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Increases in Biogenic Volatile Organic Compound Concentrations Observed after Rains at Six Forest Sites in Non-Summer Periods

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Abstract: Since biogenic volatile organic compounds (BVOCs) are important precursors of ozone, the monitoring of the BVOC concentration distributions is needed. In general, forest BVOC concentrations increase in summer as well as in other seasons. This study aims to detect temporally sporadic increases in BVOC concentrations in the non-summer months and to analyze the occurring climatic conditions. Using a uniform sampling system and shared gas chromatography–mass spectrometry, the concentrations of isoprene and monoterpenes in six Japanese forests were observed approximately once a month for 3 years. Using the observed data, the relations between the BVOC concentration increases and meteorological factors were evaluated. Twenty instances of temporal increases in BVOC concentrations were observed. These mainly occurred in spring for isoprene and in autumn for monoterpenes. Most of the increases in the non-summer months were observed after a rainfall event, when the daily temperature range was large, suggesting that wind, rain, and a rapid diurnal temperature rise could be factors in the non-summer months. Thus, the network monitoring of BVOC concentrations might be effective for understanding the effects of factors other than temperature, and the mechanisms and frequency of the temporal increases, on the BVOC concentrations in various forests.

Keywords: ozone precursor; biogenic volatile organic compound (BVOC); isoprene; monoterpene; forest; ATD-GC–MS

1. Introduction

Forests are a large source of biogenic volatile organic compounds (BVOCs) in terrestrial ecosystems. Globally, BVOC emissions are estimated to be much higher than the anthropogenic volatile organic compound (AVOC) emissions [1]. Moreover, BVOCs are important precursors for tropospheric

ozone [2–4] and secondary organic aerosols (SOAs) [5]. High surface ozone concentration could harm human health and decreases crop yields [6]. In Japan in particular, high ozone concentrations have been observed around forests in recent years, which might be due to the BVOC emissions from forests. Recent simulation studies have shown that the use of a gridded database to estimate the BVOC emissions throughout Japan has led to significant differences in the ozone concentrations in air quality simulations [7,8]. However, most measurements of BVOC concentrations have been conducted in suburban forests and not in deep forests; thus, uncertainty remains regarding the spatial distribution and temporal variation of BVOCs around forests.

Isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$) are major components of BVOCs, and in Japan they are mainly emitted from broad-leaved and coniferous forests, respectively. The BVOC concentration in forest air is considerably dependent on the vegetation type and temperature. Modeling studies indicate that isoprene emissions from tropical forests constitute more than 50% of the global annual isoprene flux [9]. Monoterpenes are considered to be more important than isoprene as ozone precursors as, according to one estimate, they can produce more than 10 times the amount of ozone generated by isoprene [10].

To accurately evaluate global BVOC emissions, multisite field observations are needed because the presence of terpenoid emissions is unlikely to be categorized by plant functional types or climate range, and the seasonal variations are also high [11]. Volatile isoprenoid emissions with a high dependency on leaf temperature that protect against stressors (high temperature, and oxidative and mechanical stress) have been reported, and occasionally, the emission rate increases with these stressors [12]. On the other hand, water stress associated with drought has been reported to reduce BVOC emissions [13]. Note that in coniferous forests, the monoterpene emissions were occasionally higher in spring than in summer, despite the cooler temperatures [14]. The increase in spring was due to strong winds, but some cases of increased emissions were reported after a rainfall event [15]. These previous studies suggested that further studies of temporal increases in BVOC concentrations in the non-summer months were needed.

Understanding the factors related to temporal increases in BVOC concentrations, other than temperature, requires considerable field observation data. Three main types of observations exist: foliar emission observations using the enclosure method, forest–atmosphere flux observations based on the micrometeorological method, and BVOC concentration monitoring. The BVOC emission characteristics of individual trees have been investigated since the 1970s, using the enclosure method. From North America to Europe, and in many other regions, screening has been done. However, only a limited number of individual tall woody plants of vascular plant species have been measured for short periods and seasonal variation has not been adequately evaluated. In particular, the lack of emission data for understory vegetation and soil poses a major problem of representativeness [12]. Concerning micrometeorological methods, performing long-term, stable, and continuous observations at multiple sites is technically difficult. However, the BVOC concentration monitoring method that uses a unified sampling system and an analyzer is highly advantageous for comparing seasonal characteristics among multiple sites, including emissions from small plants and soil, even though it cannot directly estimate the flux.

To detect the temporally sporadic increases in BVOC concentrations in the non-summer months and to analyze the occurring climatic factors, we collected data on the seasonal variations in BVOC concentrations in six Japanese forest sites with different vegetation types, from Hokkaido (LAT 43N) to Okinawa (LAT 26.5N). Data were collected approximately once a month for 3 years using a uniform sampling system and automated thermal desorption–gas chromatography–mass spectrometry (ATD-GC–MS). In particular, we focused on the relation between high BVOC concentration events in the non-summer months and the effects of wind, precipitation, and daily air temperature variation.

2. Site and Method

2.1. Site

The regular interval field sampling of BVOCs is difficult because accessing forests far from cities is time consuming. However, many flux researchers regularly visit the forest sites of the FLUXNET for maintenance and flux data collection, which can be an effective solution for collaboration for BVOC sampling. Thus, the cooperation of the flux and analytical researchers can be key to future global BVOC observation networks.

FLUXNET is a global network built from more than 500 micrometeorological flux measurement tower sites in the world, and it unites regional and organizational networks [16]. The Forestry and Forest Products Research Institute FLUXNET (FFPRI FluxNet) is one of the organizational networks for researching the exchange of energy, water, carbon dioxide (CO_2), and trace gases between the atmosphere and forest ecosystems since 1999 [17]. The FFPRI FluxNet has been operating five tower sites between the cool temperate and warm temperate zones, where the tower sites are a part of the JapanFlux and AsiaFlux networks [18]. The University of the Ryukyus has also been conducting tower flux observations in the subtropical forest of the Yona Field in Okinawa Island since 2013. Furthermore, with the cooperation of the University of the Ryukyus, the seasonal variation in the isoprene and monoterpene concentrations of various forests was evaluated using the six tower sites in Japan (Figure 1). For accurate flux observation, all the sites have enough fetch, and the towers were built in sites far from industrial districts, residential areas, and roads. Thus, the towers' situations are suitable for measuring the concentration of the biogenic gases with reduced artificial effects. These six towers are visited by researchers about once or twice a month. The detailed site information is shown in Table 1.

