Review: Exchanges of volatile organic compounds between terrestrial ecosystems and the atmosphere

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Abstract

Many VOCs are reactive in the atmosphere, may produce secondary organic aerosol (SOA), and keep photochemical ozone concentrations high by VOC-involved reactions. Accumulated studies have shown the importance of terrestrial ecosystems which can be sinks and sources of VOCs. The research progress in the exchange of volatile organic compounds (VOCs) between terrestrial ecosystems and the atmosphere was reviewed in this paper. Representative VOCs emitted from terrestrial ecosystems are low-molecular-weight oxygenated VOCs including methanol, acetone, formic and acetic acids, and terpenoids, including isoprene and monoterpenes. Terpenoid emissions have been intensively investigated from the leaf to the canopy level using advanced analytical systems, including proton-transfer-reaction mass spectrometry. Environmental factors, including temperature, light intensity, carbon dioxide and ozone concentrations, and water stress have been reported to affect terpenoid emissions from plants. The combined effects of these environments influence terpenoid emission additively or interactively, and are important in terms of VOC emission estimates against ongoing climate change. Isoprene is most abundantly released into the atmosphere among VOCs; the potential reasons why some plants release such large amounts of carbon as isoprene were summarized in this study. Among oxygenated VOCs, some compounds, including isoprene oxygenates methacrolein and methyl vinyl ketone, are bidirectionally exchanged, and both atmospheric chemical reactions and reactions under oxidative stress in leaves have been regarded as involved in bidirectional VOC exchanges. Bottom-up process-based models and top-down inverse models have been developed to estimate global and local terpenoid emissions. To validate the accuracy and precision of the models, the collection of additional in-situ ground truth data, such as long-term flux measurement data, at various sites is required. Otherwise, these models may still leave large uncertainties compared with CO₂ flux models that can be validated with a large number of ground truth flux data.

Key words: Bidirectional exchange, Canopy flux, Isoprene, Monoterpene, Process-based models, Volatile organic compounds

1. Introduction

In addition to greenhouse gases, many kinds of trace gas species are exchanged between terrestrial ecosystems and the atmosphere (Fig. 1). Some of them are emitted from biogenic sources, and others are anthropogenically produced. Several species are exchanged bilaterally.

Some of them are highly reactive in the atmosphere and have a short lifetime. These gases can produce other gas species via chemical reactions, and in some cases, the reactions are important in terms of atmospheric chemistry. More than 100 volatile organic compound (VOC) species are detectable in the atmosphere, even in forest air. Most of them are at sub-ppb (v/v) level. VOCs are considered to be involved in producing photochemical ozone and secondary organic aerosols (SOAs).

VOC and NO_x emissions are believed to form photochemical

ozone and degrade air quality in urban and sub-urban areas. NO in the atmosphere is produced from NO₂ during daytime by sunlight (wavelength < 398 nm). This NO is easily oxidized by O₃ and peroxides to produce NO₂. This is the reason why the NO concentration is very low compared with that of NO₂. Peroxides are produced through a series of chemical reactions between VOCs and OH radicals. If the VOC concentration is high, NO reacts more frequently with the peroxides than with O₃. This results in maintaining the ozone concentration at a higher level. In urban areas, the reduction of NO_x and VOC emissions is essential to decrease the O₃ concentration.

SOA is also produced from VOCs and affects human health and the climate. SOAs absorb and scatter shortwave radiation and affect cloud properties, as they serve as cloud condensation nuclei (CCN) or ice nuclei by providing their surface for water vapor condensation to form liquid droplets and ice particles (Shrivastava *et al.*, 2017). VOCs are degraded in the atmosphere by a number of reactions with OH, ozone, NO₃, and HO₂ (Carlton *et al.*, 2009). These oxidized products undergo gas-particle conversion processes such as nucleation, condensation, and heterogeneous and multiphase chemical reactions. The formation and growth of SOA depend on the original oxidized products. By mass balance calculation, Goldstein and Galbally (2007) estimated that 510–910 TgC yr⁻¹

Received; April 21, 2020

Accepted; August 15, 2020

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DOI: 10.2480/agrmet.D-20-00025

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Fig. 1. Trace gas species exchanged between terrestrial ecosystem and atmosphere

of SOA was formed from globally emitted VOCs with an annual emission of 1300 TgC yr^{-1} . As annual emission of terpenoids including isoprene and monoterpenes is estimated to be at least more than half of annual VOC emission (Arneth *et al.*, 2008), terrestrial ecosystems may be strongly involved in the formation of photochemical ozone and SOA.

