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Secondary Production of Organic Aerosols from Biogenic VOCs over Mt. Fuji, Japan

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Supporting Information

ABSTRACT: We investigated organic molecular compositions of summertime aerosols collected at the summit of Mt. Fuji (3776 m a.s.l.) in July– August 2009. More than 120 organic species were identified using GC/MS. Concentrations of both primary and secondary organic aerosol (SOA) tracers in whole-day samples were 4–20 times higher than those in nighttime samples, suggesting that valley breeze is an efficient mechanism to uplift the aerosols and precursors from the ground surface to mountaintop in daytime. Using a tracer-based method, we estimated the concentrations of secondary organic carbon (SOC) derived from isoprene, α/β -pinene, and β caryophyllene to be 2.2–51.2 ngC m⁻³ in nighttime and 227–1120 ngC m⁻³ during whole-day. These biogenic SOCs correspond to 0.80–31.9% and 26.8–57.4% of aerosol organic carbon in nighttime and whole-day samples, respectively. This study demonstrates that biogenic SOA, which is controlled



by the valley breeze, is a significant fraction of free tropospheric aerosols over Mt. Fuji in summer.

INTRODUCTION

Organic aerosols are important constituents in the Earth's atmosphere because they can influence the chemical composition, radiative balance, and hydrological cycle on the Earth.¹ In general, primary organic aerosols (POA) are directly emitted from primary sources such as plant material, soil dust, biomass and fossil fuel burning, while secondary organic aerosols (SOA) are formed by the oxidation of gas-phase precursors emitted from both anthropogenic and biogenic sources.^{2–4} For example, SOA can be formed via the oxidation of biogenic volatile organic compounds (VOCs) such as isoprene, monoterpenes, and sesquiterpenes with OH radicals, ozone, and nitrate radicals (NO₃).⁵ Owing to the complexity of the emitted VOC mixture, the variation of ambient oxidation capacity, as well as the changing meteorology such as wind, temperature, relative humidity, clouds, and precipitation, molecular compositions of organic aerosols are quite variable in the troposphere depending upon geographical situations.^{1,6–10}

During the past decade, particular attention has been paid to atmospheric chemistry in East Asia (e.g., ACE-Asia campaign), where severe biomass burning, dust storms, and industrial and residential emissions are important sources of atmospheric aerosols and precursors.^{11–14} For example, Wang et al.¹⁵ reported high loadings of organic aerosols from fossil fuel combustion and plastic emission in Chinese megacities. In addition, Asian outflow of continental pollutants to the East China Sea and western North Pacific has increasingly been recognized.⁷ Long-range atmospheric transport of Asian dust has also been identified in the Asian-Pacific regions.¹⁶

Heald et al.¹⁷ reported a large, sustained source of SOA in the free troposphere (FT) from the oxidation of long-lived volatile organic compounds in East Asia. Henze and Seinfeld¹⁸ reported that inclusion of isoprene as a source of SOA in a global model substantially increases SOA concentrations in the free troposphere. These studies highlight the need to investigate the molecular composition of organic aerosols at high altitudes. In a previous study at the summit of Mt. Tai (1534 m a.s.l.) in the North China Plain during the MTX2006 campaign,^{19,20} high levels of both POA and SOA tracers were observed as a result of crop-residue burning on the ground level in early summer and the photochemical processing during the atmospheric transport.

The objective of this study is to investigate the molecular compositions of organic aerosols over Mt. Fuji (3776 m a.s.l.) in summer. The summit of Mt. Fuji exists in the free troposphere for most of the year due to the high and independent peak of the mountain.²¹ It is believed that ground surface aerosols and precursors can be uplifted along the mountain slope to the FT during daytime over the Japanese Islands and that the air quality at the summit of Mt. Fuji represents the regional FT condition of East Asia or the

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western North Pacific.²² Thus, the summit of Mt. Fuji provides an ideal site for the study of chemical compositions of free tropospheric aerosols. In the present study, we measured more than 120 organic compounds including POA and SOA tracers in the aerosol particles collected at the summit of Mt. Fuji. Here, we compare the molecular compositions of the aerosols collected during nighttime and whole-day to better understand the influences of long-range atmospheric transport via mountain and valley breezes at high altitudes in East Asia.