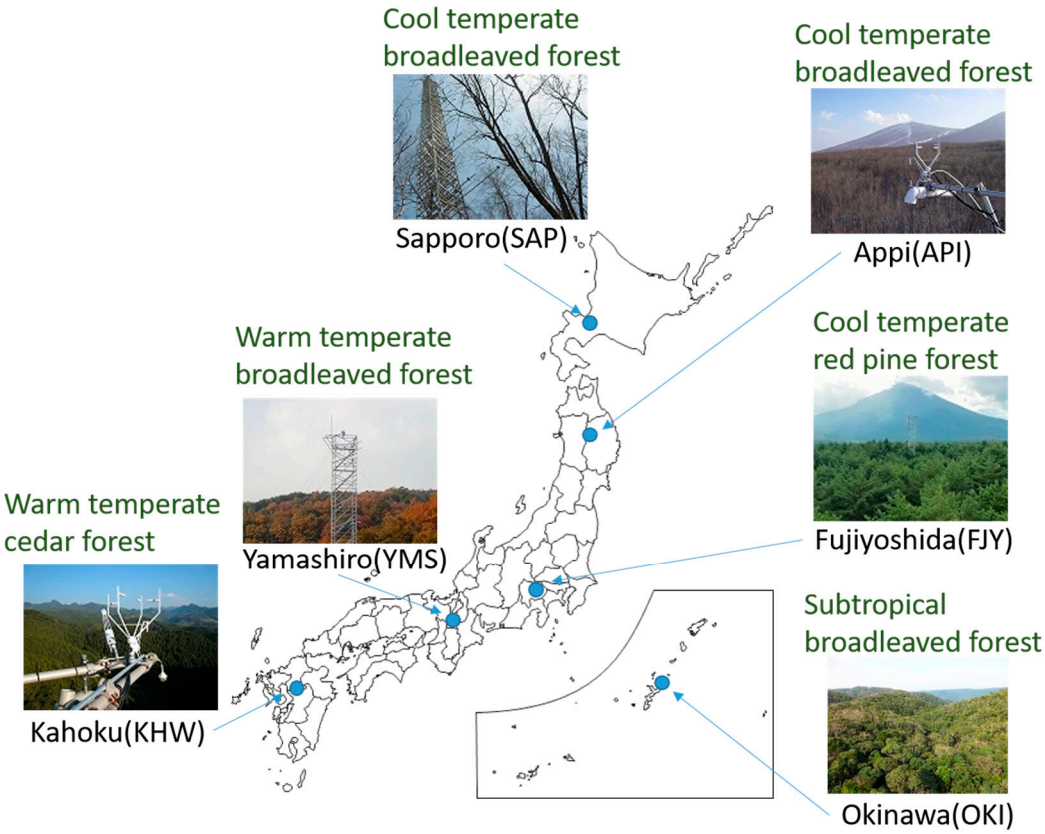


Figure 1. Locations of the six measurement sites in Japan.

Table 1. General information of the six measurement sites.

Site (Code)	Location	Altitude (m)	Area (ha)	Ta (C°)	P (mm)	Climate	Dominant Tree Species	H (m)	LAI (Min.)	LAI (Max.)
Sapporo (SAP)	42°59′ N, 141°23′ E	182	80	7.4	1150	Continental (Dfb)	*Betula platyphylla* *Quercus crispula* *Kalopanax septemlobus*	20	-	4
Appi (API)	40°00′ N, 140°56′ E	825	44	5.9	1869	Continental (Dfb)	*Fagus crenata* *Quercus crispula* *Quercus serrata*	19	-	4.8
Fujiyoshida (FJY)	35°27′ N, 138°46′ E	1030	3600	9.5	1954	Temperate (Cfb)	*Pinus densiflora* *Ilex pedunculosa* *Quercus serrata*	20	2	5
Yamashiro (YMS)	34°47′ N, 135°51′ E	180–255	100	14.7	1095	Temperate (Cfa)	*Quercus serrate* *Ilex pedunculosa* *Pinus densiflora*	6–20	2.7	4.4
Kahoku (KHW)	33°08′ N, 130°43′ E	165	13	15.1	2106	Temperate (Cfa)	*Cryptomeria japonica* *Chamaecyparis obtuse* *Castanopsis cuspidata*	10–35	3.6	5.2
Okinawa (OKI)	26°45′ N, 128°13′ E	380	318	20.7	2673	Temperate (Cfa)	*Castanopsis sieboldii* *Myrsine seguinii* *Ilex liukiuensis*	7	2.3	2.8

Ta: annual mean air temperature (°C); P: annual mean precipitation (mm); H: mean canopy height (m); LAI: leaf area index (m^2 m^{-2}).

2.2. Method

2.2.1. Sampling

At the beginning of the BVOC concentration monitoring, unified portable air sampling systems were distributed to the six sites. The monitoring was conducted from June 2016 to November 2018. The sampling systems comprised an ozone scrubber (eight layers of MnO_2-coated copper nets) at the inlet for reducing the ozonolytic decomposition of terpenes [19], a stainless-steel adsorbent tube (6.35 mm o.d. filled with 200 mg of Tenax TA (GL Science, Tokyo, Japan), and 100 mg of Carbotrap (Supelco, Bellefonte, PA, USA) for BVOC sampling in air, polytetrafluoroethylene (PTFE) tubes for plumbing, ethylene chlorotrifluoroethylene (ECTFE) connectors, and a micropump with a mass flow controller for sucking air in the most downstream part (MP-Σ30NII, Shibata, Souka, Japan). The sampling flow rate, sampling period, total sampling volume, sampling point height, and sampling interval were 0.2 L min^{-1}, 30 min, 6 L, 2–5 m above the ground level (which exceeds the snow depth in winter), and about once a month, respectively. The sampling tubes were tightly sealed using metal caps (B-400-C, Swagelok, Solon, OH, USA), shipped to the Tsukuba main office of FFPRI by regular mail, and stored at 5 °C before analysis. The air temperature was measured near the sampling locations at around the same height. The lack of regular observation data was due to analysis troubles and the delayed delivery of the sampling tubes during the tower maintenance interval.