Hereinafter, we describe the characteristics of VOC, especially terpenoids, the effects of environmental factors on the exchange of these gases, and the perspective of their behavior affected by ongoing climate change.

2. Trace gas species and atmospheric impacts

2.1 Isoprene

2.1.1 General

Isoprene is an important secondary metabolite of plants and has a molecular formula of C_5H_8 . It is volatile (b.p. = 34°C) and released into the atmosphere immediately after being produced. Isoprene is produced from dimethylallyl diphosphate (DMAPP) by isoprene synthase in chloroplasts. DMAPP is produced via the mevalonate pathway in cytosol and the methylerythritol 4-phosphate (MEP) pathway in chloroplasts.

As isoprene is very reactive with OH radicals, lifetime of isoprene in the reaction with OH radicals at a typical concentration ($2.0 \times 10^6 \text{ molecules cm}^{-3}$) is 1.4 h (Atkinson and Arey, 2003). Isoprene is less reactive with ozone than with OH radicals, with a lifetime of 1.3 days at a typical ozone concentration ($7.0 \times 10^{11} \text{ molecules cm}^{-3}$). Because of its reactivities, isoprene is easily oxidized into methacrolein (MAC), methyl vinyl ketone (MVK), glycolaldehyde, and other compounds (Carlton *et al.*, 2009). Further reactions of these compounds can lead to the formation of SOA and ozone. Even

if the SOA yield from isoprene is $\sim 1\%$, the large global source strength of isoprene may significantly contribute to the formation of SOA (Carlton *et al.*, 2009). Details of SOA formation from isoprene have been described by Carlton *et al.* (2009).

Isoprene is emitted from many broadleaved trees and several coniferous trees (Table 1). Isoprene-emitting and non-emitting species can be found even within the same genus. There may be no consistent taxonomic relationships in the presence or absence of isoprene emission (Pacífico *et al.*, 2009), but Harley *et al.* (1999) suggested that the occurrence of isoprene emissions may be involved in evolutionary history. In the genus *Quercus*, trees in section *Cerris* are non-emitters, whereas others in sections *Rubrae*, *Quercus*, and *Protobalanus* are isoprene emitters (Harley *et al.*, 1999). In *Quercus* spp. occurring in East Asia, Tani and Kawawata (2008) revealed that *Q. serrata*, *Q. crispula*, *Q. dentata*, and *Q. aliena* in the *Quercus* section were all strong isoprene emitters, but some species in the *Cerris* section were non-emitters. The presence and absence of isoprene emission is unlikely to be categorized by functional type or climate range (Pacífico *et al.*, 2009). The annual global emission of isoprene is estimated to be 459–601 TgC by several models (Arneth *et al.*, 2008), which is higher than the annual emission estimates of anthropogenic VOCs (98–158 TgC y^{-1}) (Boucher *et al.*, 2013).

2.1.2 Cost and benefit of isoprene production

The ratio of carbon emitted in the form of isoprene to photosynthetically fixed carbon is 0.2%–5% depending on temperature and other environmental factors (e.g., Tani and Kawawata, 2008). Isoprene production requires 20 ATP and 14 NADPH per molecule (Sharkey and Yeh, 2001), and this significant cost is paid by isoprene-emitting species, but not by others. The physiological reason why some plants release such

Table 1. Plant classification based on terpenoid emissions.

category	storage or non-storage	plant type	representative species
isoprene emitter	non-storage	many deciduous trees and grass	<i>Quercus serrata</i> , <i>Quercus crispula</i> Blume, <i>Quercus robur</i> , <i>Pueraria montana</i> , <i>Liquidambar styraciflua</i> , <i>Elaeocarpus serratus</i> , <i>Phyllostachys pubescens</i>
monoterpene emitter	storage	most coniferous trees, limited number of deciduous trees, herbs	<i>Cryptomeria japonica</i> , <i>Chamaecyparis obtusa</i> , <i>Pinus densiflora</i> , <i>Abies firma</i> , <i>Picea jezoensis</i> , <i>Picea abies</i> , <i>Cinnamomum camphora</i> , <i>Eucalyptus globulus</i> , <i>Salvia rosmarinus</i>
	non-storage	limited number of deciduous trees	<i>Fagus sylvatica</i> , <i>Quercus ilex</i> , <i>Quercus phillyraeoides</i> , <i>Castanopsis cuspidata</i>
non-emitter		some deciduous and coniferous trees	<i>Fagus crenata</i> , <i>Quercus acutissima</i> , <i>Quercus variabilis</i> , <i>Castanea crenata</i> , <i>Cornus florida</i> , <i>Zelkova serrata</i> , <i>Liriodendron tulipifera</i> , <i>Ilex rotunda</i> , <i>Nerium indicum</i>

Some plant species emit both isoprene and monoterpenes, but based on dominant terpenoid species, they are categorized into either isoprene or monoterpene emitter.

large amounts of carbon as isoprene is not fully understood and many studies have been conducted. Thermal tolerance seems to be a plausible reason (Sharkey *et al.*, 2007) as isoprene emission increases up to ~40 °C. Many studies have been undertaken to prove the thermotolerance hypothesis.

