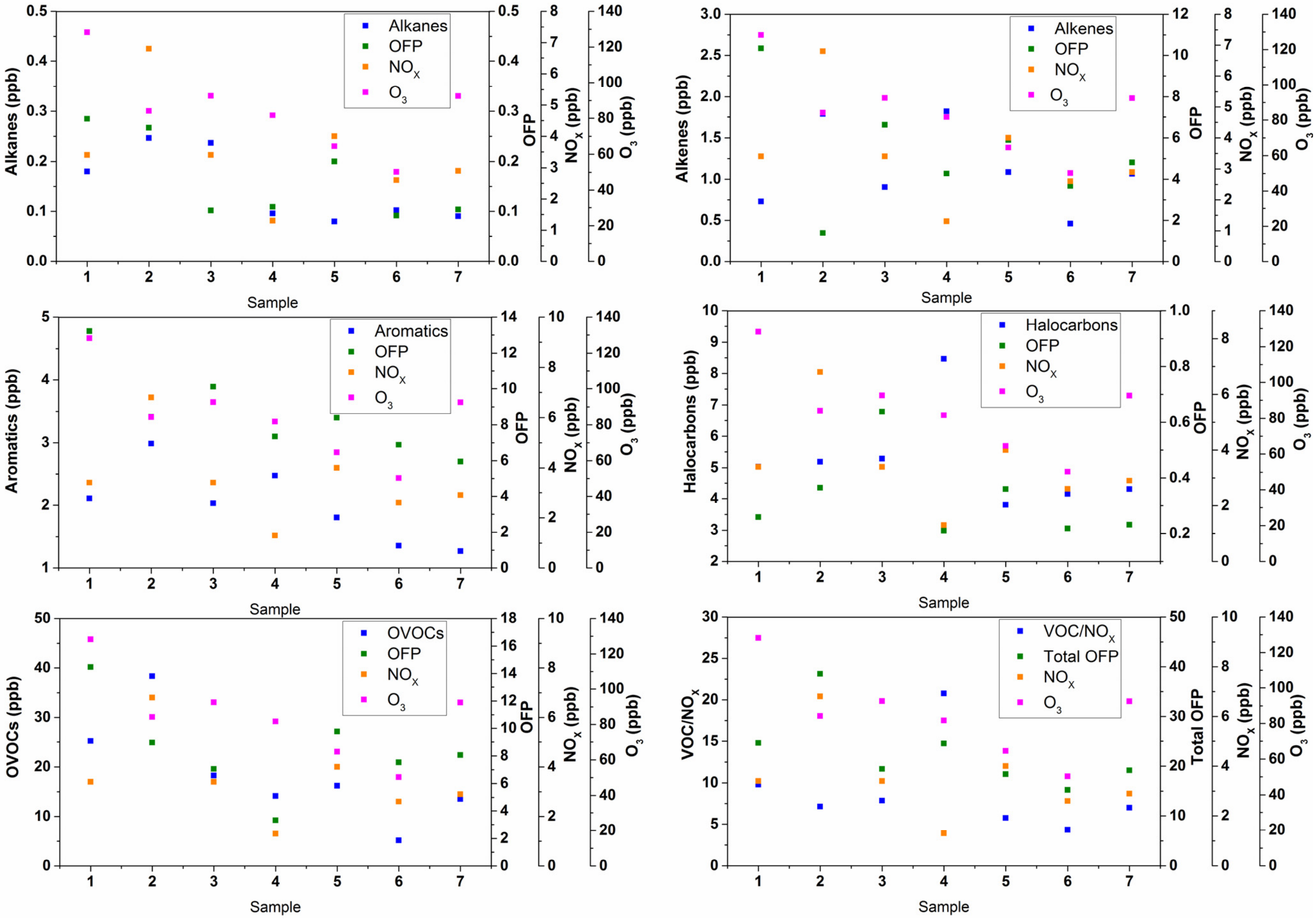

Fig. 7. The variation patterns of VOC/NO$_x$ ratio, five kinds of VOC concentration and their OFP, NO$_x$ and O$_3$ concentration.

on cloudy/foggy than non-cloudy/foggy days. Aromatics had the largest contribution to the total OFP on cloudy/foggy days, while OVOCs had the largest contribution on non-cloudy/foggy days. This agrees with the comparison of the OVOCs concentration between cloudy/foggy and non-cloudy/foggy days. In addition, the main ozone precursor and the value of OFP differ between cloudy/foggy and non-cloudy/foggy days, changing from aromatics to OVOCs and from 24 ppb to 21 ppb.

Overall, cloud and fog have an impact on the deposition and removal of atmospheric VOCs by a series of physical and chemical processes. This process has a significant effect on the characteristics of VOCs at high mountains under special weather conditions. However, to get more accurate result, specific model simulation study and longer field measurements are needed.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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