MATERIALS AND METHODS

Sample Collection. Total suspended particle (TSP) samples were collected at the summit of Mt. Fuji (35.4° N, 138.7° E) in the summer of 2009. Mt. Fuji is the highest mountain in Japan, located to the west of Tokyo and near the Pacific coast of Honshu Island (Supporting Information (SI) Figure S1). The sampling campaign lasted for one month from 27 July to 26 August 2009 during the 2-month period when climbing is permitted. The nighttime and whole-day samples were collected using two high-volume samplers (Kimoto AS-810B) with a flow rate of 1.0 m³ min⁻¹. Nighttime samples were collected during 23:00-8:00 (local time, sample ID MF07-10) from 27 July to 12 August on a 3- or 4-day basis due to clean condition in the free troposphere. Whole-day TSP samples (MF12-15) were collected on the basis of 2-4 days during 13-26 August (SI Table S1). All samples were collected onto precombusted (450 °C for 6 h) quartz fiber filters (20 cm × 25 cm, Pallflex 2500QAT-UP). Before the sampling, each filter was placed in a precombusted (450 °C for 6 h) glass jar with a Teflon-lined cap during the transport and storage. After sampling, filters were recovered into the glass jar, transported to the laboratory, and stored at -20 °C prior to analysis. A field blank was taken by placing the filter on the filter cartridge of the sampler for a few seconds without pumping.

Extraction and Derivatization. Filter aliquots (30–50 cm²) of the aerosol samples were extracted three times with dichloromethane/methanol (2:1, ν/ν) under ultrasonication for 10 min. The solvent extracts were filtered through quartz wool packed in a Pasteur pipet, concentrated by the use of a rotary evaporator under vacuum, and then blown down to dryness with pure nitrogen gas. The extracts were reacted with 50 μ L of *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, Sigma-Aldrich) containing 1% trimethylsilyl chloride and 10 μ L of pyridine at 70 °C for 3 h. After the reaction, derivatives were diluted by addition of 140 μ L of *n*-hexane containing 1.43 ng μ L⁻¹ of internal standard (C₁₃ *n*-alkane) prior to GC/MS injection.¹⁹

GC/MS Analyses. GC/MS analyses of the samples were performed with a Hewlett-Packard model 6890 GC coupled to a mass-selective detector (Hewlett-Packard model 5973). The GC was equipped with a split/splitless injector and a DB-5MS fused silica capillary column (30 m \times 0.25 mm i.d., 0.25 μ m film thickness). The mass spectrometer was operated on the electron impact (EI) mode at 70 eV and scanned from 50 to 650 Da. Individual compounds were identified by comparison of mass spectra with those of authentic standards or literature data. Detailed quantification of the organic tracers has been mentioned elsewhere.^{19,23} The field blank filter was treated as a real sample for quality assurance. No contamination was found for the target compounds. The limits of detection (LODs) for different chemicals reported here ranged from 1 to 10 pg m^{-3} . Recoveries for the authentic standards or surrogates that were spiked into precombusted quartz filters were generally better

than 80% except for polyacids and pinonic acid, whose recoveries were around 60%. Relative standard deviation of the concentrations based on duplicate analysis was generally <10%.

Organic Carbon (OC) and Elemental Carbon (EC) Measurements. OC and EC were measured using a Sunset Lab carbon analyzer, following the Interagency Monitoring of Protected Visual Environments (IMPROVE) method.²⁴ Duplicate analyses of filter samples showed uncertainties of $\pm 10\%$.

RESULTS AND DISCUSSION

During the sampling period, no rainfall events were recorded, although fog/cloud events occasionally occurred in nighttime and early in the morning. Ambient temperatures ranged from 1.0 to 16.7 °C (mean 7.9 °C), whereas relative humidity (RH) ranged from 13.0% to 100% (75.2%). Detailed sample information with mean ambient temperature and RH for each sample is presented in SI Table S1. Concentrations of OC in the Mt. Fuji samples were relatively low with 0.029–0.16 μ gC m⁻³ (mean 0.095 μ gC m⁻³) in nighttime, which are more than ten times lower than those $(0.85-1.95 \ \mu \text{gC m}^{-3}$, mean 1.3 μgC m^{-3}) of the whole-day samples. OC values of the whole-day samples were 1-2 orders of magnitude lower than those reported in urban and rural sites in China.^{14,25} However, the OC values from the summit of Mt. Fuji were similar to those $(0.11-2.9 \ \mu \text{gC m}^{-3})$ of summertime marine aerosols collected in the Arctic Ocean during the MALINA campaign,² suggesting a representative background level in the Earth's atmosphere.