Singsaas *et al.* (1997) showed that when air containing several ppm isoprene was passed around leaf discs of an isoprene-emitting plant kudzu (*Pueraria lobata*), the temperature limit of thermal tolerance evaluated by chlorophyll fluorescence increased by as much as 4 °C in the least intense light and by as much as 10 °C in the more intense light. This suggests that exogenous and endogenous isoprene may help photosynthetic resistance against high temperatures. Sharkey *et al.* (2001) used fosmidomycin, which can inhibit isoprene emission without affecting photosynthesis for several hours. The decreased photosynthetic rate of *P. lobata* caused by a temperature treatment at 46 °C for 2 min, recovered less in fosmidomycin-fed leaves than in leaves fed water or fosmidomycin-fed leaves in isoprene-containing air. The non-isoprene-emitting plant *Phaseolus vulgaris* exhibited increased photosynthetic recovery under a high temperature treatment when air containing 2–22 ppm isoprene was supplied. These results indirectly suggest that isoprene can mitigate heat stress. Additionally, they show that other short-chain alkenes can also improve thermotolerance, while alkanes reduce thermotolerance.

A genetic approach seems to provide evidence that is more direct. Behnke *et al.* (2007) produced transgenic grey poplar (*Populus × canescens*) plants in which the gene expression of isoprene synthase (ISPS) was silenced by RNA interference (RNAi). The authors showed that lack of capacity for isoprene emission decreased the net photosynthetic rate and photosynthetic electron transport of poplars by heat stress. Velikova *et al.* (2014) suggested that a rearrangement of the chloroplast protein profile occurs in non-isoprene-emitting poplars, probably to minimize the negative stress effects caused by the absence of isoprene. As isoprene synthase was found to bind to the thylakoid membrane (Wildermuth and Fall, 1996), the results of Velikova *et al.* (2014) may support the idea that isoprene improves or stabilizes the thylakoid membrane structure under heat stress.

Other indirect approaches have been made from an ecosystem perspective. Taylor *et al.* (2018) estimated the proportional abundance of isoprene-emitting trees at 103 lowland tropical sites and revealed that the proportional abundance increased with the mean annual temperature of the sites. Taylor *et al.* (2019) compared the photosynthetic temperature responses of 26 co-occurring tropical trees and liana species to test whether isoprene-emitting species are more tolerant of high temperatures. They revealed that the maximum temperatures for net photosynthesis were ~1.8 °C higher in isoprene-emitting species than in non-emitters.

The theory of isoprene defense against thermal stress has been expanded to other oxidative stresses (Sharkey and Yeh, 2001; Vickers *et al.*, 2009a), as isoprene may act as an antioxidant in leaves owing to its high reactivity. Loreto and Velikova (2001) showed that fosmidomycin-fed leaves of isoprene-emitting plants were less tolerant to ozone. They estimated that isoprene quenched reactive oxygen species (ROS), including H₂O₂ and singlet delta oxygen (Zeinali *et al.*, 2016) formed in leaves, and reduced the lipid peroxidation of cellular membranes caused by ozone. Vickers *et al.* (2009b) used transgenic tobacco plants capable of emitting isoprene and found that the isoprene-emitting plants were more resistant to ozone-induced oxidative damage than non-emitting controls. They also found that the content of reduced ascorbate in leaves, which functioned as an antioxidant, was higher in transgenic isoprene-emitting plants than in non-emitting plants, implying that the former contained antioxidant compounds in higher abundance. Isoprene directly reacts with ozone in leaves, producing hydroperoxides that are toxic to plants (Hewitt *et al.*, 1990). However, the isoprene reaction with ozone is not fast (Atkinson and Arey, 2003), meaning that it may not work effectively even though the isoprene concentration inside the leaves is high (~several tens ppm). Isoprene may scavenge ROS generated in plants under other abiotic stresses, including intense light, water deficit, mechanical damage, salinity in soil, and other air pollutants (Vickers *et al.*, 2009a). So far, it has become evident that isoprene acts as a ROS scavenging system in leaves.

