Characteristics of Summertime Volatile Organic Compounds in the Lower Free Troposphere: Background Measurements at Mt. Fuji

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ABSTRACT

Air samples were collected at Mt. Fuji Research Station (FRS) for the measurements of volatile organic compounds (VOCs) in the summers of 2015 and 2016. In this study, 24 compounds were analyzed, of which only 12 halocarbons were quantified in 2015. The average total concentrations of target VOCs were 2.62 ± 1.38 and 2.99 ± 0.95 ppb in 2015 and 2016, respectively. The concentrations of individual VOCs ranged from a few ppt to a few ppb, indicating a highly inhomogeneous feature at the FRS. A cluster analysis of 3-day backward trajectories was performed for the sampling time. Except for the aromatic compounds, the VOCs showed relatively low concentrations in association with air masses originating from the coastal region in the low latitudes (15°N–35°N) of East Asia in 2015. By contrast, the clusters with elevated VOC concentrations mainly came from the high latitudes (35°N–60°N) of the Asian continent in 2016. No particular diurnal pattern was found for VOCs and CO, which might have resulted from suppressed mountain-valley winds at the FRS. Halocarbons regulated by the Montreal Protocol showed low variability and were in favorable agreement with background values at the Gosan station (GSN) and those reported in the literature. Other partially halogenated compounds with higher variability, such as CH_3Cl and $CHCl_3$, showed discrepancies at the FRS and GSN. 1,2-dichloroethane (R-150), 1,1-dichloroethane (R-150a), and 1,4-dichlorobenzene (*p*-DCB) were also measured at the FRS with concentrations of 24 ± 14, 38 ± 13, and 13 ± 10 ppt, respectively, in 2015. A close relationship between *n*-pentane and *i*-pentane with R^2 more than 0.85 was found in both 2015 and 2016. Low ratios of *n*/*i*-pentane ranging from 0.25 to 0.67 were observed in the free troposphere at the FRS, comparable to most mountain stations.

Keywords: Mt. Fuji Research Station (FRS); Mt. Fuji Weather Station (FWS); Volatile organic compound (VOC); Ozone-depleting substance (ODS); Halocarbons; Pentane; Dichloroethane; 1,4-dichlorobenzene; Chlorofluorocarbon (CFC).

INTRODUCTION

Volatile organic compounds (VOCs) are primary precursors to the photochemical formation of ground-level ozone (Cardelino and Chameides, 1995) and aerosols (Kanakidou *et al.*, 2005), which are the two main components of smog. VOCs are emitted from various anthropogenic and natural sources (Blake and Blake, 2002; Litvak, 2003). The dominant anthropogenic sources of VOCs include vehicle exhaust, liquefied petroleum gas leakage, industrial and residential solvent evaporation, extraction and refining of fossil fuels, and biomass burning. Once released, the VOCs are transported and reacting with hydroxyl (OH) radicals and nitrogen oxides ($NO_x = NO + NO_2$) to produce ozone in the presence of sunlight (Le Bras, 2003). Depending on their reactivity with oxidants, such as OH radicals, some VOCs can travel over a long distance because of their relatively long lifetime in the atmosphere (Parrish *et al.*, 2007). Most halocarbons such as anthropogenic chlorofluorocarbons (CFCs) poorly react with OH radicals and can persist in the atmosphere for decades, which is long enough for these compounds entering stratosphere and to destroy the ozone layer (Carpenter *et al.*, 2014). The Montreal Protocol and

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its subsequent amendments set out a mandatory timetable for the phase out of ozone-depleting substances (ODS) for developed and developing countries (UNEP, 1987, 1992). As a result of a global emission reduction, the concentration of major tropospheric ODS has steadied and been decreasing for more than a decade as reported in literature (Rigby *et al.*, 2013; Carpenter *et al.*, 2014; Ou-Yang *et al.*, 2015).

In recent years, a higher growth rate of tropospheric ozone has been observed in East Asia than in other regions (Cooper *et al.*, 2014). For instance, a significant increase in ozone of 0.23 DU yr^{-1} was observed in the free troposphere over eastern China for the period of 2005–2010, which was nearly two-fold greater (0.13 DU yr^{-1}) than that over the western US (Verstraeten *et al.*, 2015). Air pollutants such as ozone released in the boundary layer of East Asia are sent into free troposphere predominately through the process of frontal lifting (Liu *et al.*, 2003). The increased ozone in East Asia can therefore be rapidly spread over the northern Pacific (Hoell *et al.*, 1997; Zhang *et al.*, 2008) and transport to North America (Jaffe *et al.*, 1999; Parrish *et al.*, 2009; Cooper *et al.*, 2010; Verstraeten *et al.*, 2015; Lin *et al.*,

2017). A deeper understanding of the characteristics of VOCs and photochemical mechanisms underlying the Asian continental outflow can be gained by obtaining measurements on the rim of the western Pacific.

The characteristics of VOCs in the lower free troposphere have been examined using several approaches. Measurements have been obtained using aircrafts (Blake *et al.*, 1996; Bechara *et al.*, 2008; Baker *et al.*, 2010) and tethered balloons (Helmig *et al.*, 1998; Spirig *et al.*, 2004) operated at different heights. Ground-based measurements of VOCs at high-altitude stations have also been conducted in various locations, such as North America (Swanson *et al.*, 2003; Khwaja and Narang, 2008; Burley *et al.*, 2016), Europe (Karl *et al.*, 2001; Li *et al.*, 2005; Helmig *et al.*, 2008; Lanz *et al.*, 2009; Lo Vullo *et al.*, 2016a, b), Africa (Schmitt and Volz-Thomas, 1997), East Asia (Sharma *et al.*, 2000; Suthawaree *et al.*, 2010; Xue *et al.*, 2013; Yang *et al.*, 2016), and Hawaii (Greenberg *et al.*, 1992, 1996).

The Mt. Fuji Research Station (FRS, 35.37°N, 138.73°E, 3776 m above sea level, Fig. 1), formerly Mt. Fuji Weather Station (FWS), was established in 1932 and is operated by
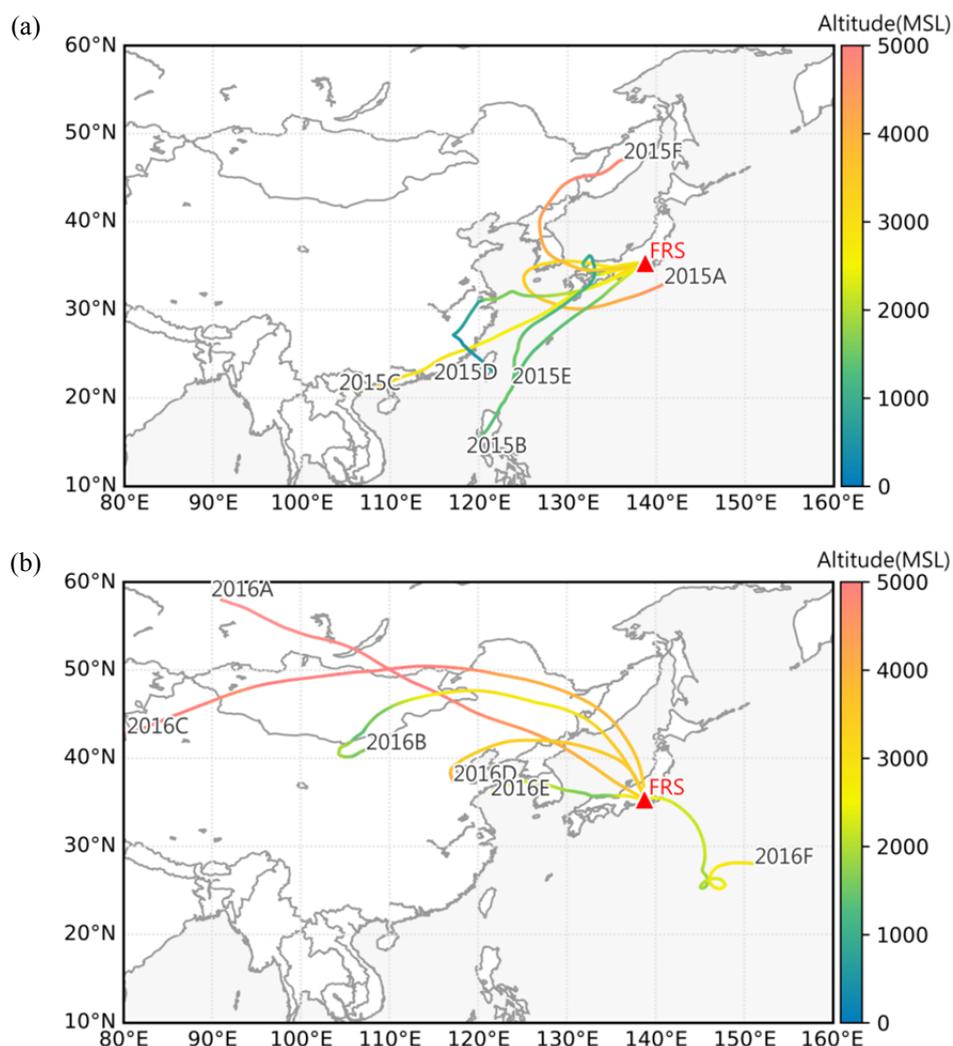
Fig. 1. Location of the Mt. Fuji Research Station (FRS) and the mean backward trajectory of each group during the (a) 2015 and (a) 2016 campaigns.

the Japan Meteorological Agency (JMA). Yearlong and multiple-year measurements of tropospheric ozone (Tsutsumi *et al.*, 1994; Dokiya *et al.*, 2001), water-soluble ions from aerosol samples (Suzuki *et al.*, 2008), and rainwater (Dokiya *et al.*, 2001) have been successfully obtained at the FRS. Short-term observations from a few weeks to several months have also been performed for various atmospheric constituents including gaseous pollutants (Nakazawa *et al.*, 1984; Sekino *et al.*, 1997; Tsutsumi *et al.*, 1998; Tsutsumi and Matsueda, 2000; Igarashi *et al.*, 2004; Igarashi *et al.*, 2006; Kato *et al.*, 2016), precipitation chemistry (Dokiya *et al.*, 1995; Sekino *et al.*, 1997; Hayashi *et al.*, 2001; Watanabe *et al.*, 2006; Wai *et al.*, 2008), and radioactive elements (Tsutsumi *et al.*, 1998; Igarashi *et al.*, 2004; Igarashi *et al.*, 2006). Episodic aerosols in Japanese volcanic plumes (Naoe *et al.*, 2003), Siberian forest fire smoke (Kaneyasu *et al.*, 2007), and Asian dust (Suzuki *et al.*, 2008; Suzuki *et al.*, 2010) were observed at the FRS. The in-cloud aging process of aerosols along the Mt. Fuji slope was also investigated (Ueda *et al.*, 2014).