Thirteen organic compound classes were detected in the Mt. Fuji aerosol samples (Figure 1). They are *n*-alkanes, fatty acids,



Figure 1. Chemical compositions of organic compounds detected in the tropospheric aerosols collected at the summit of Mt. Fuji, Japan. Sample ID numbers for nighttime (MF07–10) and whole-day (MF12–15) samples are presented in the figure.

fatty alcohols, sugar compounds, lignin products, sterols, phthalates, aromatic acids, hydroxy-/poly acids, polycyclic aromatic hydrocarbons (PAHs), and biogenic SOA tracers produced by the photooxidation of isoprene, monoterpenes, and β -caryophyllene. Total concentrations of the identified organic species ranged from 86 to 363 ng m⁻³ (201 ng m⁻³) for the whole-day samples, which are more than 10 times higher

Table 1. Summary of Organic Carbon (OC) Concentrations (ngC m⁻³) from Biogenic Primary Emission (Biomass-Burning OC and Fungal-Spore OC) and Photochemical Formation (Anthropogenic SOC and Biogenic SOC) and Their Contributions in Aerosol OC (%) in the Mt. Fuji Aerosol Samples

component	nighttime aerosols			whole-day aerosols		
	range	mean	std	range	mean	std
	Concentration	(ngC m ⁻³)				
OC	29-161	95	66	850-1950	1330	459
biomass burning OC	0.44-3.1	1.5	1.2	18.3-46.0	29.7	13.1
fungal spore OC	1.1-9.1	4.5	4.0	5.6-68.5	29.6	27.1
naphthalene SOC	0.93-5.5	2.5	2.6	46.6-192	86.7	70.5
isoprene SOC	0.72-48.4	13.7	23.2	112-694	339	258
α -pinene SOC	1.3-2.8	1.8	0.67	96.5-354	170	123
β -caryophyllene SOC	nd ^a	na ^b	na	15.8-70.5	32.1	25.8
MBO SOC	nd	na	na	0.45-1.8	1.1	0.64
sum of biogenic SOC	2.2-51.2	15.5	23.8	227-1120	542	399
subtotal	4.6-68.9	23.5	30.5	305-1370	688	478
	Percentage in Ae	erosol OC (%)				
biomass burning OC	0.34-2.0	0.90	0.73	1.6-3.6	2.3	0.88
fungal spore OC	0.39-7.0	3.4	3.4	0.66-5.3	2.2	2.1
naphthalene SOC	0.16-3.4	1.3	1.5	3.8-9.9	6.1	2.8
isoprene SOC	0.27-30	8.9	14.2	13.2-35.6	23.0	10.4
α -pinene SOC	0.53-1.8	1.2	0.51	8.2-18.2	12.0	4.3
β -caryophyllene SOC	na	na	na	1.3-3.6	2.2	1.0
MBO SOC	na	na	na	0.05-0.11	0.08	0.03
sum of biogenic SOC	0.80-31.9	10.1	14.7	26.8-57.4	37.3	14.3
subtotal	1.7-42.9	15.7	18.9	34.5-70.3	47.9	16.6
^{<i>a</i>} nd = not detected. ^{<i>b</i>} na = not available.						

than those of nighttime samples (9.3–19 ng m⁻³, 16 ng m⁻³) (SI Table S2). Isoprene oxidation products were found as the dominant compound class (69 ± 57 ng m⁻³ during whole-day versus 2.9 \pm 4.1 ng m⁻³ during nighttime), which account for one-third of the mass concentrations of the measured organics.

Significant Contributions of Biogenic SOA. Isoprene is the most abundant biogenic volatile organic compound (BVOC) emitted from terrestrial vegetation to the atmosphere.²⁷ Eight compounds were identified as isoprene SOA tracers in the Mt. Fuji aerosols, including 2-methylglyceric acid (2-MGA), three C_5 -alkene triols, two isomers of 2-methyltetrols (2-methylthreitol and 2-methylerythritol), and two isomers of 3-methyltetrahydrofuran-3,4-diols (3-MeTHF-3,4diols) (SI Table S2).