2.2 Monoterpene and other terpenoids

Monoterpene is the general name of a group of secondary metabolites produced by plants. The molecular formula of monoterpenes is $C_{10}H_{16}$. Monoterpenes are reactive in the atmosphere and emitted substantially. Monoterpenes are produced from geranyl diphosphate (GPP) by monoterpene synthase in plastids. Monoterpene alcohols $C_{10}H_{18}O$ and ketones $C_{10}H_{16}O$ are also included in the monoterpene family. They are volatile, but their boiling points are $> 150^\circ\text{C}$, suggesting that they are produced in the liquid phase. Most monoterpene-emitting plants have specific storage organs and tissues, including oil glands and trichomes on leaf surfaces and resin ducts inside leaves, stems, or roots. Most coniferous trees have resin ducts and are classified as storage-type monoterpene emitters. Some broad-leaved trees, including those in the *Eucalyptus* genus and the *Lauraceae* family (Table 1), are categorized into the storage-type monoterpene emitters. Plants that have no storage organs are exceptions. They emit monoterpenes immediately after producing them. Some *Quercus* species, including *Q. ilex* (Staudt and Seufert, 1995) and *Q. phillyraeoides* (Okumura *et al.*, 2008) are of the non-storage type.

Some of the monoterpene compounds are very reactive with OH radicals and ozone (Atkinson and Arey, 2003) in the atmosphere, causing the formation of SOA and ozone. The lifetimes of monoterpenes α -pinene, β -pinene, and d-limonene with OH radicals at a typical concentration (2.0×10^6 molecules cm^{-3}) are 2.6 h, 1.8 h, and 49 min, respectively, (Atkinson and Arey, 2003). Their lifetimes in the reaction with ozone at a typical ozone concentration (7.0×10^{11} molecules cm^{-3}) are 4.6 h, 1.1 days, and 2.0 h, respectively. The annual global emission of monoterpenes is estimated by several models to be 32–127 TgC (Arneth *et al.*, 2008).

The molecular formula of sesquiterpenes is $C_{15}H_{24}$. Because of their low volatility, their emission rate is generally low. However, they are produced and emitted after being fed to insects (Holopainen and Gershenzon, 2010). Sesquiterpene ketones and aldehydes are also often detected in plant emissions. Diterpenes are rarely detected in the atmosphere and is emitted by a very limited number of tree species. A large amount of kaur-16-ene was reported to be produced and emitted by *Cryptomeria japonica* (Matsunaga *et al.*, 2012). Many of sesquiterpenes and diterpenes are reactive and low volatile, therefore easily converted to SOA in the atmosphere.

2.3 Other biogenic gases

Methanol and acetone are among the most abundant VOCs in the atmosphere (Jacob *et al.*, 2002; 2005). Atmospheric methanol is oxidized by OH radicals to produce formaldehyde (Riemer *et al.*, 1998). Methanol and formaldehyde are toxic organic air pollutants, and their emissions are regulated by the United States Environmental Protection Agency (EPA) and the Ministry of the Environment (Japan). Acetone is an important source of HO_x radicals (Singh *et al.*, 1995) that contribute to the formation of ozone in the atmosphere.

Formic and acetic acids in the gas phase are the dominant organic acids in the atmosphere (Kawamura *et al.*, 2000; Mochizuki *et al.*, 2019). Gaseous formic and acetic acids are

adsorbed on existing alkaline particles (Alexander *et al.*, 2015). As formic and acetic acids are highly water soluble, they can alter the hygroscopic properties of atmospheric particles (Kanakidou *et al.*, 2005). It should be noted that organic acids contribute to the acidity of wet deposition (e.g., Kawamura *et al.*, 1996).

Atmospheric concentrations of methanol, acetone, and formic and acetic acids range from a few ppt to several ppb (see Seco *et al.*, 2007 and the references therein). The lifetimes of gaseous methanol and acetone reacting with OH radicals at a typical concentration (2.0×10^6 molecules cm^{-3}) are 12 and 61 days, respectively (Atkinson and Arey, 2003). The lifetimes of gaseous formic and acetic acids reacting with OH radicals at a typical concentration (2.0×10^6 molecules cm^{-3}) are 13 and 7.2 days, respectively (NIST Standard Reference Database Number 69), suggesting that their lifetimes are much longer than those of reactive hydrocarbons, such as isoprene and monoterpenes.