2.2.2. ATD-GC–MS Analysis

We utilized the analysis methods mentioned in previous studies [20,21]. The isoprene and seven monoterpenes (myrcene, sabinene, limonene, 3-carene, t-β-ocimene, α-pinene, and β-pinene) in the Model of Emissions of Gases and Aerosols from Nature (MEGAN) [22] were quantified. The sampling tube was mounted on an automated two-stage thermal desorber (ATD:TD-100, MARKES International, Llantrisant, UK) and heated to 280 °C for 3 min. BVOCs were desorbed and reconcentrated into a thin cold trap part cooled to −10 °C. The cold trap part was then rapidly heated to 280 °C, and the desorbed BVOCs were introduced into a capillary column (DB-5MS, 60 m × 0.25 mm, 1 μm, Agilent Technology, Santa Clara, CA, USA) and settled in a gas chromatograph–mass spectrometer (GC–MS:7890B (GC), 5977A (MSD), Agilent Technology, Santa Clara, CA, USA). Helium gas was used as the carrier gas for GC. An internal standardization method was applied using toluene-D8 (1.0 ppmv, Sumitomo Seika, Tokyo, Japan). The column was maintained at 35 °C for 5 min and heated to 200 °C at 5 °C min^{-1} and then to 250 °C at 10 °C min^{-1}. The split ratio was set to 1:17.7 with one-stage splitting. The sampling tubes for calibration were prepared by spiking the liquid samples as standard.

3. Results and Discussions

3.1. Isoprene Concentration

The relations between the air temperature (Ta) and concentrations of isoprene or monoterpene are shown in Figure 2. Since the annual minimum and maximum air temperatures were observed in February and August in Japan, respectively, we defined January to March as winter, July to September as summer, April to June as spring, and October to December as autumn. The temperatures were separately plotted for each season, by color. Moreover, twenty data items for high BVOC concentrations observed in the non-summer months were numbered. The details of these temporal data are described in Section 3.3.

In general, isoprene is emitted from the leaf surface of a part of broad-leaved trees during daytime with photosynthesis. *Quercus serrata* was already reported as a strong isoprene emitter in Japan [20]. Because the sites, except for OKI, were in the distribution area of *Q. serrata* or its close relative *Quercus crispula*, these species were thought to be strong isoprene emitters in these forests. The isoprene concentration was high in the summer in the broad-leaved (OKI, YMS, API, and SAP) and coniferous (KHW and FJY, Figure 2a) forests. In comparison, the concentration of isoprene was low under

temperature conditions below 20 °C, and it rapidly increased above 20 °C. In the coniferous forests (KHW and FJY), rapid increases in isoprene concentrations, corroborating the rises in air temperature, were observed in the summer. In the deciduous broad-leaved forests (YMS, API, and SAP), the isoprene variation between the spring and autumn was relatively large compared to that in the coniferous forests. In the subtropical evergreen broad-leaved forest (OKI), a high isoprene concentration was observed in not only the summer but also the spring and autumn, and the variation of the period between 19 °C and 24 °C was large.

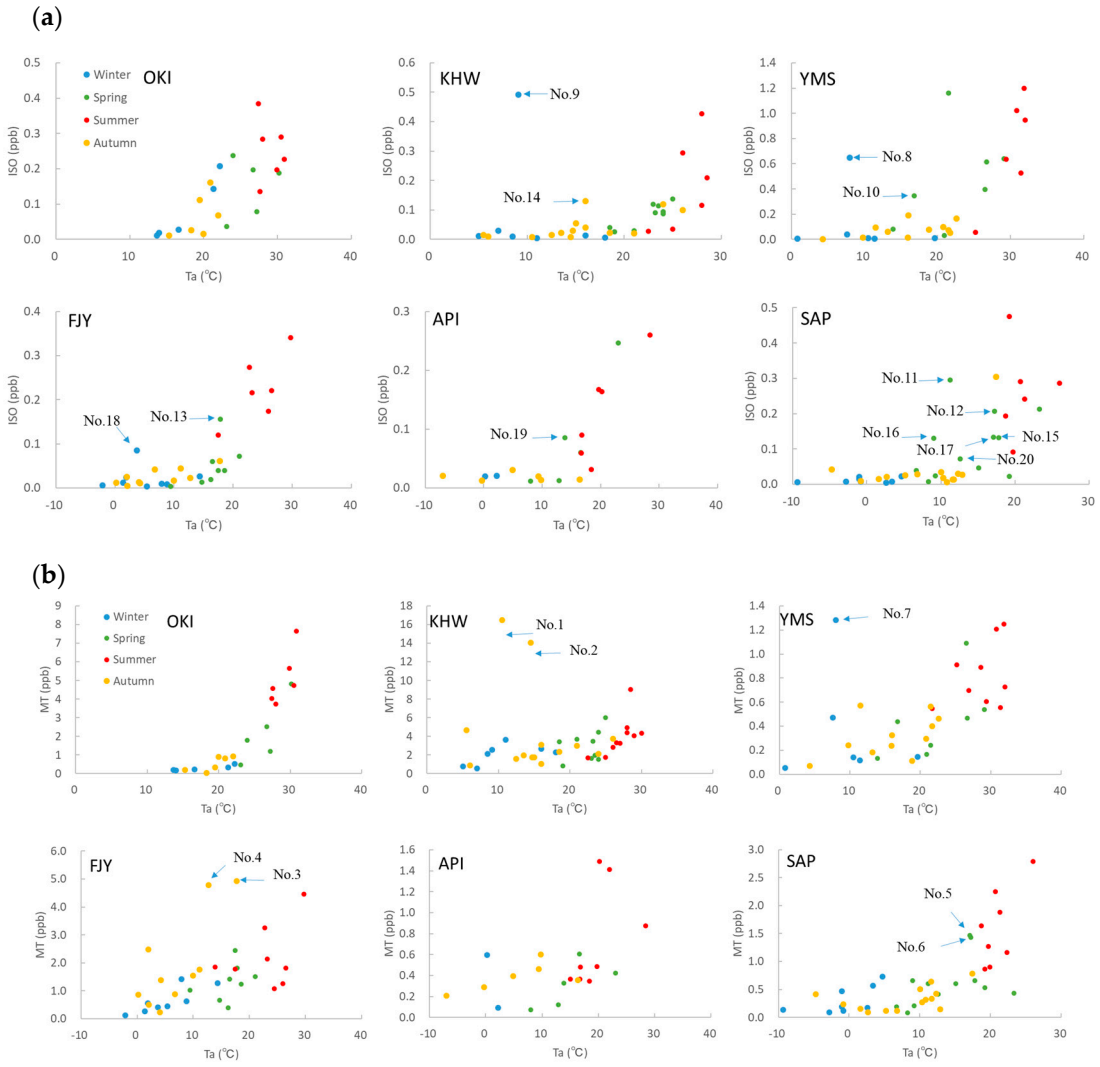
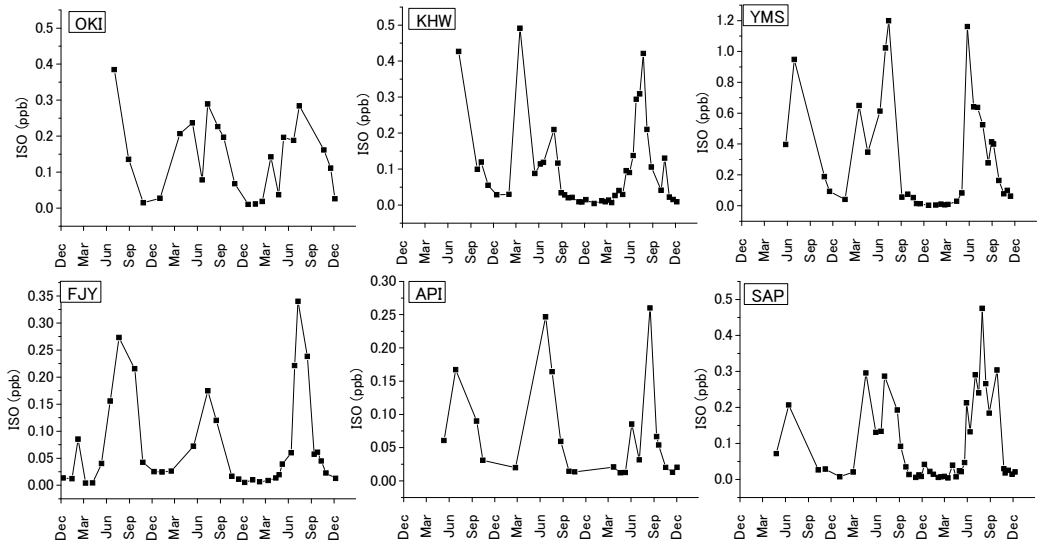