Unattended operation was initiated in the FRS in 2004. Since then, only automated instruments have been used to collect meteorological data throughout the year. The nonprofit organization Valid Utilization of Mount Fuji Research Station (http://npofuji3776-english.jimdo.com/) was established in 2007 to evaluate the further benefits of the facility. After the organization received permission from the JMA to use the FRS, the station became available to private individuals for summer research. We took the opportunity to participate in summer campaigns at the FRS in 2015 and 2016 to collect whole air samples for the measurement of VOCs and halocarbons. Since the FRS is considered as the gateway to monitor air masses transported before entering the Pacific, results from the campaigns can be used to improve our understanding of VOCs seriously perturbed by anthropogenic activities in East Asia. In addition, a regional-scale perspective of the VOCs and halocarbons can also be provided in the lower free troposphere of northern East Asia.

METHODS

Air Sampling

Sampling was performed at the FRS from August 12, 2015 to August 17, 2015 and from August 10, 2016 to August 17, 2016. In total, 24 and 30 air samples were collected in 2015 and 2016 campaigns, respectively. The FRS is located at the summit of Mt. Fuji, which is the highest mountain with a nearly perfect conical profile in Japan. Mt. Fuji is a non-active volcano lying in the free troposphere for most of the year, and it ideally acts as a baseline representative in the northeast Asian region. A detailed description of the FRS has been provided in previous studies (Tsutsumi and Matsueda, 2000; Igarashi *et al.*, 2004). Air samples were collected using a prevacuumed 2-L electropolished stainless steel canister four times a day, with a time interval of more than 3 hours. A deactivated stainless steel tube (1.6 mm OD, 0.25 mm ID, 40 cm length) serving as a restrictor was attached to the inlet of the canister to collect a 1-hour integrated air sample.

Samples were analyzed within 1 month after the campaign.

Chemical Analysis and Calibration of VOCs and Halocarbons

Analytical methods used for measuring VOCs in the 2015 and 2016 campaigns were generally identical. A gas chromatography (GC) equipped with a mass spectrometer (MS) was employed for the analysis of VOCs and halocarbons. In total, 24 compounds measured by the GC-MS were targeted in this study; however, of the 24 compounds, 12 halocarbons were quantified only in 2015. The list and the statistical information of the compounds targeted in this study are provided in Table 1. The GC-MS instruments used in 2015 and 2016 were Model 450-GC/240-MS (Varian, USA) and 7890B/5977A (Agilent, USA), respectively. The sample air was first passed through a stainless steel cryotrap (1/8 in × 8 cm) packed with fine glass beads cooled with liquid nitrogen at –170°C. Then, thermal desorption was performed by flash heating the trap to 120°C and purging it with a stream of ultrapure helium (99.9999%) to inject analytes into the GC. A PLOT column (Chrompack; 30 m × 0.32 mm × 5.0 μm) and a DB-1 column (J&W; 60 m × 0.3 mm × 1.0 μm) were used to separate C_2–C_4 and the remaining heavier VOCs, respectively. The m/z scanning range of the MS was set at 35–180. Only the primary ion was used to quantify compounds monitored in this study. The details of the analytical system have been addressed in our previous study (Wang *et al.*, 2012).

Several standard gases were used to calibrate VOCs and other air pollutants in this study. Tertiary standards purchased from the National Oceanic and Atmospheric Administration/Global Monitoring Division (NOAA/GMD) were used for the calibration of specific halocarbons, i.e., CFC-12, CFC-11, CFC-113, carbon tetrachloride (CCl_4), chloromethane (CH_3Cl), and chloroform ($CHCl_3$). VOCs and the remaining halocarbons were calibrated using a standard gas mixture containing 65 C_2–C_{11} VOC compounds (Scott-Marrin, USA).

Methodologies for CH_4 and CO Measurements

CH_4 was analyzed using a cavity ring-down spectrometer (G2401, Picarro, USA). An oil-free vacuum pump with a shut-off valve was used to evacuate residual air in the manifold before the sample was introduced. A series of NOAA/GMD tertiary standards ranging from 1599 to 2024 ppb were employed for the calibration of CH_4. The standard scale used was NOAA04 CH_4 mole fractions. Additional detailed information of the canister CH_4 analysis has been provided in our previous study (Wang *et al.*, 2013).

CO was monitored onsite using a nondispersive infrared absorption analyzer (Model 48C, Thermo Electron, USA). A standard gas of 1.96 ppm CO (Taiyo Nissan, Japan) was used to calibrate the analyzer in the laboratory prior to and after the field campaigns. CO-free air was fed into the instrument from a heated Pt catalyst (Model 96, Thermo Electron, USA) during the first 15 min at every hour for the zeroing correlation. Ambient air was measured in the remaining 45 min. A detailed description of the CO measurement can be found elsewhere (Kato *et al.*, 2016).

Table 1. Statistical results of target compounds observed at the Mt. Fuji Research Station (FRS).

Compound	2015 (N = 24)		2016 (N = 30)		Atmospheric Lifetime	Reference[†]
	MDL	Mean (± 1σ)	MDL	Mean (± 1σ)		
alkanes (ppt)						
ethane	38	610 ± 203	38	999 ± 376	47 days	1
propane	40	276 ± 172	40	402 ± 241	10.5 days	1
n-butane	45	133 ± 90	33	166 ± 126	4.8 days	1
n-pentane	8	29 ± 19	7	27 ± 23	2.8 days	1
i-pentane	10	47 ± 37	6	64 ± 41	3.0 days	1
alkenes (ppt)						
ethene	39	234 ± 104	34	585 ± 642	1.4 days	1
propene	51	103 ± 49	51	198 ± 61	0.44 day	1
ethyne (ppt)	85	139 ± 40	57	182 ± 78	14.2 days	1
aromatics (ppt)						
benzene	2	337 ± 982	20	181 ± 147	8.3 days	1
toluene	2	593 ± 698	10	193 ± 87	1.9 days	1
ethylbenzene	2	21 ± 23	2	16 ± 10	1.6 days	1
m,p-xylene	3	95 ± 114	3	19 ± 16	0.49–0.84 day	1
halocarbons (ppt)						
chloromethane (CH_3Cl)	25	598 ± 36			1.0 year	2
dichlorodifluoromethane (CFC-12)	2	535 ± 20			100 years	2
trichlorofluoromethane (CFC-11)	1	232 ± 9			45 years	2
carbon tetrachloride (CCl_4)	1	84 ± 2			26 years	2
trichlorotrifluoroethane (CFC-113)	1	72 ± 2			85 years	2
1,2-dichlorotetrafluoroethane (CFC-114)	1	16 ± 1			190 years	2
methyl chloroform (CH_3CCl_3)	1	4[*]			5 years	2
bromomethane (CH_3Br)	3	8 ± 2			0.8 year	2
chloroform ($CHCl_3$)	2	39 ± 11			0.4 year	2
1,2-dichloroethane (R-150)	2	24 ± 14			65 days	2
1,1-dichloroethane (R-150a)	3	38 ± 13			~2 months	3
1,4-dichlorobenzene (*p*-DCB)	1	13 ± 10			~1 month	4
others						
CH_4 (ppb)	0.4	1879 ± 24	0.4	1914 ± 30	9.1 years	2
CO (ppb)	22.6	99.2 ± 21.1	22.6	100.6 ± 29.5	1–3 months	5

[*] Estimated standard deviation (1σ) < 0.5 ppt.
[†] References: (1) Jobson *et al.* (1998); (2) IPCC (2013); (3) ATSDR (1990); (4) ATSDR (2006); (5) Ou-Yang *et al.* (2014).

Backward Trajectory Analysis

Three-day (72 h) backward trajectories arriving at the FRS were computed for each sample by using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, version 4, 2016 (http://ready.arl.noaa.gov/HYSPLIT_traj.php), developed and provided by the NOAA/Air Resources Laboratory (Stein *et al.*, 2015; Rolph, 2016). Meteorological data employed were the Global Data Assimilation System half-degree archive provided by the National Center for Environmental Prediction, with a time resolution of 6 h, a horizontal grid of 0.5° × 0.5°, and a hybrid sigma-pressure level of 55.

RESULTS AND DISCUSSION

Overview of the Observed VOCs

Air samples were analyzed for VOCs including alkanes, alkenes, ethyne, and aromatics. The total concentrations of target VOCs were 2.62 ± 1.38 ppb and 2.99 ± 0.95 ppb in 2015 and 2016, respectively. Alkanes constituted the largest proportion of VOCs, accounting for 41.8% in 2015 and 55.3% in 2016 (Fig. 2). Because of the relatively long atmospheric lifetime of ethane (Table 1), it contributed most of the measured alkane concentration in both years. This result is similar to those obtained at other mountain stations, irrespective of locations and seasons (Greenberg *et al.*, 1996; Schmitt and Volz-Thomas, 1997; Sharma *et al.*, 2000; Swanson *et al.*, 2003; Helmig *et al.*, 2008; Suthawaree *et al.*, 2010; Xue *et al.*, 2013). Alkyne, as represented solely by ethyne, had the lowest contribution among all VOC types, accounting for 5.3%–6.1% of total VOCs. As illustrated in Fig. 3, concentrations were sorted generally on the basis of the atmospheric lifetimes of respective VOC types. Furthermore, the concentrations of individual VOCs ranged from few ppt to few ppb, with large variability (Fig. 3), indicating a highly inhomogeneous distribution, particularly for short-lived VOCs.