Methanol, acetone, and formic and acetic acids are directly emitted from plant leaves, leaf litter, and dead plant matter (Seco *et al.*, 2007). Briefly, methanol is a product of pectin demethylation in the plant cell wall. Acetone is produced after the decarboxylation of acetoacetate, which is derived from acetyl-CoA in plant leaves. Formic acid is a product of the decarboxylation of glycolic acid during photorespiration. It is also produced through the oxidation of formaldehyde in plant leaves. Acetic acid is a product of the hydrolysis of acetyl-CoA. Several studies have found that emissions of methanol, acetone, and formic and acetic acids from plant leaves varied with temperature, light intensity, and stomatal conductance (Nemecek-Marshall *et al.*, 1995; Kesselmeier *et al.*, 1997; Janson and Serves, 2001). However, the available data on these compounds that are directly emitted by vegetation are limited, and their controlling factors are unclear. Formic and acetic acids are also produced secondarily from the photochemical oxidations of terpenoids, including isoprene and monoterpenes in the atmosphere (Paulot *et al.*, 2011).

Methanol, acetone, and formic and acetic acids are emitted from a variety of anthropogenic and biogenic sources. The annual global emissions of methanol and acetone are estimated to be 187 Tg yr^{-1} (Stavrakou *et al.*, 2011) and 95 Tg yr^{-1} (Jacob *et al.*, 2002), respectively. The annual emissions of methanol and acetone from terrestrial vegetation account for approximately 53% and 35% of the annual global emissions, respectively. The annual global emissions of formic and acetic acids are estimated to be 57 Tg yr^{-1} and 85 Tg yr^{-1} , respectively (Paulot *et al.*, 2011). The emissions of formic and acetic acids from terrestrial vegetation account for 4.5% and 3.0% of the global emissions, respectively; conversely, the secondary production of formic and acetic acids via the photochemical oxidation of biogenic VOCs is estimated to account for 74% and 67% of the global emissions, respectively.

2.4 Anthropogenic VOCs

The fossil fuel burning and solvent industry release a wide variety of anthropogenic VOCs, including aliphatic hydrocarbons, aromatic hydrocarbons, ketones, aldehydes, and alcohols. Toluene is the most abundant compound in urban and rural atmosphere. Benzene is also ubiquitous and the second abundant compound. In general, the reactivity of

these compounds is low compared with those of isoprene and monoterpenes. However, compounds with double or triple bonds, including acrolein, are more easily oxidized in the atmosphere.

Partitioning of anthropogenic VOCs from air phase to water phase is explained by Henry's law constant. Small amounts of benzene and toluene are partitioned into water phase but oxygenated VOCs including aldehydes, ketones and alcohols are largely partitioned into water phase. As plant leaves include water at a volume ratio of >80%, substantial amounts of these oxygenated compounds are partitioned in leaves. Some of them are metabolized in plant cells (Trapp and Karlson, 2001). Octanol/water partition coefficient is another index that determines the degree of partition of VOCs between plants and outside environments. Toluene is substantially stored in lipids of plant leaves (Keymeulen *et al.*, 1997). Mobility of VOCs within plants from roots to leaves depends on the octanol/water partition coefficient and differs for different VOC species (Burken and Schnoor, 1998).

3. Leaf, plant, and soil level exchanges

3.1 Isoprene emissions from leaves, branches, and individual trees

Isoprene emissions from plants on the leaf and branch levels have been intensively measured in terms of plant physiology and atmospheric chemistry. By using a real-time isoprene analyzer, such as a chemiluminescence analyzer (Hills and Zimmerman, 1990) and a proton-transfer-reaction mass spectrometer (PTR-MS) (Lindinger *et al.*, 1997), it is evident that isoprene emission is not affected by the degree of stomatal opening. This is different from

the CO₂ exchange on the leaf surface that is governed by stomatal conductance. This is because isoprene synthesis is not affected by the intercellular isoprene concentration. When the opening area of the stomata becomes narrow, the intercellular concentration immediately increases to equilibrate the isoprene production rate with its emission rate (Fall and Monson, 1992).