Figure 2. Relation between the air temperature (Ta) and (**a**) isoprene (ISO, above) and (**b**) monoterpene (MT, below) concentrations.

The seasonal variation in the isoprene and monoterpene concentrations of each site is shown in Figure 3. Remarkable seasonal variations in the isoprene concentration were observed in all the sites (Figure 3a). Since OKI is an evergreen forest in the subtropical zone, the low isoprene period was limited to the short period from December to February, while the other regions had longer periods from September to May. In OKI, the isoprene slowly increased from February to August and then gradually decreased. However, the isoprene of YMS, *Q. serrata* forest, rapidly increased in May in synchronization with the leaf expansion, and it then rapidly decreased in relation to the leaf fall. These characteristics of seasonality are the cause of the inter-site differences in the relations between air temperature and concentrations shown in Figure 3a.

(**a**)



(**b**)

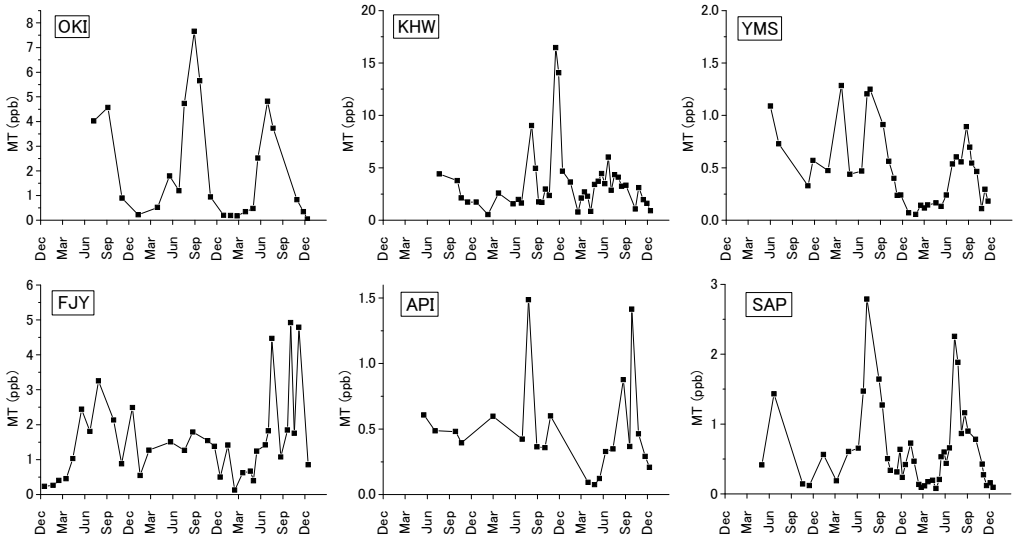


Figure 3. Seasonal variation in the (**a**) isoprene (ISO, above) or (**b**) monoterpene (MT, below) concentration.

The five-number summary and statistics of the isoprene and monoterpene concentrations of each site are shown in Figure 4 and Table 2. A comparison of the mean concentrations during the observation period using the Bonferroni post-hoc test showed that the isoprene and monoterpenes concentrations were significantly higher at YMS and KHW than at the non-OKI sites ($p < 0.05$). As has been reported, *Q. serrata* accounts for 33% of the woody biomass in YMS [23]. The maximum isoprene concentration was highest in YMS, which is due to the strong isoprene emitter *Q. serrata* trees. However, the median concentration of isoprene at OKI was higher than that at YMS. This concentration was strongly influenced by both vegetation and climatic zone.