Fig. 4(a) presents the time series of total alkanes, ethyne, and CH_4 concentrations during the two campaigns. The concentrations of these relatively long-lived species varied but were generally in close agreement. By contrast, the behavior of highly reactive VOCs, such as alkenes and aromatics,

changed incoherently with other compounds throughout the observations (Fig. 4(b)). In 2015, the concentration of aromatics peaked at 5.71 ppb in association with a long-range transport episode originating from the Yangtze River

Delta (YRD) region; this massively boosted the contribution of aromatics to approximately 40.0% of all VOCs in that year (Fig. 2(b)). Previous studies have demonstrated a considerable amount of VOC emissions contributed to solvent
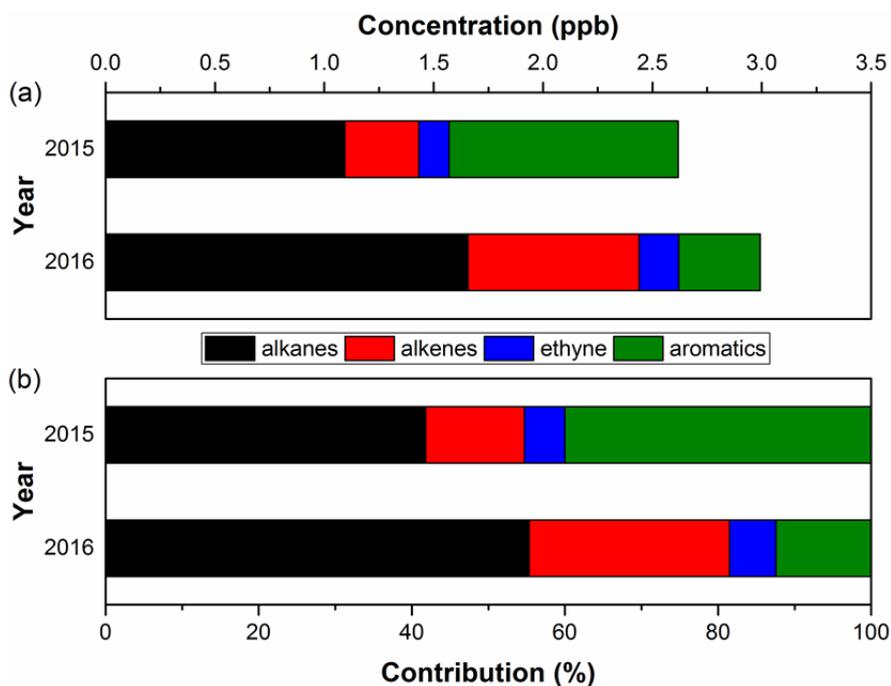
Fig. 2. (a) Cumulative concentrations and (b) percentage contributions of the mean values of VOC types in the 2015 and 2016 campaigns. Halocarbons are excluded here and discussed in the later section.
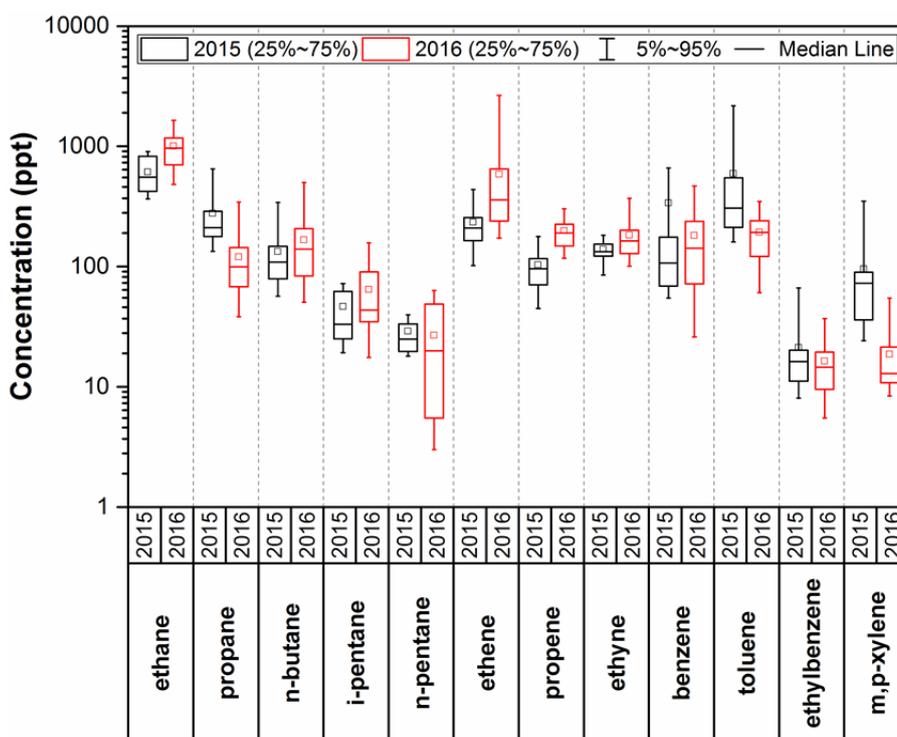
Fig. 3. Concentration distributions of VOCs measured at the Mt. Fuji Research Station (FRS) in summer. Boxes and whiskers define 25%–75% and the outlying 5% of the data, respectively. The median is the line within the box. The open squares represent the mean values of the data.
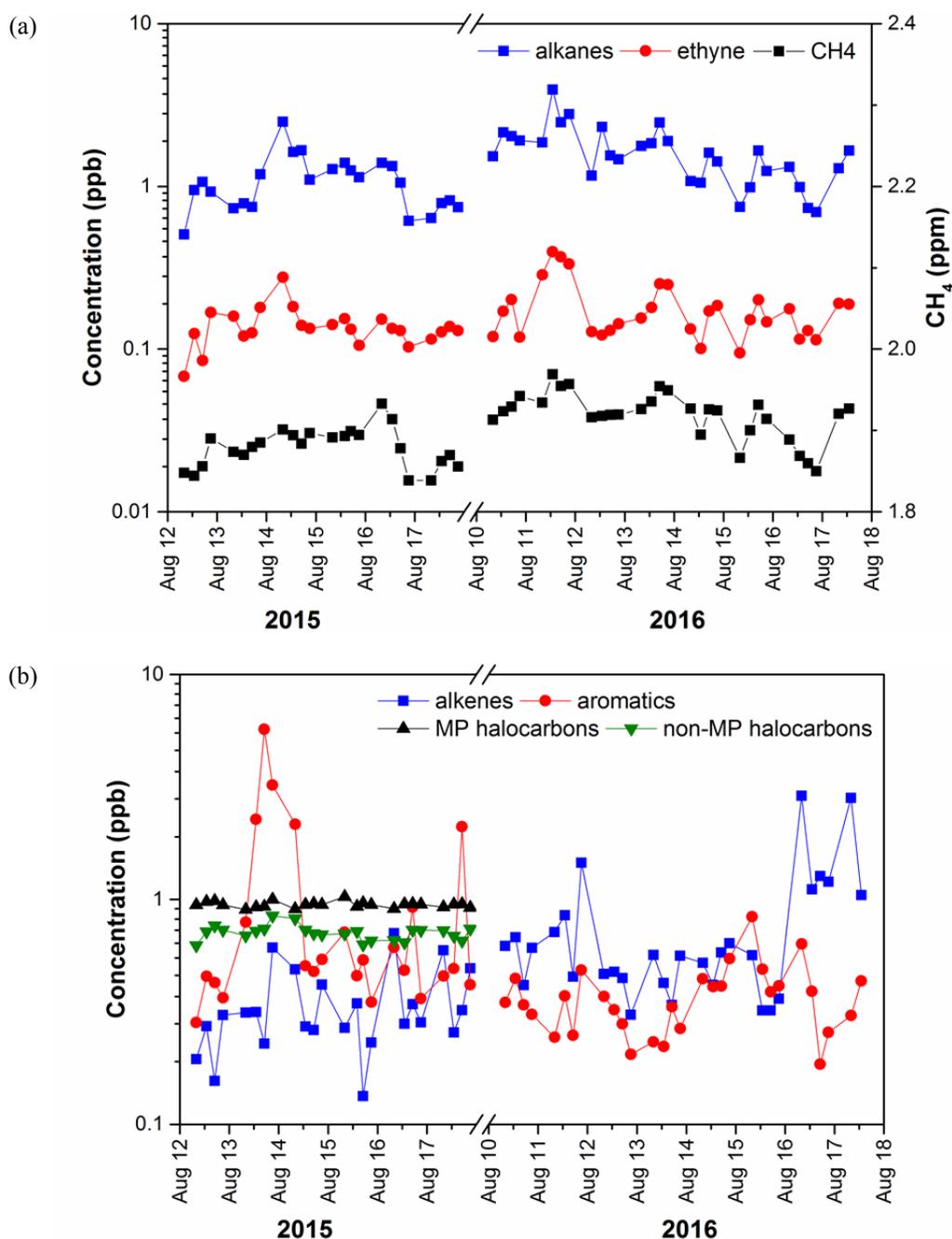
Fig. 4. Observed concentration variation of (a) alkanes, ethyne, and CH_4 and (b) alkenes, aromatic compounds, and halocarbons at the Mt. Fuji Research Station (FRS) in the summers of 2015 and 2016. Halocarbons are classified into two groups: halogenated compounds regulated by the Montreal Protocol (MP) and those not regulated by the MP (non-MP). Note that the concentrations are plotted using logarithmic scale.

use and industrial production in YRD, which could be the major source of aromatics in that region (Huang *et al.*, 2011; Wang *et al.*, 2014). The alkene concentration, which is the sum of ethene and propene concentrations, varied dramatically from sub-ppb to a few ppb in both summers. Studies have also shown highly inconsistent concentrations of alkenes in summertime at mountain sites, such as 397 ppt at Happo, Japan (Sharma *et al.*, 2000); 167.8 ppt at Mt. Waliguan, China (Xue *et al.*, 2013); 32 ppt at Izana, the Canary Islands (Schmitt and Volz-Thomas, 1997); and 5 ppt

in the free troposphere at Mauna Loa, Hawaii (Greenberg *et al.*, 1996). The halocarbons showed much lower variability than did VOCs, regardless of whether they were controlled according to the Montreal Protocol (MP; Fig. 4(b)).

Halocarbons

We examined 12 halocarbons (Table 1) at the FRS in the summer of 2015. No correlation was observed between the halocarbons and individual VOC types (Fig. 3). CH_3Cl and CFC-12 were the largest contributors to atmospheric

halocarbons (Fig. 5 and Table 1), which were amounted to approximately 68.2%. Most of the ozone-depleting substances regulated under the MP (e.g., CFC-11, CCl$_4$, CFC-113, CFC-114, and CH$_3$CCl$_3$) showed a concentration with low variability, as expressed by box-whiskers in Fig. 5. The other two MP compounds, CFC-12 and CH$_3$Br, also showed low variability, expressed as standard deviations (1σ) of 20 and 2 ppt, respectively. By contrast, the non-MP compounds such as CH$_3$Cl, CHCl$_3$, 1,2-dichloroethane (R-150), 1,1-dichloroethane (R-150a), and 1,4-dichlorobenzene (*p*-DCB) varied noticeably as shown in Fig. 5. Except for CH$_3$Cl, CFC-12, and CHCl$_3$, most of the halogenated compounds differed within approximately 2 ppt between the FRS and Gosan station (GSN, 33.28°N, 126.15°E, 72 m above sea level), Jeju Island, South Korea. See Table S1 for the comparison in Supplementary Materials. GSN is a regional baseline station located at similar latitude to the FRS in East Asia. Note that the difference in the mean concentration of CFC-12 between the two sites was less than 3%. Furthermore, the data of the MP compounds were generally in favorable agreement with global baseline values, which have been reported recently (Carpenter *et al.*, 2014).