Concentrations of 2-MGA were 2.5-5.3 ng m⁻³ (3.5 ng m^{-3}) in the whole-day samples, which are more than ten times higher than those in the nighttime samples. 2-MGA is formed by photooxidation of isoprene under high-NO_x (NO_x = NO + NO₂) conditions, while the other isoprene SOA tracers identified in this study are higher generation products formed under low-NO_x or NO_x-free conditions from the photooxidation of epoxydiols of isoprene (IEPOX = β -IEPOX + α -IEPOX).^{28,29} Concentration ranges of 2-methyltetrols were 15–102 ng m⁻³ (49 ng m⁻³) in the whole-day samples, which are even higher than those (mean 30.5 ng m⁻³) reported in the forest aerosols in north Japan.³⁰ In the whole-day samples, 2methyltetrols were about three times higher than those (4.2-44 ng m⁻³, mean 17 ng m⁻³) of C₅-alkene triols. In the nighttime samples, 2-methyltetrols $(0.13-7.1 \text{ ng m}^{-3}, 2.5 \text{ ng m}^{-3})$ were found to be 30 times higher than those $(0.02-0.14 \text{ ng m}^{-3})$. 0.08 ng m⁻³) of C₅-alkene triols. The higher concentration ratios of 2-methyltetrols to C5-alkene triols in the nighttime samples could be explained by the photochemical aging of organic aerosols during long-range transport, because C_5 -alkene triols are easily oxidized due to the presence of a double bond.

Oxidation products of α -/ β -pinene, including pinonic acid, pinic acid, 3-hydroxyglutaric acid (3-HGA), 3-(2-hydroxyethyl)-2,2-dimethylcyclobutane carboxylic acid, 3-acetylglutaric acid, 3-acetyladipic acid, 3-isopropylglutaric acid and 3methyl-1,2,3-butanetricarboxylic acid (MBTCA), were detected in the Mt. Fuji aerosols. Their total concentrations ranged from 22 to 82 ng m⁻³ (mean 39 ng m⁻³) in the whole-day samples, which was 2 orders of magnitude higher than those (0.31–0.65 ng m⁻³, 0.45 ng m⁻³) in the nighttime samples.

 β -Caryophyllinic acid, an ozonolysis or photooxidation product of β -caryophyllene,³¹ was detected only in the wholeday samples with a concentration range of 0.36–1.6 ng m⁻³. 2,3-Dihydroxyisopentanol (DHIP) is proposed to be a specific tracer for the photooxidation of 2-methyl-3-buten-2-ol (MBO).³² Concentrations of DHIP were relatively low with an average of 0.11 ± 0.06 ng m⁻³ (SI Table S2).

To evaluate the relative abundances of organic aerosols from primary and secondary sources, some tracer-based methods are used to estimate their contributions to aerosol OC. The measured concentrations of mannitol are used to calculate the contributions of fungal spores to OC.^{33,34} The mass percent ratios (8.0–8.2%) of levoglucosan to OC (LG/OC) are calculated from various types of biomass burning emissions;^{6,35} the average ratio of 8.14% is used here to estimate the biomassburning-derived OC. The measured biogenic SOA tracers are used to estimate the secondary organic carbon (SOC) formation due to the oxidation of isoprene, α -pinene, β caryophyllene, and MBO using a tracer-based method developed by Kleindienst et al.³⁶ and Jaoui et al.³² In addition, the formation of anthropogenic SOC from the photooxidation of naphthalene is calculated using phthalic acid as a tracer.³⁷ These methods use the laboratory-generated mass fractions





($f_{\rm soc}$) of marker compounds derived from given precursors into SOC concentrations. It should be noted that such approaches were developed using a series of smog chamber experiments under relatively high NO_x conditions (0.11–0.63 ppm);³⁶ the $f_{\rm soc}$ of 0.155 \pm 0.039 for isoprene is similar to those ($f_{\rm soc, isoprene}$ from 0.117 to 0.231, mean 0.156) in the absence of NO_x.³⁸ These similar values suggest that the tracer-based method is applicable to the high mountain aerosols where the ambient NO_x levels are generally low. Although little is known about the differences of $f_{\rm soc}$ values for α -pinene and β -caryophyllene between high and low NO_x levels, we consider that the tracerbased method is the best technique available at present.³⁹ The uncertainties of such estimation have been discussed in details by Yttri et al.⁴⁰ and El Haddad et al.⁴¹

The results of the tracer-based methods are presented in Table 1. In the whole-day samples, biomass-burning-derived OC ranged from 18.3-46 ngC m^{-3} (29.7 ngC m^{-3}), which account for only 1.6-3.6% (2.3%) of OC in the Mt. Fuji aerosols. Concentrations of fungal-spore-derived OC (5.6-68.5 ngC m⁻³, 29.6 ngC m⁻³) are comparable with those of biomass-burning-derived OC. These primary OC are lower than those of naphthalene-derived SOC (46.6-192 ngC m⁻³, 86.7 ngC m⁻³). However, concentrations of biogenic SOC (227-1120 ngC m⁻³, 542 ngC m⁻³) are about 1 order of magnitude higher than those of primary OC, among which isoprene SOC is dominant. For example, isoprene SOC account for 13.2-35.6% (23%) of OC, doubling that (8.2-18.2%, 12.0%) of α -pinene SOC. The contribution of β caryophyllene SOC to OC (2.2%) is comparable with those of biomass-burning- and fungal-spore-derived OC.