The conifers of the cedar–cypress (*Cryptomeria japonica–Chamaecyparis obtusa*) trees in KHW and the red pine (*Pinus densiflora*) trees in FJY are not isoprene emitters, but a high isoprene concentration was observed in KHW and FJY in the summer. The understory vegetation of coniferous forests, such as ferns and oak seedlings, is known to emit isoprene in the summer in the daytime [15]. In general,

isoprene emission from the understory vegetation of coniferous forests has been neglected. However, our observed data suggest that observing the isoprene flux above the coniferous forests and on the leaf surface of understories in the summer is necessary to clarify the sources of the isoprene.

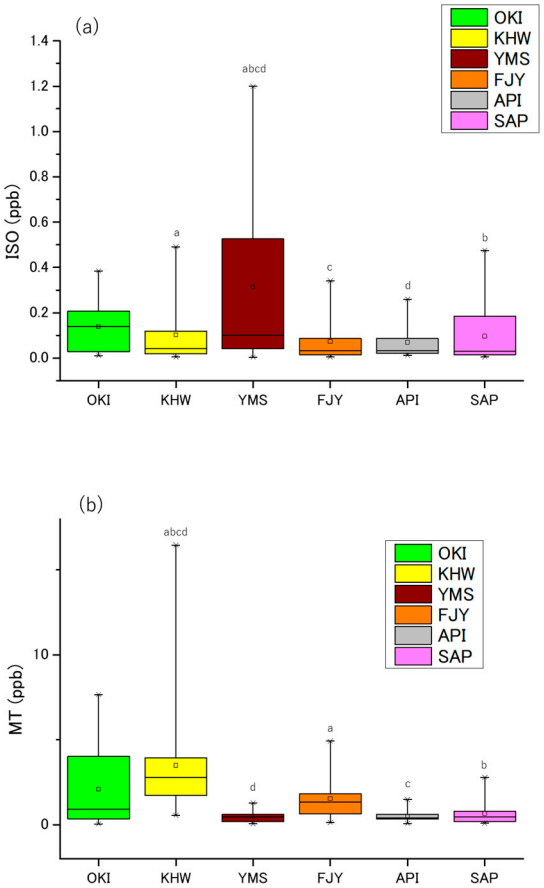


Figure 4. Box plot of the (**a**) isoprene (ISO, left) and (**b**) monoterpene (MT, right) concentrations. The blank small squares, symbols, whiskers, and boxes indicate the mean, outlier, minimum, maximum, and 25, 50, and 75 percentiles, respectively. The means, identified by letters, significantly differ ($p < 0.05$) based on the Bonferroni post-hoc tests.

Table 2. Statistics of the concentration of the isoprene (ISO, upper) (**a**) or monoterpene (MT, lower) (**b**) at the six measurement sites (unit: ppb).

(a)	**OKI**	**KHW**	**YMS**	**FJY**	**API**	**SAP**
Maximum	0.38	0.49	1.2	0.34	0.26	0.48
Mean	0.14	0.1	0.31	0.07	0.07	0.1
SD	0.11	0.13	0.36	0.09	0.08	0.12
Median	0.14	0.04	0.1	0.03	0.03	0.03
n	22	40	33	34	21	42
(b)	**OKI**	**KHW**	**YMS**	**FJY**	**API**	**SAP**
Maximum	7.66	16.46	1.28	4.92	1.49	2.79
Mean	2.08	3.5	0.49	1.55	0.49	0.64
SD	2.25	3.19	0.36	1.24	0.37	0.62
Median	0.92	2.77	0.46	1.33	0.4	0.45
n	22	40	33	34	21	42

3.2. Monoterpene Concentration

The relations between the air temperature (Ta) and total monoterpene concentration are shown in Figure 2b. Using the most common monoterpene emission algorism [24], it was simulated that the monoterpene concentrations exponentially increase with the temperature. The closest relation to these ideal emission characteristics was observed in OKI (Figure 2b). The seasonal variation in the total monoterpene concentration is shown in Figure 3b. The season wherein the peak concentration was observed in OKI correlated with the peak temperature. Due to this characteristic, the variance of the temperature–monoterpene relation was small in OKI. Site OKI is in a subtropical zone, and monoterpenes hardly accumulated in the leaves for freeze resistance. In other words, the leaves at this site might have a relatively constant low pool of monoterpenes during the year.

The maximum monoterpene concentration was the highest in the cedar–cypress forest in KHW (Figure 4b, Table 2b), followed by OKI and FJY. The mean concentration of monoterpenes at KHW during the monitoring period was significantly higher ($p < 0.05$) than that at the other sites except for OKI. Fifty-year-old *C. japonica* is believed to be a strong emitter of monoterpenes in KHW. Ryukyu pine (*Pinus luchuensis*) in OKI and red pine (*P. densiflora*) in FJY were also thought to be strong monoterpene emitters. Site KHW had extremely high maximum monoterpene concentrations compared to the other sites, and they were not observed in the summer. Since about 20% of Japan is covered by cedar–cypress forests, their remarkably high rate of monoterpene emissions is noteworthy. Understanding the factors and frequency of such high emissions is thought to be important for estimating the mean annual monoterpene emissions of the cedar–cypress forest in Japan.

3.3. Temporal Increases in BVOC Concentrations

Thirteen and seven temporal increases in the isoprene and monoterpenes concentrations, respectively, were observed during the 3 years of periodic observations at the six sites (Tables 3 and A1). We defined a temporal increase as an event wherein high concentrations (in the top 25th percentile of each site data) under low air temperature conditions (below 20 °C) are observed in the non-summer months.

Temporal increases in isoprene and monoterpene concentrations were not observed at OKI. Observations in other subtropical forests will be needed in the future to confirm whether isoprene and monoterpene are a common feature of subtropical forests. Event Nos. 1 and 2 were observed at consecutive 12-day intervals for monoterpenes at KHW. These events, which occurred in cedar–cypress forests, showed remarkably high concentrations of monoterpenes. They are noteworthy because ignoring them could result in a considerable underestimation of the mean annual concentrations. Sixty-nine percent of the temporal increase in isoprene concentrations occurred independently from the increase in monoterpene concentrations. More than 69% and 57% of the temporal increase events occurred in autumn and spring for isoprene and monoterpene concentrations, respectively, suggesting that the mechanisms responsible for the increases in concentration might not be common.