The relatively short atmospheric lifetime of non-MP compounds means that they present large temporal and regional variability. For instance, CH$_3$Cl and CHCl$_3$ concentrations differed by 51 and 24 ppt between FRS and GSN, respectively. It was the first time that R-150, R-150a, and *p*-DCB were measured in the lower free troposphere of northern East Asia, with mean concentrations ranging from 13 to 38 ppt. (Table 1). Singh *et al.* (1983) first reported a baseline concentration of 37 ppt for R-150 in the Northern Hemisphere. An assessment by Carpenter *et al.* (2014) has summarized that the concentration of R-150 ranged from

0.7 to 14.5 ppt in the marine boundary layer. R-150a and *p*-DCB are rarely observed in the background atmosphere but are found at ppb levels in urban air (Logue *et al.*, 2010). It has been reported that the average concentration of R-150a was 55 ppt in ambient air across the United States (ATSDR, 1990). The outdoor levels of *p*-DCB range from 0.01 to 1 ppb and are much lower than its indoor levels (ATSDR, 2006). More recently, Yang *et al.* (2016) reported summertime concentrations of 0.60, 0.02, and 0.08 ppb for R-150, R-150a, and *p*-DCB, respectively, at the top of Lushan, a mountain in China. Although R-150, R-150a, and *p*-DCB have been observed in both background and urban atmosphere, no reliable estimates of their global emissions or inventories are available to date (Carpenter *et al.*, 2014).

Cluster Analysis of Backward Trajectories

Trajectory simulations are often used to examine atmospheric trace substances in association with particular events. Three-day backward trajectories were simulated and classified into six groups based on the routes and origins of air masses in each year. As illustrated in Fig. 1, air masses which arrived at the FRS show different patterns between the two summers. See also Fig. S1 in Supplementary Materials for the mean wind flows at 650 hPa (~3600 m above sea level) during the two campaigns. Most of the clusters originated from the coastal region in the low latitudes (15–35°N) of East Asia in 2015, whereas air masses mainly came from the high latitudes (35–60°N) of the Asian continent in 2016. Only one cluster (2016F) was influenced by a tropical cyclone originating from the Pacific region. A recent study also indicated that in the summer of 2015, wind currents moved along the western Pacific from South
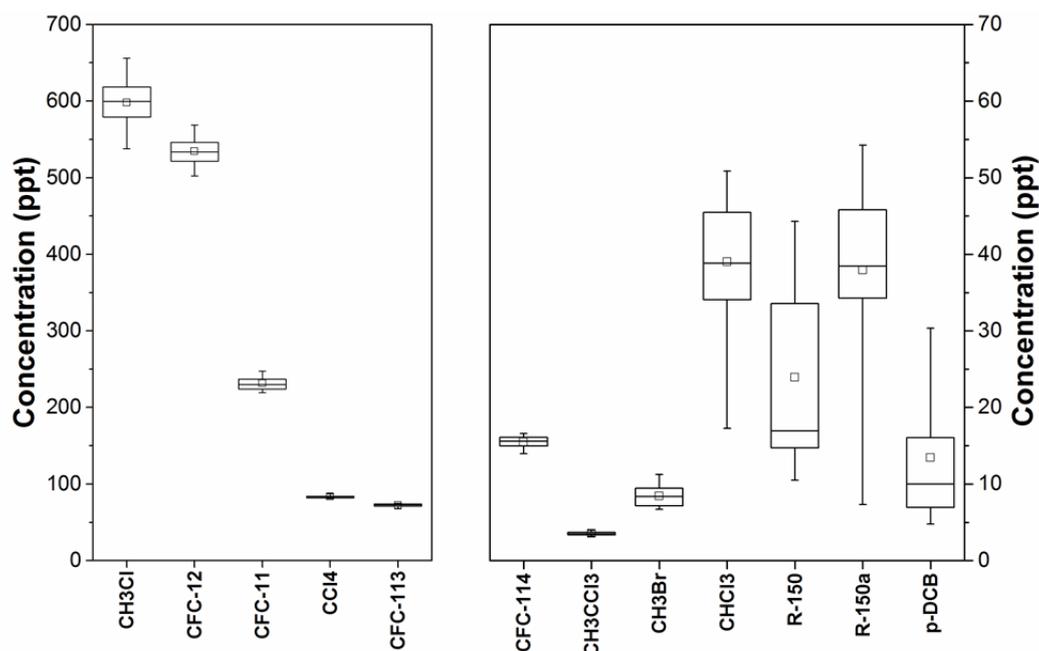
Fig. 5. Concentration distributions of observed halocarbons at the Mt. Fuji Research Station (FRS) in the summer of 2015. The box represents 25%–75% of the data. Whiskers define the outlying 5% of the data. The median or the 50th percentile is the line within the box. The open squares represent the mean values of the data.

China Sea, through southern China and Taiwan, to southern Japan (Wang *et al.*, 2017). Furthermore, air masses mainly traveled near the surface (< 2500 m above sea level; e.g., 2015B–E) in 2015, whereas they were mostly transported at high elevations (> 2500 m above sea level) in 2016 (e.g., 2016A–D).

Table 2 lists the statistical results of VOC levels in association with each trajectory group in the two summers. In 2015, the MP compounds showed a consistent reading of total concentration ranging from 941 to 963 ppt, whereas the non-MP compounds were present with larger variations (670–758 ppt). Except for aromatics, the concentrations of most VOCs were higher in 2016 than in 2015, which might be due to different origins of air masses between the 2 years (Fig. 1). For instance, the mean alkene level in 2016 was approximately 2.3 times higher than that in 2015. This phenomenon coincides with the findings of previous studies indicating that the levels of VOCs increased in the mid-high altitudes of the Northern Hemisphere (Herbin *et al.*, 2009; González Abad *et al.*, 2011; Simpson *et al.*, 2012; Helmig *et al.*, 2016). The same phenomenon was observed for CO and CH_4 in this study (Table 1). Only the group 2016F originated from the Pacific and was induced by the typhoon Chanthu, which brought air masses containing the lowest levels of most VOCs, except for alkenes, among the 2016 groups (Table 2).

Significantly enhanced aromatics were observed in 2015D, which were possibly affected by air masses originating from the YRD region. The YRD is one of the most developed areas in East Asia, with extensive urbanization and industrialization. As shown in Fig. 6(a) for the backward trajectory of the aromatic peak observed on August 13, 2015, the air mass could be lifted by a tropical depression (TD, in Fig. 6(b)) from the boundary layer to the free troposphere around the YRD region on August 10, 2015. The average

concentrations of benzene and toluene in 2015D were 1.09 ± 2.13 and 1.75 ± 0.78 ppb, with maximum concentrations of 4.91 and 2.72 ppb, respectively. These values were significantly higher than the mean levels of 337 ± 982 ppt for benzene and 593 ± 698 ppt for toluene in 2015. Alkenes and ethyne were only slightly elevated but still had the highest concentrations among all the 2015 groups, indicating the effects of mixed industrial and urban sources. However, no obvious enhancement of alkanes and halocarbons was coherently observed during this event.

Diurnal Pattern

Diurnal variations in air pollutants sculptured by upslope/downslope circulations have been distinguished at many mountain sites (Greenberg *et al.*, 1992; Ou-Yang *et al.*, 2012; Ou-Yang *et al.*, 2014; Sarkar *et al.*, 2015). To examine the diurnal characteristics of VOCs at the FRS, air samples were collected deliberately at four local time periods (i.e., 8:00–9:00 AM, 13:00–14:00 PM, 17:00–18:00 PM, and 21:00–22:00 PM). As shown in Fig. 7, no particular diurnal pattern for CO and VOCs was found at the FRS in 2015 or 2016. The concentrations of all VOC types changed mainly because of their different origins. However, Hayashi *et al.* (2001) observed diurnal variations of sulfate in aerosol samples during a period with poor wind speeds at the FRS in the summers of 1997–1999. Tsutsumi and Matsueda (2000) revealed a minor diurnal cycle of ozone at the FRS. However, they argued that these diurnal variations were probably not caused by air masses uplifted by valley winds from lower elevations, but by photochemical ozone destruction with water vapor during the transport. In addition, the wind speed at the peak could reach approximately 10 m s^{-1} even in summer (Naoe *et al.*, 2003; Igarashi *et al.*, 2004). Suppressed mountain-valley winds were suggested due to the minimal sunlight received and reduced thermal

Table 2. Statistical results of VOCs for different trajectory cluster groups at the Mt. Fuji Research Station (FRS).

Cluster group	N	Alkanes (ppt)	Alkenes (ppt)	ethyne (ppt)	Aromatics (ppt)	MP compounds[†] (ppt)	non-MP compounds[†] (ppt)
2015							
A	2	729 ± 314	234 ± 55	96 ± 40	369 ± 121	963 ± 23	673 ± 68
B	5	768 ± 180	321 ± 164	118 ± 28	506 ± 167	944 ± 31	721 ± 32
C	3	910 ± 156	381 ± 100	143 ± 22	569 ± 310	941 ± 19	735 ± 4
D	5	1207 ± 741	393 ± 154	168 ± 65	3095 ± 153	943 ± 36	758 ± 78
E	3	1464 ± 315	317 ± 87	152 ± 26	509 ± 32	952 ± 7	713 ± 17
F	6	1299 ± 98	328 ± 199	137 ± 18	526 ± 127	957 ± 40	670 ± 36
Mean		1094 ± 435	337 ± 145	139 ± 40	1047 ± 1257	950 ± 29	712 ± 54
2016							
A	4	1908 ± 270	582 ± 114	153 ± 41	361 ± 59		
B	4	2434 ± 1084	582 ± 247	299 ± 114	267 ± 73		
C	4	1955 ± 732	712 ± 498	179 ± 103	365 ± 89		
D	9	1545 ± 528	513 ± 98	169 ± 56	412 ± 192		
E	6	1360 ± 260	1295 ± 1244	176 ± 22	444 ± 111		
F	3	808 ± 161	1194 ± 81	120 ± 9	277 ± 104		
Mean		1656 ± 690	783 ± 640	182 ± 78	372 ± 137		

[†] MP compounds refer to the halocarbons in this study which are regulated by the Montreal Protocol (e.g., CFC-12, CFC-11, CCl_4, CFC-113, CFC-114, CH_3CCl_3, and CH_3Br). Other halocarbons (CH_3Cl, $CHCl_3$, R-150, R-150a, and *p*-DCB) are summarized as the non-MP compounds.