The temperature dependency of isoprene is governed by isoprene synthase. Analogous to most enzymes, its optimum temperature is ~40 °C. The isoprene emission rate increases with an increase in temperature up to ~40 °C (Fig. 2). The light dependency of isoprene is closely related to the DMAPP production rate, which is affected by CO₂ fixation via photosynthesis. The isoprene emission rate curve against light intensity is very similar to the curve of photosynthetic rate against light (Fig. 2). The light saturation point is between 200 and 1000 $\mu\text{mol m}^{-2}\text{s}^{-1}$, depending on the sun exposure conditions of leaves (Harley *et al.*, 1996, 1997; Hayward *et al.*, 2004; Tani and Kawawata, 2008). The equations that express the isoprene emission rate depending on temperature and light intensity were developed by Guenther *et al.* (1993) and have been called the G93 algorithm. These equations have been widely used to estimate the isoprene emission rate not only on the leaf area and branch bases, but also on the plant and canopy levels.

The effect of elevated CO₂ concentration on plant isoprene emissions has been investigated. Short-term fumigation can decrease the isoprene emission rate compared with ambient CO₂ fumigation (e.g., Tingey *et al.*, 1981). The isoprene precursor DMAPP is produced by the MEP pathway in chloroplasts, and phosphoenolpyruvate (PEP) is converted to pyruvate, which is

Fig. 2. Models describing temperature-dependent (A) and light-dependent (B) isoprene and temperature-dependent (C) monoterpene emissions.

a substance of the MEP pathway. The elevated CO₂ may result in a higher concentration of total leaf PEP, but cause a lower PEP concentration in the stroma when compared with ambient CO₂ concentration. This stromal PEP contributes to isoprene production, and this change in this metabolic balance may cause an isoprene emission reduction. The details of this hypothesis are described by Sharkey and Monson (2014). Many reports suggest that long-term fumigation experiments with elevated CO₂ may also result in the inhibition of isoprene emission (Rosenstiel *et al.*, 2003; Scholefield *et al.*, 2004; Monson *et al.*, 2007), although a few reports have shown that it may increase the isoprene emission capacity (Sun *et al.*, 2012; 2013). The inhibition of isoprene emission may be caused by a decreased activity of isoprene synthase (Scholefield *et al.*, 2004; Possell and Hewitt, 2011) in addition to the lower PEP concentration in the stroma mentioned above.

Elevated O₃ has been reported to increase isoprene production in several short-term fumigation experiments. Increased isoprene emission under ~300 ppb O₃ quenched H₂O₂ formed in the ozone-exposed leaves of *Phragmites australis* and reduced lipid peroxidation in the cellular membranes (Loreto and Velikova, 2001; Velikova *et al.*, 2005). However, this protective effect was not obvious under long-term exposure with a possible concentration of O₃ (ambient + 40 ppb in many cases). The isoprene emission rate was reduced by long-term exposure, probably by the suppressed gene expression and protein level of isoprene synthase (Calfapietra *et al.*, 2007, 2008) or the decreased production of DMAPP (Yuan *et al.*, 2016; Tani *et al.*, 2017). Under enriched O₃ conditions, biomass was reported to be less decreased in aboveground parts, including leaves, than in the roots, in order to mitigate the decreased photosynthesis on the leaf area basis (Agathokleous *et al.*, 2018). If this is the case, the isoprene emission rate of individual trees may be less decreased than the isoprene emission rate on the leaf area basis.

The effect of water stress on isoprene emission has been intensively investigated. The isoprene emission rate of *Q. pubescens* (Brüggemann and Schnitzler, 2002), *Populus alba* (Brilli *et al.*, 2007), *Q. rubra* (Funk *et al.*, 2005), *P. deltoides* (Funk *et al.*, 2004; Pegoraro *et al.*, 2004), and *Liquidambar styraciflua* (Fang *et al.*, 1996) is reduced by water stress, but the degree of reduction is smaller than that of the photosynthetic reduction. *Quercus serrata* and *Q. crispula*, which are major tree species native to East Asia, continue to produce isoprene even when the gross photosynthetic rate becomes lower than the respiration rate during daytime (net photosynthetic rate < 0) (Tani *et al.*, 2011). Under normal conditions, DMAPP is supplied mainly from chloroplastic sources, but it may be supplied substantially from an alternative source in the cytosol. The cytosol source may be the primary precursor of isoprene under drought conditions (Karl *et al.*, 2002; Schnitzler *et al.*, 2004). Under severe drought conditions, the alternative source is so limited that the isoprene emission rate is low.

A change in land use may enhance the emission of isoprene from modified vegetation, including spreading bamboo forests (Okumura *et al.*, 2018; Chang *et al.*, 2019) and palm oil plantations (Wilkinson *et al.*, 2006; Misztal *et al.*, 2011; Dislich *et al.*, 2017).