To evaluate the relationship between meteorological conditions and increases in BVOC concentrations, data from automated weather monitoring stations near the sites were referenced (Table 3). Under the conditions of a large daily air temperature range of more than 10 °C, about 62% and 71% of the temporal increase events occurred for isoprene and monoterpene concentrations, respectively. Observations were typically made on sunny or cloudy days with low wind, but it had rained the week before the observation date. The total precipitation of 15 mm or more within a week before the event was 77% and 57% for isoprene and monoterpenes, respectively. Especially in autumn, typhoons are a major disturbing factor in Japanese forests. In late October, before the No. 4 event, two typhoons (25W and 27W, code of Joint Typhoon Warning Center: JTWC) brought strong wind and heavy rain. On October 29, 2017, at Kawaguchiko station, 108 mm of precipitation was observed. The typhoon (28W, JTWC) also brought a total of 176.5 mm of rainfall in the 3 days before the No. 3 event.

Table 3. Climatological conditions of the temporal biogenic volatile organic compound (BVOC) increase events in non-summer months.

No.	Date	Site	BVOC	ppb	Station	P	P_week	WS_max	WS_max_week	Ta_max	Ta_min	Ta_delta	L
1	2017/11/16	KHW	MT	16.46	Kahoku	0.0	6.5	4.5	5.7	13.4	1.8	11.6	9.3
2	2017/11/28	KHW	MT	14.06	Kahoku	0.0	8.0	1.6	6.8	20.1	2.4	17.7	7.0
3	2018/10/3	FJY	MT	4.92	Kawaguchiko	0.0	273.5	4.7	17.6	21.6	9.7	11.9	6.1
4	2018/11/6	FJY	MT	4.79	Kawaguchiko	6.0	0.0	2.8	6.0	14.6	11.9	2.7	0.0
5	2017/6/27	SAP	MT	1.47	Sapporo	0.0	89.0	7.2	12.2	22.2	11.6	10.6	4.2
6	2016/6/21	SAP	MT	1.43	Sapporo	0.0	93.5	7.4	12.1	25.4	16.5	8.9	9.9
7	2017/3/23	YMS	MT	1.28	Kyotanabe	0.0	32.0	2.9	6.5	14.1	2.1	12.0	2.8
8	2017/3/23	YMS	ISO	0.65	Kyotanabe	0.0	32.0	2.9	6.5	14.1	2.1	12.0	2.8
9	2017/3/24	KHW	ISO	0.49	Kahoku	0.0	38.5	3.3	6.2	13.3	0.3	13.0	1.5
10	2017/4/27	YMS	ISO	0.35	Kyotanabe	1.0	14.5	4.7	6.0	19.1	7.5	11.6	7.9
11	2017/4/27	SAP	ISO	0.3	Sapporo	0.5	18.5	7.1	10.3	13.9	5.4	8.5	4.5
12	2016/6/21	SAP	ISO	0.21	Sapporo	0.0	93.5	7.4	12.1	25.4	16.5	8.9	9.9
13	2016/6/23	FJY	ISO	0.16	Kawaguchiko	7.0	12.5	3.8	5.3	26.9	17.6	9.3	4.5
14	2018/10/26	KHW	ISO	0.13	Kahoku	24.0	5.5	1.6	4.7	20.7	6.6	14.1	0.8
15	2018/6/19	SAP	ISO	0.13	Sapporo	0.0	55.5	6.7	10.7	24.4	15.2	9.2	13.8
16	2017/6/6	SAP	ISO	0.13	Sapporo	0.0	42.0	12.2	12.2	23.8	7.6	16.2	13.5
17	2017/6/27	SAP	ISO	0.13	Sapporo	0.0	89.0	7.2	12.2	22.2	11.6	10.6	4.2
18	2016/2/15	FJY	ISO	0.09	Kawaguchiko	0.0	40.0	7.3	9.0	10.9	−4.2	15.1	1.2
19	2018/6/11	API	ISO	0.09	Okunakayama	13.0	17.0	3.2	3.9	16.9	11.4	5.5	0.0
20	2016/5/2	SAP	ISO	0.07	Sapporo	0.0	22.5	9.1	12.3	17.0	1.7	15.3	10.0

Date: date of events; Site: name of observed tower site; BVOC: increased compound (MT: monoterpene, ISO: isoprene); ppb: concentration of BVOCs (ppb); Station: the nearest weather monitoring station for each site [25]; P: daily precipitation (mm); P_week: weekly total precipitation before the event (mm); WS_max: daily maximum wind speed (m s^{-1}, 10 min average); WS_max_week: weekly maximum wind speed before the event (m s^{-1}, 10 min average); Ta_max: maximum daily air temperature (°C); Ta_min: minimum daily air temperature (°C); Ta_range: daily temperature range (°C); and L: daylight hours (h).

In particular, note that Mochizuki et al. indicated a strong correlation between the soil water content (SWC) and monoterpene flux [15]. They reported that the annual monoterpene emissions are underestimated by about 50% if the increased effect after precipitation is not considered. In the No. 4 event, high monoterpene concentrations were observed even 8 days after the typhoon rain, suggesting that strong monoterpene emissions after a storm could continue for more than a week and that the pool size of the monoterpene source might be large for continuous emission. After storms, many fresh needle leaves were blown by the wind onto the wet soil surface. Fresh fallen leaves with damaged resin pools could be strong monoterpene emitters, and the emission rate should be evaluated in future studies. Moreover, increases in the SWC after a rain might be related to increases in soil BVOC emissions. As has been reported, BVOCs are emitted from tree roots [26] and high concentrations of BVOCs are accumulated in the soil, especially in the lower part of the slopes [27]. BVOCs in the micropores of the soil might be pushed out by the water and emitted after the rain. The relation between precipitation and soil BVOC emission rates needs to be evaluated further.

Most of the temporal increases in non-summer were observed after rainfall, when the daily temperature range was large. This suggests that a rapid diurnal temperature rise could be a factor in the sporadic increase in BVOC concentrations in the non-summer months. A variety of previous studies on the seasonal variation of BVOCs have reported observational examples of increased isoprene emissions in spring [28] and fall [29], and monoterpene emissions in spring [30] after rainfall [31] and wind events [14]. Temporally high monoterpene concentrations in winter were also reported, which have been explained by the much longer atmospheric lifetime of monoterpenes in winter [4]. Moreover, it has been reported that the seasonal change in leaf isoprene emission capacity has a particularly high temperature dependency and that some cases of drought stress reduce the emission rate [13,32–34]. The detailed internal mechanisms are unknown, but the high isoprene concentration events in spring might be linked to warm conditions without drought stress or rapid oxidation in the atmosphere.