(a)

(b)
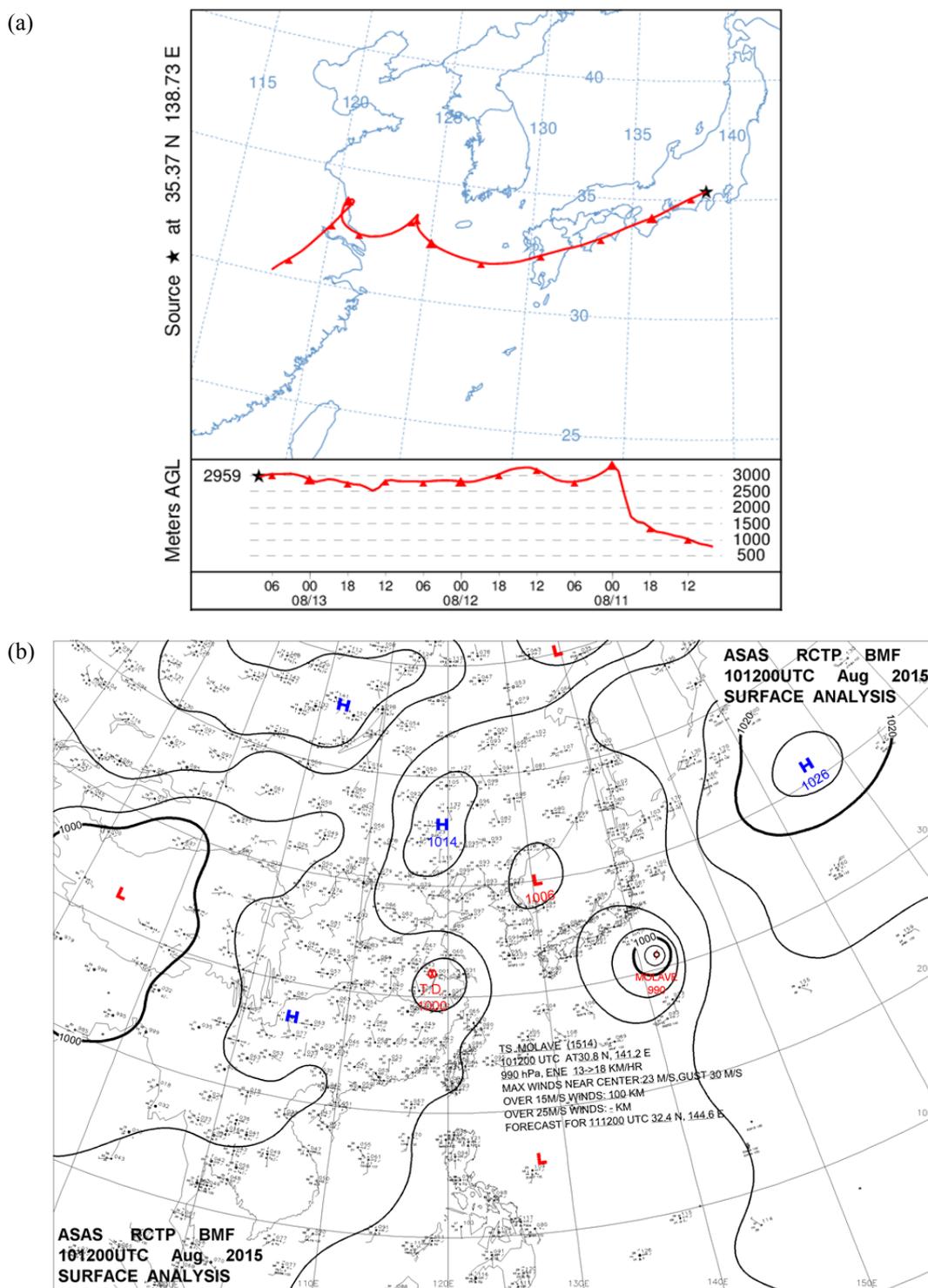
Fig. 6. (a) Three-day backward trajectory arriving at the Mt. Fuji Research Station (FRS) on August 13, 2015. (b) Surface weather map of East Asia on August 10, 2015, provided by Central Weather Bureau, Taiwan.

radiation from the small surface area of the isolated mountaintop (Tsutsumi *et al.*, 1994; Igarashi *et al.*, 2006).

Isomeric Pairs of Pentanes

VOC ratios are useful for investigating the sources and aging/mixing processes of air masses during transport. Isomeric pairs of alkanes usually have a similar reactivity

with OH in the atmosphere, such as *n*-pentane (3.8×10^{-12} cm^3 molecule^{-1} s^{-1}) and *i*-pentane (3.6×10^{-12} cm^3 molecule^{-1} s^{-1}) (Atkinson and Arey, 2003), as targeted here. Pentanes are mainly found in vehicle exhausts and gasoline vapors but are released at different emission rates (Swarthout *et al.*, 2013). As illustrated in Fig. 8, the relationship between the isomeric pair of pentanes presented a
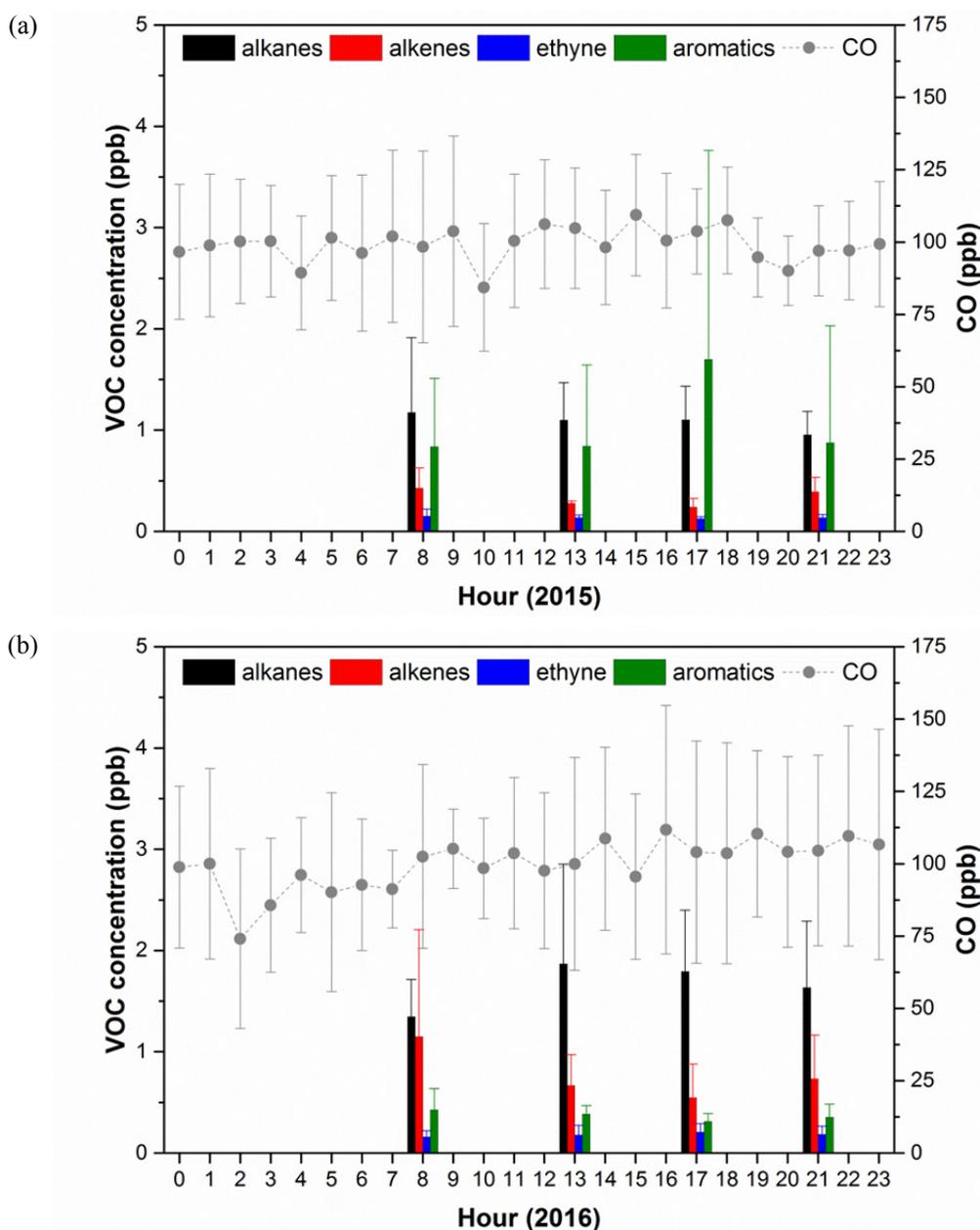
Fig. 7. Diurnal patterns of VOCs and CO observed at the Mt. Fuji Research Station (FRS) in the summer of (a) 2015 and (b) 2016.