In nighttime samples, isoprene-derived SOC also dominates in OC (0.27-30%, 8.9%), followed by fungal spore (3.4%) and biomass burning emissions (0.90%). However, the total contributions of these sources to OC are much lower (1.7-42.9%, 15.7%) in the nighttime samples than those (34.5-70.3%, 47.9%) in the whole day samples.

Primary biological aerosol particles (PBAP) have often been observed at high altitudes in the atmosphere; they can act as cloud condensation nuclei or ice nuclei for water vapors, and thus have an important influence on cloud formation and precipitation.⁴² As seen in SI Figure S2, the relative abundance of fungal spores to OC is more significant in nighttime samples (22%) than that of whole-day samples (5%). Such an enhanced contribution from fungal spore in nighttime highlights an importance of PBAP during long-range transport in the free troposphere, especially during late July to early August when the air masses were mainly transported over the East China Sea and West/North Pacific Ocean (SI Figure S3). In total, these biogenic primary and secondary sources can account for 34.5– 70.3% (47.9%) of OC in the whole-day samples, among which biogenic SOC accounts for 26.8–57.4% (37.3%) of OC. The contribution of biogenic SOC to OC in the Mt. Fuji aerosols is much more significant than those reported in other mountain sites such as Mt. Tai, China $(1.0-23\%)^{19}$ and Godavari, Nepal (6-23%).⁴³ Previous studies have shown that anthropogenic SO₂ emission and pre-existing acidic sulfate aerosols can favor isoprene SOA formation.^{29,44} Recently, Froyd et al.⁴⁵ reported that isoprene oxidation products, especially isoprene-derived organosulfates, can contribute to free tropospheric aerosol mass through acidity-dependent IEPOX uptake.

Article

Minor Contributions of Biomass Burning. Biomass burning is one of the major sources of organic aerosols in the atmosphere.¹ Levoglucosan and its two isomers, galactosan and mannosan, are specific tracers of biomass burning.⁴⁶ The ratios of levoglucosan to mannosan (L/M) can be used to distinguish the biomass categories with lower ratios for soft wood burning³⁻⁵ and higher ratios (>10) for hard wood and crop residue burning.⁴⁷ In the whole-day samples, the ratios were found to range from 4.6 to 7.6 with an average of 5.5, suggesting that the influence of biomass burning over Mt. Fuji may be mostly associated with soft wood burning.

In the present study, the atmospheric levels of biomass burning tracers such as levoglucosan, lignin and resin acids, and β -sitosterol are generally low. For example, concentrations of levoglucosan (0.04–3.7 ng m⁻³) in the Mt. Fuji aerosols are slightly higher than those (0.01–0.93 ng m⁻³) from the marine aerosols in the Arctic Ocean²⁶ and were within those (0.008– 27 ng m⁻³, 2.9 ng m⁻³) from the marine aerosols collected during a round-the-world cruise⁹ and those (0.01–5.2 ng m⁻³) from a remote island in the western North Pacific.⁴⁸ However, they are lower than those of the Indian Ocean aerosols collected at Gan (12.3–25.4 ng m⁻³) and Hanimaadhoo (1.97–8.62 ng m⁻³),⁴⁹ and those (14.2–436 ng m⁻³) in the Kanto Plain⁵⁰ and Hokkaido forest (1.5–21 ng m⁻³),⁵¹ Japan, and are much lower than those in urban/rural aerosols in China and India, which can reach several thousand ng m⁻³.^{10,19}

Thus, our study provides the background level of levoglucosan in the free troposphere in East Asia; such low levels of levoglucosan and other biomass-burning tracers in high mountain aerosols indicate that biomass burning is not an important source of organic aerosols in the free troposphere over Japan, especially during night when the mountaintop is far above the planetary boundary layer (PBL). The low level of levoglucosan over Mt. Fuji could be explained by the removal through both dry and wet depositions of smoke particles, as well as photodegradation of levoglucosan by free radicals such as OH⁵² during its upward transport from the ground surface to mountaintop, although biomass burning sources are generally



Figure 3. Schematic diagram of the effect of mountain and valley breezes on the organic molecular composition of tropospheric aerosols over Mt. Fuji (3776 m a.s.l.).

not significant in Japan. Moreover, atmospheric dilution of levoglucosan during the transport could be responsible for its low levels in the free troposphere.