3.2 Monoterpene emissions from leaf, branch, and individual tree

Monoterpene emissions from non-storage types depend on temperature and light intensity, as does isoprene emission. It increases with temperatures of up to ~40 °C and with photosynthetic photon flux density (PPFD) of up to ~1000 μmol m⁻² s⁻¹ (Staudt and Seufert, 1995; Staudt and Bertin, 1998). Monoterpene emissions from storage type plants depend on temperature because monoterpene evaporates from storage organs following the temperature-dependent equation of saturated vapor pressure, which is similar to the Antoine equation. A more simplified equation was proposed by Guenther *et al.* (1993), as shown in Fig. 2. In this equation, coefficient β determines the slope of the fitted curve. Coefficient β can be calculated using datasets of the emission rate and temperature, and it is reported to have a wide range of values, that is, 0.02–0.13 within a strain of *C. japonica* (Miyama *et al.*, 2019).

The effects of CO₂, ozone, and water stress on monoterpene emissions from non-storage type trees are similar to those on isoprene emission (e.g., Loreto *et al.*, 2001). However, the effects on monoterpene emissions from storage-type trees are not the same as those on isoprene emission and are not consistent among reports. No effects of elevated CO₂ on the total monoterpene emission rate were observed for the evergreen coniferous tree *Pinus sylvestris* (700 μmol mol⁻¹ throughout a 5 year period) (Räsänen *et al.*, 2008) and deciduous broadleaved tree *Betula pendula* clones (twice as much as the ambient CO₂ concentration for two growing seasons) (Vuorinen *et al.*, 2005). A negative effect of elevated CO₂ on total monoterpene emissions was found for hybrid larch F₁ (*Larix gmelinii* var. *japonica* × *Larix kaempferi*) (Mochizuki *et al.*, 2017). Elevated O₃ levels increase the total monoterpene emissions of deciduous *Ginkgo biloba* (Li *et al.*, 2009) and *C. japonica* (Miyama *et al.*, 2018), but they do not affect the total monoterpene emissions of deciduous *B. pendula* (Hartikainen *et al.*, 2012) and hybrid larches (Mochizuki *et al.*, 2017). However, ozone causes a change in the monoterpene composition in hybrid larch leaves; less reactive monoterpenes are abundantly emitted because O₃ may react with monoterpenes in leaves (Mochizuki *et al.*, 2017).

3.3 Terpenoid emissions from soil

Leaf litter, roots, forest floor plants, and the microbiological decomposition of organic matter are monoterpene sources (Hayward *et al.*, 2001; Leff and Fierer, 2008; Ludley *et al.*, 2009; Tsuruta *et al.*, 2018). Their source strengths are diverse and differ among vegetation types. As for forest soil, the soil monoterpene emission rates in coniferous *P. sylvestris* (Ketola *et al.*, 2011) and *P. sitchensis* (Hayward *et al.*, 2001) forests were 0.86 nmol m⁻² s⁻¹ (8 °C in soil temperature) and 0.08 nmol m⁻² s⁻¹ (18 °C in air chamber temperature), respectively. The soil monoterpene emission rate in a broadleaved *Q. ilex* forest was 0.004 nmol m⁻² s⁻¹ (8 °C in soil temperature) (Asensio *et al.*, 2007). As for the forest floor including ground vegetation (e.g., herbaceous plants, fungi, and mosses), the monoterpene emission rate of the floor of *P. sylvestris* forests was reported to be 1.9 nmol m⁻² s⁻¹ (28 °C in air chamber temperature) (Aaltonen *et al.*, 2013) and 0.013 nmol m⁻² s⁻¹ (7.5 °C in air chamber

temperature) (Aaltonen *et al.*, 2011).

Smolander *et al.* (2006) reported that the monoterpene concentration in the aerial space of soil in coniferous *Picea abies* and *P. sylvestris* forests were significantly higher than that in broadleaved *Betula pendula* forest. The monoterpene concentration in the aerial space of soil in a coniferous *P. mariana* (black spruce) forest was significantly higher than the atmospheric concentration above the forest (Morishita *et al.*, 2019). Hayward *et al.* (2001) reported that monoterpene emission rates differed among soil depths, and needle litter was a strong source of monoterpenes. The monoterpene emission rate of the *P. sylvestris* forest floor was the highest in autumn (Aaltonen *et al.*, 2011) and the observed seasonality was attributed to an increase in litter fall in autumn as the needle litter included monoterpenes. Coniferous forests floor/soil may be an important source of monoterpenes in the atmosphere.