close correlation at the FRS in the two summers. Regardless of the similar slopes in the 2 years (Fig. 8), the mean n/i-pentane ratios were considerably different (0.67 ± 0.18 with a range from 0.39 to 1.04 in 2015 and 0.38 ± 0.19 with a range from 0.10 to 0.76 in 2016). The lower ratio in 2016 than that in 2015 was caused by the elevated i-pentane level in 2016 (Table 1 and Fig. 3). Since i-pentane is the primary component in gasoline evaporation (McLaren *et al.*, 1996), a low n/i-pentane ratio (0.26–0.41) can be utilized to identify the VOC source signature of oil and nature gas operation (Gilman *et al.*, 2013). The ratios of air masses affected by gasoline evaporation fall in a similar range to the FRS but had much higher pentane levels. This is a plausible explanation for the enhanced i-pentane level

and the low mean ratio of n/i-pentane at the FRS in 2016. However, Khwaja and Narang (2008) also reported a low ratio of 0.36 during nighttime for free tropospheric subsidence at Whiteface Mountain in the northeastern United States. Xue *et al.* (2013) observed an even lower ratio of 0.25 at Mt. Waliguan in summer. Lo Vullo *et al.* (2016b) obtained slightly higher n/i-pentane ratios of 0.45 and 0.50 at European mountain background stations (Mt. Cimone, Italy, and Hoenpeissenberg, German, respectively) without clear influences of gasoline vapor in summer. By contrast, they also observed enhanced ratios of n/i-pentane (> 1.5) for some cases of prevailing southwesterly winds at Mt. Cimone in the same season (Lo Vullo *et al.*, 2016b). See Table 3 for the summary of n/i-pentane observed at
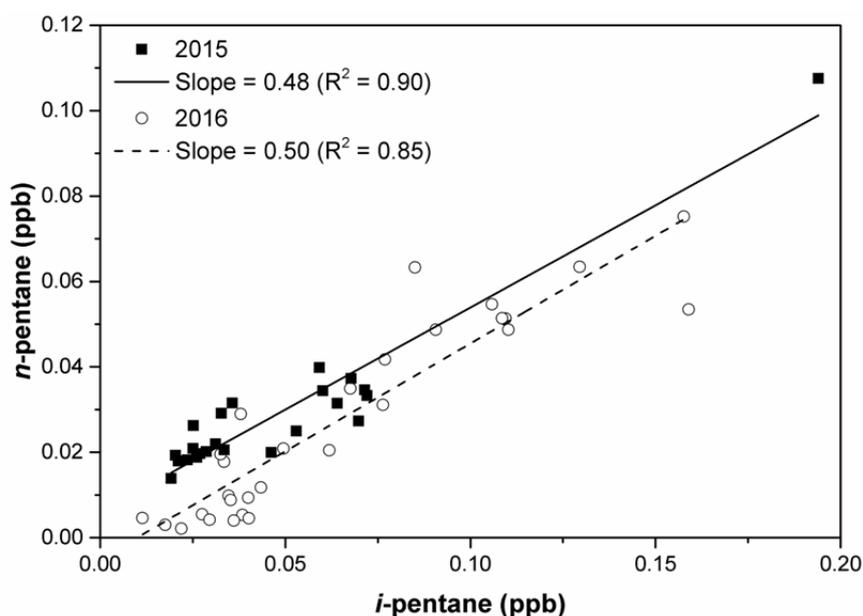
Fig. 8. Relationships between *n*-pentane and *i*-pentane in 2015 and 2016 at the Mt. Fuji Research Station (FRS).

Table 3. Summary of *n*/*i*-pentane ratios observed at mountain sites.

Mountain Site	Elevation (m a.m.s.l.)	Location	Average *n*/*i*-pentane ratio	Observation Time	Reference
Mt. Fuji Research Station (FRS)	3776	35.37°N, 138.73°E	0.67 0.38	12–17 August, 2015 10–17 August, 2016	This study
Whiteface Mountain	1483	44.37°N, 73.90°W	0.36	12–16 July, 1994	Khwaja and Narang (2008)
Mt. Waliguan	3810	36.28°N, 100.90°E	0.25	15 July–16 August, 2003	Xue *et al.* (2013)
Mt. Cimone	2165	44.18°N, 10.70°E	0.45	June–August of 2010–2014	Lo Vullo *et al.* (2016b)
Hoenpeissenberg	985	47.80°N, 11.02°E	0.50	June–August of 2010–2014	Lo Vullo *et al.* (2016b)
Pico Mountain	2225	38.47°N, 28.40°W	0.62	June–August, 2005	Helmig *et al.* (2008)

mountain sites in summer. Oceanic sources preferentially release *n*-pentane relative to *i*-pentane, resulting in a high *n*/*i*-pentane ratio of approximately 1.7–2 (Broadgate *et al.*, 1997; Hopkins *et al.*, 2002). However, although trajectories mainly passed through the East China Sea in the western Pacific in 2015 (Fig. 1(a)), no significant difference in *n*-pentane levels between 2015 and 2016 was observed (*p*-value = 0.707, 95% confidence interval, two-tailed).

Air masses impacted by biomass burning in the tropical and extratropical forest were revealed to exhibit a high *n*/*i*-pentane ratio of 1.75–2.00 (Andreae and Merlet, 2001). Helmig *et al.* (2008) reported a *n*/*i*-pentane ratio of 1.37 for summer samples affected by boreal fires at Pico Mountain, the Azores, whereas the ratio was 0.62 during non-fire-influenced events. An *n*/*i*-pentane ratio of 1.32 was observed at Mace Head, Ireland, in summer, but it was not claimed to be impacted by biomass burning (Yates *et al.*, 2010). The increase in the *n*/*i*-pentane ratio might have resulted from the reaction of nitrate radicals (NO_3) with *i*-pentane

because the reaction with *i*-pentane is approximately two times faster than that with *n*-pentane (Atkinson and Arey, 2003; Penkett *et al.*, 2007). However, it has been argued that the required NO_3 level for enhancing the *n*/*i*-pentane ratio is unrealistically high (Helmig *et al.*, 2008; Yates *et al.*, 2010; Lo Vullo *et al.*, 2016b).

CONCLUSIONS

The characteristics of trace gases, including 12 VOCs and 12 halocarbons, were investigated at the FRS in the summers of 2015 and 2016. In the analysis of backward trajectories, the origination of air masses arriving at the FRS showed diverse patterns between the two campaigns, causing the concentrations to differ. The diurnal patterns of VOCs were most likely governed by air masses originating from different latitudes or altitudes. No distinguished diurnal cycles were found for VOCs and CO at the FRS, as demonstrated by a similar feature that has been previously

reported. Isomeric pairs of pentanes exhibited robust relationships at the FRS during the two summers. Low ratios of summertime *n/i*-pentane ranging from 0.25 to 0.67 were observed in the lower free troposphere at the FRS and many mountain stations. It is possible that the *n/i*-pentane ratio can be altered to some extent by the effects of anthropogenic or natural emissions.

Our study has demonstrated that the concentrations of VOCs at the FRS can be considerably varied by air masses transported from East Asia. On the other hand, MP halocarbons with longer atmospheric lifetimes showed homogeneous or well-mixed features compared with VOCs, resulting in concentrations unchanged from all origins. As expected, the non-MP compounds had a large variability, in contrast to the MP compounds. Besides the compounds measured in this study, the behavior of other VOCs could differ according to their chemical nature and role in the lower free troposphere, which remains to be determined.

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SUPPLEMENTARY MATERIAL

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

REFERENCES

Andreae, M.O. and Merlet, P. (2001). Emission of trace gases and aerosols from biomass burning. *Global Biogeochem. Cycles* 15: 955–966.

Atkinson, R. and Arey, J. (2003). Atmospheric degradation of volatile organic compounds. *Chem. Rev.* 103: 4605–4638.

ATSDR (1990). Toxicological profile for 1,1-dichloroethane, U.S. Public Health Service, Atlanta, GA.

ATSDR (2006). Toxicological profile for dichlorobenzenes, U.S. Public Health Service, Atlanta, GA.

Baker, A.K., Slemr, F. and Brenninkmeijer, C.A.M. (2010). Analysis of non-methane hydrocarbons in air samples collected aboard the CARIBIC passenger aircraft. *Atmos. Meas. Tech.* 3: 311–321.

Bechara, J., Borbon, A., Jambert, C. and Perros, P.E. (2008). New off-line aircraft instrumentation for non-methane hydrocarbon measurements. *Anal. Bioanal.* *Chem.* 392: 865–876.

Blake, D.R., Chen, T.Y., Smith, T.Y., Wang, C.J.L., Wingenter, O.W., Blake, N.J., Rowland, F.S. and Mayer, E.W. (1996). Three-dimensional distribution of nonmenthane hydrocarbons and halocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Mission (PEM-West A). *J. Geophys. Res.* 101: 1763–1778.

Blake, N.J. and Blake, D.R. (2002). Tropospheric chemistry and composition / VOCs: Overview, In *Encyclopedia of atmospheric sciences*, Holton, J.R., Pyle, J.A. and Curry, J.A. (Eds.), Academic Press, London, pp. 2438–2445.

Broadgate, W.J., Liss, P.S. and Penkett, S.A. (1997). Seasonal emissions of isoprene and other reactive hydrocarbon gases from the ocean. *Geophys. Res. Lett.* 24: 2675–2678.

Burley, J.D., Bytnerowicz, A., Buhler, M., Zielinska, B., Schweizer, D., Cisneros, R., Schilling, S., Varela, J.C., McDaniel, M., Horn, M. and Dulen, D. (2016). Air quality at devils postpile national monument, Sierra Nevada Mountains, California, USA. *Aerosol Air Qual. Res.* 16: 2315–2332.

Cardelino, C.A. and Chameides, W.L. (1995). An observation-based model for analyzing ozone precursor relationships in the urban atmosphere. *J. Air Waste Manage. Assoc.* 45: 161–180.

Carpenter, L.J., Reimann, S., Burkholder, J.B., Clerbaux, C., Hall, B.D., Hossaini, R., Laube, J.C. and Yvon-Lewis, S.A. (2014). *Update on Ozone-Depleting Substances (ODSs) and other gases of interest to the montreal protocol, scientific assessment of ozone depletion: 2014, global ozone research and monitoring project - Report No.55.* World Meteorological Organization, Geneva.

Cooper, O.R., Parrish, D.D., Stohl, A., Trainer, M., Nedelec, P., Thouret, V., Cammas, J.P., Oltmans, S.J., Johnson, B.J., Tarasick, D., Leblanc, T., McDermid, I.S., Jaffe, D., Gao, R., Stith, J., Ryerson, T., Aikin, K., Campos, T., Weinheimer, A. and Avery, M.A. (2010). Increasing springtime ozone mixing ratios in the free troposphere over western North America. *Nature* 463: 344–348.

Cooper, O.R., Parrish, D.D., Ziemke, J., Balashov, N.V., Cupeiro, M., Galbally, I.E., Gilge, S., Horowitz, L., Jensen, N.R., Lamarque, J.F., Naik, V., Oltmans, S.J., Schwab, J., Shindell, D.T., Thompson, A.M., Thouret, V., Wang, Y. and Zbinden, R.M. (2014). Global distribution and trends of tropospheric ozone: An observation-based review. *Elem. Sci. Anth.* 2: 29.

Dokiya, Y., Tsuboi, K., Sekino, H., Hosomi, T., Igarashi, Y. and Tanaka, S. (1995). Acid deposition at the summit of Mt. Fuji: Observations of gases, aerosols and precipitation in summer,1993 and 1994. *Water Air Soil Pollut.* 85: 1967–1972.

Dokiya, Y., Yoshikawa, T., Komada, T., Suzuki, I., Naemura, A., Hayashi, K., Naoe, H., Sawa, Y., Sekiyama, T. and Igarashi, Y. (2001). Atmospheric chemistry at the summit of Mt. Fuji: A challenging field for analytical chemists. *Anal. Sci.* 17: i809–i812.