Furthermore, high-concentration events in the non-summer months also occurred without storms or heavy rains. Another possible reason for the increase in monoterpenes in non-summer months is the temporary high emissions caused by insect attacks on tree trunks. Between 2014 and 2017, severe mass attacks by ambrosia beetles, *Platypus quercivorus*, occurred in YMS [35]. The beetles made many holes in the trunks of the broad-leaved trees and *P. densiflora*. Beetle attacks on the conifers might be the reason for the increase in monoterpenes of the No. 7 event in 2017.

Our one-time sampling for only 30 min is a useful technique for network monitoring, but a problem of spatial representativeness exists. Ideally, the technique should be improved to multiple-time sampling with lower labor intensity for flux researchers. In general, the concentrations of BVOCs (isoprene and monoterpenes) outside of forests are very low and close to zero; thus, BVOCs are thought to be emitted into the atmosphere from the forests when the concentrations are high. However, the emitted BVOC amounts cannot be directly estimated from their concentrations, which may also change with storage changes, advection, oxidization, and deposition. A more continuous mulch-site BVOC monitoring, using eddy covariance methods, micrometeorological observation tower networks, and high-speed analyzers, would be better for accurate annual emission estimates.

The isoprene and monoterpene concentrations reported in this study are within the range previously reported [36]. The repeated air samplings performed in this study suggest that there are temporally strong BVOC emissions in non-summer and complicated seasonal emission characteristics with site dependency that are difficult to assess through temporary observations at one site. Since the BVOC was estimated to produce more ozone than AVOC in Japan [37], the enhancement of the wide-area evaluation of the BVOC emissions using the flux network can be the key for improving the simulation accuracy of the ozone formation.

4. Conclusions

The network monitoring of BVOCs, in collaboration with flux tower networks, detected a temporal increase in BVOC concentrations in the non-summer months. Twenty temporal increase events of isoprene or monoterpene concentrations were observed in six Japanese forests in 3 years. The present study revealed the climatic conditions in which high BVOC concentration events occurred in Japanese forests in non-summer months. The temporal increase events occurred mainly after rainfall with a large daily air temperature range in spring for isoprene and in autumn for monoterpene. This suggests that wind, rain, and a rapid diurnal temperature increase could be factors causing the sporadic rises in BVOC concentrations in the non-summer months. In particular, the monoterpene concentrations in cedar–cypress forests can occasionally be remarkably high; therefore, the effect on ozone concentrations should be noted. BVOCs are an important ozone precursor. Continuous wide-area monitoring and careful evaluation of the BVOC distributions in various forests are required.

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Appendix A. Information of the Network Monitoring

Table A1. Observed data at the six tower sites.