Source Apportionment of Identified Organics. To better understand the sources of organic aerosols in the troposphere over Mt. Fuji, the quantified organic species in the high mountain aerosols can be roughly apportioned to six emission sources and atmospheric oxidation products as follows:^{7,53} (a) "higher plant waxes" characterized by the sum of the mass concentrations of plant wax n-alkanes, higher molecular weight (MW) fatty acids, and fatty alcohols (> C_{20}); (b) "microbial/marine sources" reflected by lower MW fatty acids and fatty alcohols ($\leq C_{20}$), cholesterol, and ergosterol; (c) "biomass burning" characterized by levoglucosan and its isomers, β -sitosterol, 4-hydroxybenzoic acid, and lignin/resin acids; (d) "fossil fuel combustion" characterized by petroleumderived *n*-alkanes and PAHs; (e) "soil resuspension" characterized by primary saccharides and reduced sugars; (f) "plastic emission" characterized by phthalate esters; and (g) "photooxidation" reflected by biogenic SOA tracers, aromatic acids, and hydroxy-/polyacids (see SI Table S3).

On the basis of the above-categorized organic tracers, source strengths are apportioned for the Mt. Fuji samples (Figure 2). In the nighttime aerosols, microbial/marine sources (43.5%) are found to be the main contributor, followed by photo-oxidation (19.8%) and plastic emission (17.1%). In the whole-day samples, photooxidation (62.4%) is the dominant contributor, followed by microbial/marine sources (11.2%); the contributions of other sources are relatively minor (<8%). With the same method of source apportionment, we find that the contribution of photooxidation (62.4%) in the whole-day samples is much more significant than those (8.6–23%) from tropical urban aerosols in India⁵³ and (17%) from Mt. Tai (1534 m a.s.l.) aerosols collected during a severe wheat-straw burning season in the North China Plain.¹⁹

Influence of Mountain and Valley Breezes. Under the conditions of higher relative humidity (RH) and higher loadings of biogenic VOC and NO_{xy} SOA can be significantly formed in cloud droplets and aqueous particles.⁵⁴ In the present study, RH was high only in nighttime (SI Table S1). Thus, cloud processing may not contribute significantly to the high loadings of biogenic SOA over Mt. Fuji. However, cloud processing may be important even during daytime-uplifting transport of aerosols and precursors from the ground surface to

the mountaintop because we often observed cloud layers down the summit of Mt. Fuji (see TOC art). The large differences in both POA and SOA between the whole-day and nighttime samples indicate that the mountain/valley breezes should act as an important factor to control the organic molecular compositions of the tropospheric aerosols over Mt. Fuji. The atmospheric transport and spatial distribution of pollutants in urban-mountain regions could be driven by mountain and valley winds, as well as local atmospheric circulation.^{55–58}

As shown in Figure 3, the valley breeze can transport large amounts of ground-surface aerosols to the summit of Mt. Fuji in daytime, together with anthropogenic and biogenic VOCs, SO_{21} NO₂₂ oxidants, and so on. Biogenic VOCs such as isoprene and monoterpenes can be rapidly oxidized into semivolatile organic compounds by oxidants (O₃, OH, and nitrate radicals etc.) during the upward transport and be condensed into the aerosol phase. Rather, levels of OC (0.85-1.95 μ gC m⁻³, mean 1.3 μ gC m⁻³) in the whole-day samples were slightly lower than those (ca. $3-9 \ \mu \text{gC} \text{ m}^{-3}$) reported in fine aerosol particles at ground surface sites in the Kanto region, Japan in summer.^{50,59} In nighttime, the mountain breeze prevails and the transport of local ground-surface aerosols to the summit is negligible; the tropospheric aerosols over the summit of Mt. Fuji are mainly derived from long-range atmospheric transport, in which the major source of organics is of microbial/marine origin. Our results provide useful information to understand the sources and abundances of organic aerosols in the free troposphere over East Asia.

ASSOCIATED CONTENT

Supporting Information

Tables S1–S3 and Figures S1–S3 used in this work. This material is available free of charge via the Internet at http://pubs.acs.org/.

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The authors declare no competing financial interest.

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