Gilman, J.B., Lerner, B.M., Kuster, W.C. and de Gouw, J.A. (2013). Source signature of volatile organic compounds

from oil and natural gas operations in northeastern Colorado. *Environ. Sci. Technol.* 47: 1297–1305.

González Abad, G., Allen, N.D.C., Bernath, P.F., Boone, C.D., McLeod, S.D., Manney, G.L., Toon, G.C., Carouge, C., Wang, Y., Wu, S., Barkley, M.P., Palmer, P.I., Xiao, Y. and Fu, T.M. (2011). Ethane, ethyne and carbon monoxide concentrations in the upper troposphere and lower stratosphere from ACE and GEOS-Chem: A comparison study. *Atmos. Chem. Phys.* 11: 9927–9941.

Greenberg, J.P., Zimmerman, P.R., Pollock, W.F., Lueb, R.A. and Heidt, L.E. (1992). Diurnal variability of atmospheric methane, nonmethane hydrocarbons, and carbon monoxide at Mauna Loa. *J. Geophys. Res.* 97: 10395–10413.

Greenberg, J.P., Helmig, D. and Zimmerman, P.R. (1996). Seasonal measurements of nonmethane hydrocarbons and carbon monoxide at the Mauna Loa Observatory during the Mauna Loa Observatory Photochemistry Experiment 2. *J. Geophys. Res.* 101: 14581–14598.

Hayashi, K., Igarashi, Y., Tsutsumi, Y. and Dokiya, Y. (2001). Aerosol and precipitation chemistry during the summer at the summit of Mt. Fuji, Japan (3776 m a.s.l.). *Water Air Soil Pollut.* 130: 1667–1672.

Helmig, D., Balsley, B., Davis, K., Kuck, L.R., Jensen, M., Bognar, J., Smith, T., Arrieta, R.V., Rodriguez, R. and Birks, J.W. (1998). Vertical profiling and determination of landscape fluxes of biogenic nonmethane hydrocarbons within the planetary boundary layer in the Peruvian Amazon. *J. Geophys. Res.* 103: 25519–25532.

Helmig, D., Tanner, D.M., Honrath, R.E., Owen, R.C. and Parrish, D.D. (2008). Nonmethane hydrocarbons at Pico Mountain, Azores: 1. Oxidation chemistry in the North Atlantic region. *J. Geophys. Res.* 113: D20S91.

Helmig, D., Rossabi, S., Hueber, J., Tans, P., Montzka, S.A., Masarie, K., Thoning, K., Plass-Duelmer, C., Claude, A., Carpenter, L.J., Lewis, A.C., Punjabi, S., Reimann, S., Vollmer, M.K., Steinbrecher, R., Hannigan, J., Emmons, L.K., Mahieu, E., Franco, B., Smale, D. and Pozzer, A. (2016). Reversal of global atmospheric ethane and propane trends largely due to US oil and natural gas production. *Nat. Geosci.* 9: 490–495.

Herbin, H., Hurtmans, D., Clarisse, L., Turquety, S., Clerbaux, C., Rinsland, C.P., Boone, C., Bernath, P.F. and Coheur, P.F. (2009). Distributions and seasonal variations of tropospheric ethene (C$_2$H$_4$) from Atmospheric Chemistry Experiment (ACE-FTS) solar occultation spectra *Geophys. Res. Lett.* 36: L04801.

Hoell, J.M., Davis, D.D., Liu, S.C., Newell, R.E., Akimoto, H., McNeal, R.J. and Bendura, R.J. (1997). The Pacific exploratory mission-west phase B: February–March 1994. *J. Geophys. Res.* 102: 28223–28239.

Hopkins, J.R., Jones, I.D., Lewis, A.C., McQuaid, J.B. and Seakins, P.W. (2002). Non-methane hydrocarbons in the arctic boundary layer. *Atmos. Environ.* 36: 3217–3229.

Huang, C., Chen, C.H., Li, L., Cheng, Z., Wang, H.L., Huang, H.Y., Streets, D.G., Wang, Y.J., Zhang, G.F. and Chen, Y.R. (2011). Emission inventory of anthropogenic air pollutants and VOC species in the Yangtze River Delta region, China. *Atmos. Chem. Phys.* 11: 4105–4120.

Igarashi, Y., Sawa, Y., Yoshioka, K., Matsueda, H., Fujii, K. and Dokiya, Y. (2004). Monitoring the SO$_2$ concentration at the summit of Mt. Fuji and a comparison with other trace gases during winter. *J. Geophys. Res.* 109: D17304.

Igarashi, Y., Sawa, Y., Yoshioka, K., Takahashi, H., Matsueda, H. and Dokiya, Y. (2006). Seasonal variations in SO$_2$ plume transport over Japan: Observations at the summit of Mt. Fuji from winter to summer. *Atmos. Environ.* 40: 7018–7033.

IPCC (2013). *Climate change 2013: The physical science basis. Contribution of working Group I to the fifth assessment report of the intergovernmental panel on climate change.* Cambridge University Press, Cambridge and New York.

Jaffe, D., Anderson, T., Covert, D., Kotchenruther, R., Trost, B., Danielson, J., Simpson, W., Berntsen, T., Karlsdottir, S., Blake, D., Harris, J., Carmichael, G. and Uno, I. (1999). Transport of Asian air pollution to North America. *Geophys. Res. Lett.* 26: 711–714.

Jobson, B.T., Parrish, D.D., Goldan, P., Kuster, W., Fehsenfeld, F.C., Blake, D.R., Blake, N.J. and Niki, H. (1998). Spatial and temporal variability of nonmethane hydrocarbon mixing ratios and their relation to photochemical lifetime. *J. Geophys. Res.* 103: 13557–13567.

Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G. and Wilson, J. (2005). Organic aerosol and global climate modelling: A review. *Atmos. Chem. Phys.* 5: 1053–1123.

Kaneyasu, N., Igarashi, Y., Sawa, Y., Takahashi, H., Takada, H., Kumata, H. and Holler, R. (2007). Chemical and optical properties of 2003 Siberian forest fire smoke observed at the summit of Mt. Fuji, Japan. *J. Geophys. Res.* 112: D13214.

Karl, T., Fall, R., Crutzen, P.J., Jordan, A. and Lindinger, W. (2001). High concentrations of reactive biogenic VOCs at a high altitude site in late autumn. *Geophys. Res. Lett.* 28: 507–510.

Kato, S., Shiobara, Y., Uchiyama, K., Miura, K., Okochi, H., Kobayashi, H. and Hatakeyama, S. (2016). Atmospheric CO, O$_3$, and SO$_2$ measurements at the summit of Mt. Fuji during the summer of 2013. *Aerosol Air Qual. Res.* 16: 2368–2377.

Khwaja, H.A. and Narang, A. (2008). Carbonyls and non-methane hydrocarbons at a rural mountain site in northeastern United States. *Chemosphere* 71: 2030–2043.

Lanz, V.A., Henne, S., Staehelin, J., Hueglin, C., Vollmer, M.K., Steinbacher, M., Buchmann, B. and Reimann, S. (2009). Statistical analysis of anthropogenic non-methane VOC variability at a European background location (Jungfraujoch, Switzerland). *Atmos. Chem. Phys.* 9: 3445–3459.

Le Bras, G. (2003). Gas phase reactions, In *Encyclopedia of atmospheric sciences*, Holton, J.R., Pyle, J.A. and Curry, J.A. (Eds.), Academic Press, London, pp. 352–

359.

Li, Y.S., Campana, M., Reimann, S., Schaub, D., Stemmler, K., Staehelin, J. and Peter, T. (2005). Hydrocarbon concentrations at the Alpine mountain sites Jungfraujoch and Arosa. *Atmos. Environ.* 39: 1113–1127.

Lin, M., Horowitz, L.W., Payton, R., Fiore, A.M. and Tonnesen, G. (2017). US surface ozone trends and extremes from 1980 to 2014: Quantifying the roles of rising Asian emissions, domestic controls, wildfires, and climate. *Atmos. Chem. Phys.* 17: 2943–2970.

Litvak, M.E. (2003). Biogenic non-methane hydrocarbons, In *Handbook of weather, climate, and oceans*, Potter, T.D. and Coleman, B. (Eds.), John Wiley & Sons, Hoboken, pp. 107–124.

Liu, H.Y., Jacob, D.J., Bey, I., Yantosca, R.M., Duncan, B.N. and Sachse, G.W. (2003). Transport pathways for Asian pollution outflow over the Pacific: Interannual and seasonal variations. *J. Geophys. Res.* 108: 8786.

Lo Vullo, E., Furlani, F., Arduini, J., Giostra, U., Cristofanelli, P., Williams, M.L. and Maione, M. (2016a). Non-methane volatile organic compounds in the background atmospheres of a Southern European Mountain Site (Mt. Cimone, Italy): Annual and seasonal variability. *Aerosol Air Qual. Res.* 16: 581–592.

Lo Vullo, E., Furlani, F., Arduini, J., Giostra, U., Graziosi, F., Cristofanelli, P., Williams, M.L. and Maione, M. (2016b). Anthropogenic non-methane volatile hydrocarbons at Mt. Cimone (2165 m a.s.l., Italy): Impact of sources and transport on atmospheric composition. *Atmos. Environ.* 140: 395–403.

Logue, J.M., Small, M.J., Stern, D., Maranche, J. and Robinson, A.L. (2010). Spatial variation in ambient air toxics concentrations and health risks between industrial-influenced, urban, and rural sites. *J. Air Waste Manage. Assoc.* 60: 271–286.

McLaren, R., Singleton, D.L., Lai, J.Y.K., Khouw, B., Singer, E., Wu, Z. and Niki, H. (1996). Analysis of motor vehicle sources and their contribution to ambient hydrocarbon distributions at urban sites in Toronto during the Southern Ontario oxidants study. *Atmos. Environ.* 30: 2219–2232.

Nakazawa, T., Aoki, S., Fukabori, M. and Tanaka, M. (1984). The concentration of atmospheric carbon dioxide on the summit of Mt. Fuji (3776 m), Japan. *J. Meteorol. Soc. Jpn.* 62: 688–695.

Naoe, H., Heintzenberg, J., Okada, K., Zaizen, Y., Hayashi, K., Tateishi, T., Igarashi, Y., Dokiya, Y. and Kinoshita, K. (2003). Composition and size distribution of submicrometer aerosol particles observed on Mt. Fuji in the volcanic plumes from Miyakejima. *Atmos. Environ.* 37: 3047–3055.

Ou-Yang, C.F., Lin, N.H., Sheu, G.R., Lee, C.T. and Wang, J.L. (2012). Seasonal and diurnal variations of ozone at a high-altitude mountain baseline station in East Asia. *Atmos. Environ.* 46: 279–288.