OKI	Ta	MT	ISO	KHW	Ta	MT	ISO	YMS	Ta	MT	ISO	FJY	Ta	MT	ISO	API	Ta	MT	ISO	SAP	Ta	MT	ISO
2016/7/9	27.4	4.02	0.38	2016/7/21	28.0	4.42	0.43	2016/6/2	26.5	1.09	0.40	2015/12/17	4.1	0.23	0.01	2016/5/18	16.6	0.61	0.06	2016/5/2	12.6	0.42	0.07
2016/9/5	27.6	4.57	0.14	2016/10/4	26.0	3.77	0.10	2016/7/6	32.0	0.73	0.95	2016/1/22	1.4	0.26	0.01	2016/7/4	19.7	0.49	0.17	2016/6/21	17.2	1.43	0.21
2016/11/3	20.0	0.90	0.02	2016/10/20	24.0	2.12	0.12	2016/11/4	16.0	0.33	0.19	2016/2/15	3.7	0.40	0.09	2016/9/26	16.8	0.48	0.09	2016/10/18	12.9	0.14	0.03
2017/1/9	16.6	0.22	0.03	2016/11/16	15.0	1.73	0.05	2016/11/25	11.5	0.57	0.09	2016/3/16	5.4	0.45	0.00	2016/10/21	4.9	0.40	0.03	2016/11/15	6.8	0.12	0.03
2017/3/30	22.2	0.52	0.21	2016/12/21	14.7	1.73	0.03	2017/1/26	7.6	0.47	0.04	2016/4/13	9.4	1.03	0.00	2017/3/1	0.2	0.60	0.02	2017/1/12	3.4	0.56	0.01
2017/5/19	24.0	1.79	0.24	2017/2/8	7.0	0.54	0.03	2017/3/23	8.0	1.28	0.65	2016/5/19	17.5	2.44	0.04	2017/6/30	23.0	0.42	0.25	2017/3/7	−1.0	0.19	0.02
2017/6/27	27.2	1.20	0.08	2017/3/24	9.1	2.58	0.49	2017/4/27	16.8	0.44	0.35	2016/6/23	17.8	1.81	0.16	2017/7/26	20.2	1.49	0.16	2017/4/27	11.2	0.61	0.30
2017/7/19	30.5	4.73	0.29	2017/5/23	24.0	1.55	0.09	2017/6/15	26.7	0.47	0.61	2016/7/28	22.7	3.25	0.27	2017/8/30	16.7	0.36	0.06	2017/6/6	9.0	0.65	0.13
2017/8/29	30.9	7.66	0.23	2017/6/14	23.5	1.97	0.11	2017/7/7	30.8	1.21	1.02	2016/9/29	23.2	2.13	0.22	2017/10/2	16.4	0.36	0.01	2017/6/27	17.1	1.47	0.13
2017/9/21	29.9	5.65	0.20	2017/6/27	23.0	1.63	0.12	2017/7/20	31.9	1.25	1.20	2016/11/1	6.7	0.88	0.04	2017/10/25	9.8	0.60	0.01	2017/7/11	26.0	2.79	0.29
2017/11/5	22.0	0.94	0.07	2017/8/8	28.5	9.02	0.21	2017/9/11	25.2	0.91	0.06	2016/12/16	2.0	2.49	0.03	2018/3/30	2.2	0.09	0.02	2017/8/31	18.7	1.64	0.19
2017/12/29	15.3	0.20	0.01	2017/8/24	28.0	4.95	0.12	2017/10/5	21.5	0.56	0.07	2017/1/17	1.9	0.55	0.02	2018/4/26	8.0	0.07	0.01	2017/9/13	19.7	1.27	0.09
2018/1/27	13.7	0.19	0.01	2017/9/6	25.0	1.74	0.03	2017/10/27	21.7	0.40	0.05	2017/2/23	14.3	1.27	0.03	2018/5/16	12.9	0.12	0.01	2017/10/5	10.1	0.50	0.03
2018/2/23	14.0	0.17	0.02	2017/9/20	22.5	1.69	0.03	2017/11/9	15.9	0.24	0.01	2017/5/23	21.0	1.51	0.07	2018/6/11	13.9	0.33	0.09	2017/10/17	11.7	0.34	0.01
2018/3/30	21.3	0.34	0.14	2017/10/4	21.0	2.97	0.02	2017/11/24	9.8	0.24	0.01	2017/7/20	26.0	1.26	0.17	2018/7/11	18.4	0.35	0.03	2017/11/13	10.8	0.31	0.01
2018/4/30	23.1	0.47	0.04	2017/10/20	18.5	2.36	0.02	2017/12/27	4.3	0.07	0.00	2017/8/23	17.5	1.79	0.12	2018/8/23	28.4	0.88	0.26	2017/11/26	11.6	0.64	0.01
2018/5/20	26.7	2.52	0.20	2017/11/16	10.5	16.46	0.01	2018/1/25	0.8	0.05	0.00	2017/10/24	10.0	1.54	0.02	2018/9/19	15.0	0.37	0.07	2017/12/5	−0.8	0.24	0.01
2018/6/29	30.2	4.82	0.19	2017/11/28	14.5	14.06	0.01	2018/2/15	10.5	0.14	0.01	2017/11/21	4.2	1.38	0.01	2018/9/27	22.0	1.41	0.05	2017/12/18	−4.7	0.42	0.04
2018/7/22	28.0	3.73	0.28	2017/12/14	5.5	4.68	0.01	2018/3/2	11.4	0.12	0.01	2017/12/15	2.1	0.50	0.01	2018/10/25	9.4	0.46	0.02	2018/1/9	4.7	0.73	0.02
2018/10/29	20.9	0.83	0.16	2018/1/16	11.0	3.64	0.00	2018/3/15	19.6	0.14	0.01	2018/1/16	7.9	1.41	0.01	2018/11/22	−0.3	0.29	0.01	2018/1/23	−1.0	0.47	0.01
2018/11/25	19.5	0.35	0.11	2018/2/16	5.0	0.77	0.01	2018/4/19	20.9	0.16	0.03	2018/2/13	−2.1	0.13	0.01	2018/12/10	−7.0	0.21	0.02	2018/2/12	−9.4	0.14	0.01
2018/12/12	18.3	0.05	0.03	2018/3/2	8.5	2.11	0.01	2018/5/10	13.9	0.13	0.08	2018/3/19	8.8	0.62	0.01					2018/2/22	−2.8	0.09	0.01
				2018/3/15	16.0	2.69	0.01	2018/6/1	21.5	0.24	1.16	2018/4/19	14.7	0.67	0.01					2018/3/8	−0.8	0.11	0.01
				2018/3/28	18.0	2.28	0.01	2018/6/26	29.1	0.54	0.64	2018/5/2	16.2	0.40	0.02					2018/3/22	2.6	0.17	0.00
				2018/4/10	19.0	0.84	0.03	2018/7/12	29.4	0.60	0.64	2018/5/15	18.5	1.24	0.04					2018/4/10	6.7	0.19	0.04
				2018/4/26	18.5	3.40	0.04	2018/8/1	31.4	0.56	0.52	2018/6/20	16.5	1.42	0.06					2018/4/24	8.3	0.08	0.01

Table A1. *Cont.*

OKI	Ta	MT	ISO	KHW	Ta	MT	ISO	YMS	Ta	MT	ISO	FJY	Ta	MT	ISO	API	Ta	MT	ISO	SAP	Ta	MT	ISO
				2018/5/11	21.0	3.71	0.03	2018/8/23	28.6	0.89	0.28	2018/7/3	26.5	1.82	0.22					2018/5/8	9.2	0.21	0.02
				2018/5/25	24.0	4.44	0.10	2018/9/6	26.9	0.70	0.41	2018/7/17	29.7	4.47	0.34					2018/5/15	19.2	0.53	0.02
				2018/6/7	23.2	3.49	0.09	2018/9/14	21.7	0.54	0.40	2018/8/23	24.4	1.08	0.24					2018/5/28	15.1	0.60	0.05
				2018/6/22	25.0	6.02	0.14	2018/10/5	22.6	0.46	0.16	2018/9/20	13.9	1.84	0.06					2018/6/5	23.3	0.44	0.21
				2018/7/4	26.0	2.85	0.29	2018/10/25	18.8	0.11	0.08	2018/10/3	17.7	4.92	0.06					2018/6/19	17.8	0.66	0.13
				2018/7/18	30.0	4.34	0.31	2018/11/8	20.8	0.29	0.10	2018/10/18	11.1	1.75	0.04					2018/7/10	20.7	2.25	0.29
				2018/8/2	29.0	4.10	0.42	2018/11/21	13.2	0.18	0.06	2018/11/6	12.7	4.79	0.02					2018/7/24	21.3	1.88	0.24
				2018/8/16	27.0	3.24	0.21					2018/12/15	0.2	0.85	0.01					2018/8/7	19.2	0.86	0.48
				2018/9/3	26.5	3.33	0.11													2018/8/21	22.3	1.16	0.27
				2018/10/12	16.0	1.07	0.04													2018/9/4	19.9	0.90	0.18
				2018/10/26	16.0	3.09	0.13													2018/10/5	17.4	0.78	0.30
				2018/11/14	13.5	1.96	0.02													2018/11/2	12.3	0.43	0.03
				2018/11/29	12.5	1.60	0.02													2018/11/7	10.3	0.27	0.02
				2018/12/14	6.0	0.90	0.01													2018/11/20	5.2	0.12	0.03
																				2018/12/5	1.6	0.16	0.01
																				2018/12/17	2.7	0.09	0.02

Date (year/month/day); air temperature (Ta, °C); monoterpene concentration (MT, ppb); and isoprene concentration (ISO, ppb).

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