Ou-Yang, C.F., Lin, N.H., Lin, C.C., Wang, S.H., Sheu, G.R., Lee, C.T., Schnell, R.C., Lang, P.M., Kawasato, T. and Wang, J.L. (2014). Characteristics of atmospheric carbon monoxide at a high-mountain background station

in East Asia. *Atmos. Environ.* 89: 613–622.

Ou-Yang, C.F., Chang, C.C., Chen, S.P., Chew, C., Lee, B.R., Chang, C.Y., Montzka, S.A., Dutton, G.S., Butler, J.H., Elkins, J.W. and Wang, J.L. (2015). Changes in the levels and variability of halocarbons and the compliance with the Montreal Protocol from an urban view. *Chemosphere* 138: 438–446.

Parrish, D.D., Stohl, A., Forster, C., Atlas, E.L., Blake, D.R., Goldan, P.D., Kuster, W.C. and de Gouw, J.A. (2007). Effects of mixing on evolution of hydrocarbon ratios in the troposphere. *J. Geophys. Res.* 112: D10S34.

Parrish, D.D., Millet, D.B. and Goldstein, A.H. (2009). Increasing ozone in marine boundary layer inflow at the west coasts of North America and Europe. *Atmos. Chem. Phys.* 9: 1303–1323.

Penkett, S.A., Burgess, R.A., Coe, H., Coll, I., Hov, O., Lindskog, A., Schmidbauer, N., Solberg, S., Roemer, M., Thijsse, T., Beck, J. and Reeves, C.E. (2007). Evidence for large average concentrations of the nitrate radical (NO_3) in Western Europe from the HANSA hydrocarbon database. *Atmos. Environ.* 41: 3465–3478.

Rigby, M., Prinn, R.G., O'Doherty, S., Montzka, S.A., McCulloch, A., Harth, C.M., Muhle, J., Salameh, P.K., Weiss, R.F., Young, D., Simmonds, P.G., Hall, B.D., Dutton, G.S., Nance, D., Mondeel, D.J., Elkins, J.W., Krummel, P.B., Steele, L.P. and Fraser, P.J. (2013). Re-evaluation of the lifetimes of the major CFCs and CH_3CCl_3 using atmospheric trends. *Atmos. Chem. Phys.* 13: 2691–2702.

Rolph, G.D. (2017). Real-Time Environmental Applications and Display System (Ready) Website (Http://Ready.Arl.Noaa.Gov), Last Access: July, 2017.

Sarkar, C., Chatterjee, A., Singh, A.K., Ghosh, S.K. and Raha, S. (2015). Characterization of black carbon aerosols over Darjeeling - A high altitude himalayan station in Eastern India. *Aerosol Air Qual. Res.* 15: 465–478.

Schmitt, R. and Volz-Thomas, A. (1997). Climatology of Ozone, PAN, CO, and NMHC in the free troposphere over the southern North Atlantic. *J. Atmos. Chem.* 28: 245–262.

Sekino, H., Nara, C., Tsuboi, K., Hosomi, T., Dokiya, Y., Igarashi, Y., Tsutsumi, Y. and Tanaka, S. (1997). Chemical species in aerosol, gases, precipitation and fog at the summit of Mt. Fuji—Observations in summer, 1994 compared with summer 1993—. *Earozoru Kenkyu* 12: 311–319.

Sharma, U.K., Kajii, Y. and Akimoto, H. (2000). Seasonal variation of C_2-C_6 NMHCs at Happo, a remote site in Japan. *Atmos. Environ.* 34: 4447–4458.

Simpson, I.J., Andersen, M.P.S., Meinardi, S., Bruhwiler, L., Blake, N.J., Helmig, D., Rowland, F.S. and Blake, D.R. (2012). Long-term decline of global atmospheric ethane concentrations and implications for methane. *Nature* 488: 490–494.

Spirig, C., Guenther, A., Greenberg, J.P., Calanca, P. and Tarvainen, V. (2004). Tethered balloon measurements of biogenic volatile organic compounds at a boreal forest site. *Atmos. Chem. Phys.* 4: 215–229.

Stein, A.F., Draxler, R.R., Rolph, G.D., Stunder, B.J.B.,

Cohen, M.D. and Ngan, F. (2015). NOAA's HYSPLIT atmospheric transport and dispersion modeling system. *Bull. Am. Meteorol. Soc.* 96: 2059–2077.

Suthawaree, J., Kato, S., Okuzawa, K., Kanaya, Y., Pochanart, P., Akimoto, H., Wang, Z. and Kajii, Y. (2010). Measurements of volatile organic compounds in the middle of Central East China during Mount Tai Experiment 2006 (MTX2006): Observation of regional background and impact of biomass burning. *Atmos. Chem. Phys.* 10: 1269–1285.

Suzuki, I., Hayashi, K., Igarashi, Y., Takahashi, H., Sawa, Y., Ogura, N., Akagi, T. and Dokiya, Y. (2008). Seasonal variation of water-soluble ion species in the atmospheric aerosols at the summit of Mt. Fuji. *Atmos. Environ.* 42: 8027–8035.

Suzuki, I., Igarashi, Y., Dokiya, Y. and Akagi, T. (2010). Two extreme types of mixing of dust with urban aerosols observed in Kosa particles: 'After' mixing and 'on-the-way' mixing. *Atmos. Environ.* 44: 858–866.

Swanson, A.L., Blake, N.J., Atlas, E., Flocke, F., Blake, D.R. and Rowland, F.S. (2003). Seasonal variations of C_2-C_4 nonmethane hydrocarbons and C_1-C_4 alkyl nitrates at the Summit research station in Greenland. *J. Geophys. Res.* 108: 4065.

Swarthout, R.F., Russo, R.S., Zhou, Y., Hart, A.H. and Sive, B.C. (2013). Volatile organic compound distributions during the NACHTT campaign at the Boulder Atmospheric Observatory: Influence of urban and natural gas sources. *J. Geophys. Res.* 118: 10614–10637.

Tsutsumi, Y., Zaizen, Y. and Makino, Y. (1994). Tropospheric ozone measurement at the top of Mt. Fuji. *Geophys. Res. Lett.* 21: 1727–1730.

Tsutsumi, Y., Igarashi, Y., Zaizen, Y. and Makino, Y. (1998). Case studies of tropospheric ozone events observed at the summit of Mount Fuji. *J. Geophys. Res.* 103: 16935–16951.

Tsutsumi, Y. and Matsueda, H. (2000). Relationship of ozone and CO at the summit of Mt. Fuji (35.35°N, 138.73°E, 3776 m above sea level) in summer 1997. *Atmos. Environ.* 34: 553–561.

Ueda, S., Hirose, Y., Miura, K. and Okochi, H. (2014). Individual aerosol particles in and below clouds along a Mt. Fuji slope: Modification of sea-salt-containing particles by in-cloud processing. *Atmos. Res.* 137: 216–227.

UNEP (1987). *Montreal protocol on substances that deplete the ozone layer: Final act*. Montreal.

UNEP (1992). *The copenhagen amendment (1992): The amendment to the montreal protocol agreed by the fourth meeting of the parties*. Copenhagen.

Verstraeten, W.W., Neu, J.L., Williams, J.E., Bowman, K.W., Worden, J.R. and Boersma, K.F. (2015). Rapid increases in tropospheric ozone production and export from China. *Nat. Geosci.* 8: 690–695.

Wai, K.M., Lin, N.H., Wang, S.H. and Dokiya, Y. (2008).

Rainwater chemistry at a high-altitude station, Mt. Lulin, Taiwan: Comparison with a background station, Mt. Fuji. *J. Geophys. Res.* 113: D06305.

Wang, H.L., Qiao, Y.Z., Chen, C.H., Lu, J., Dai, H.X., Qiao, L.P., Lou, S.R., Huang, C., Li, L., Jing, S.G. and Wu, J.P. (2014). Source profiles and chemical reactivity of volatile organic compounds from solvent use in Shanghai, China. *Aerosol Air Qual. Res.* 14: 301–310.

Wang, J.L., Chang, C.C. and Lee, K.Z. (2012). In-line sampling with gas chromatography–mass spectrometry to monitor ambient volatile organic compounds. *J. Chromatogr. A* 1248: 161–168.

Wang, J.L., Jacobson, G., Rella, C.W., Chang, C.Y., Liu, I., Liu, W.T., Chew, C., Ou-Yang, C.F., Liao, W.C. and Chang, C.C. (2013). Flask sample measurements for CO_2, CH_4 and CO using cavity ring-down spectrometry. *Atmos. Meas. Tech. Discuss.* 6: 7633–7657.

Wang, S., Yuan, X. and Li, Y. (2017). Does a strong El Niño imply a higher predictability of extreme drought? *Sci. Rep.* 7: 40741.

Watanabe, K., Takebe, Y., Sode, N., Igarashi, Y., Takahashi, H. and Dokiya, Y. (2006). Fog and rain water chemistry at Mt. Fuji: A case study during the September 2002 campaign. *Atmos. Res.* 82: 652–662.

Xue, L.K., Wang, T., Guo, H., Blake, D.R., Tang, J., Zhang, X.C., Saunders, S.M. and Wang, W.X. (2013). Sources and photochemistry of volatile organic compounds in the remote atmosphere of western China: Results from the Mt. Waliguan Observatory. *Atmos. Chem. Phys.* 13: 8551–8567.

Yang, M.M., Wang, Y., Chen, J.M., Li, H.L. and Li, Y.H. (2016). Aromatic hydrocarbons and halocarbons at a mountaintop in southern China. *Aerosol Air Qual. Res.* 16: 478–491.

Yates, E.L., Derwent, R.G., Simmonds, P.G., Greally, B.R., O'Doherty, S. and Shallcross, D.E. (2010). The seasonal cycles and photochemistry of C_2-C_5 alkanes at mace head. *Atmos. Environ.* 44: 2705–2713.

Zhang, L., Jacob, D.J., Boersma, K.F., Jaffe, D.A., Olson, J.R., Bowman, K.W., Worden, J.R., Thompson, A.M., Avery, M.A., Cohen, R.C., Dibb, J.E., Flock, F.M., Fuelberg, H.E., Huey, L.G., McMillan, W.W., Singh, H.B. and Weinheimer, A.J. (2008). Transpacific transport of ozone pollution and the effect of recent Asian emission increases on air quality in North America: An integrated analysis using satellite, aircraft, ozonesonde, and surface observations. *Atmos. Chem. Phys.* 8: 6117–6136.