Contrarily, the isoprene emission rate of a *P. sylvestris* forest floor was $0.0002 \text{ nmol m}^{-2} \text{ s}^{-1}$, which was much lower than the monoterpene emission rate at the same site (Aaltonen *et al.*, 2011). The isoprene emission rate of arctic soil (*Salix-Eriophorum* community) measured at air temperature of $\sim 10^\circ \text{C}$ was $0.02 \text{ nmol m}^{-2} \text{ s}^{-1}$ (Svendsen *et al.*, 2016).

3.4 Leaf uptake of OVOCs

Oxygenated VOCs, including low-molecular-weight alcohols, ketones, and aldehydes, have been reported to be absorbed by plants via stomata (Omasa *et al.*, 2000; Tani and Hewitt, 2009; Tani *et al.*, 2013). At the concentration range of ppb to several tens ppb, measurements based on PTR-MS provide more precise data than does GCMS (Tani *et al.*, 2007). The uptake rate of ketones and aldehydes increases linearly with stomatal conductance g_s (Tani *et al.*, 2010; 2013), suggesting that the uptake is controlled by stomatal opening. However, its slope may become gentle when g_s exceeds a certain level. This phenomenon has been reported for *Spathiphyllum* fumigated in propionaldehyde and methyl ethyl ketone (Tani and Hewitt, 2009). This is because the ratio of the intercellular concentration to the fumigated concentration of the gas species becomes higher owing to the limitation of metabolic conversion.

Isoprene oxygenates MAC and MVK are also absorbed by trees (Tani *et al.*, 2010; Karl *et al.*, 2010). MAC is metabolized in tissues to produce glutathione conjugates (Muramoto *et al.*, 2015) and high-volatile compounds including isobutyl aldehyde, isobutyl alcohol, and methallyl alcohol when tomato plants are fumigated with MAC at the ppm level. Cappellin *et al.* (2019) recently reported that MVK absorbed by an isoprene-emitting species *Quercus rubra* was reduced in leaves to emit methyl ethyl ketone (MEK) or 3-buten-2-ol. Further reactions reduced MEK and 3-buten-2-ol to 2-butanol. A similar result has been reported by Tani *et al.* (2020), but they did not observe 3-buten-2-ol emission from non-isoprene-emitting species including three tree and one houseplant species. Cappellin *et al.* (2019) determined the conversion ratio of MVK to MEK to be 73%, and that of MVK to all volatiles (including MEK, 3-buten-2-ol, and 2-butanol) to be 97.6%, suggesting that the absorbed MEK was mostly converted to volatiles and scarcely remained in leaves. On the contrary, MVK conversion ratios

of the non-isoprene-emitting species determined by Tani *et al.* (2020) were much lower than those reported by Cappellin *et al.* (2019); i.e. 26–39% for MEK and 33–44% for all volatiles. The difference in the conversion ratios from MVK to volatiles between two studies might be attributed to plant materials, i.e. isoprene-emitting or non-emitting species. Isoprene-emitting trees may have more active enzymes for converting MVK to volatiles than non-emitting plants, because cells of the isoprene-emitting plants are always exposed to high concentrations of isoprene oxygenates, including MVK, during daytime. This is because that MVK and MAC are formed in leaves by isoprene reaction under oxidative stress. (Jardine *et al.*, 2010). As reactive carbonyl species including MVK and MACR are deleterious to plants at high concentrations (Mano, 2012; Farmer and Mueller, 2013), it may be safer for the isoprene-emitting plants to release the oxygenates into the atmosphere in the form of other volatiles because the pool size used for accumulating these oxygenates and their metabolites within plant tissues is limited.

It has been reported that some other VOCs are bilaterally exchanged between plants and the atmosphere (Niinemets *et al.*, 2014). Four species of low molecular weight oxygenated VOCs (acetaldehyde, formaldehyde, and acetic and formic acids) are reported to be both emitted and taken up by plants (Kesselmeier, 2001). The compensation point of the compounds within leaves may vary, depending on their atmospheric concentration and production rate of these compounds within plants (Fares *et al.*, 2015). Using an inverse model, a sink and source analysis of MACR and MVK was conducted by Wada *et al.* (2020), but their result suggests that larger amounts of data on spatial distribution of these compounds should be collected to provide a valid estimate.

4. Ecosystem scale exchange

4.1 Flux measurement by micrometeorological techniques

Flux measurement techniques employed for organic gases are theoretically the same as those employed for CO_2 flux. The eddy covariance (EC) method may be applied for terpenoid fluxes. Fast-response analytical instruments including PTR-MS have been employed (Karl *et al.*, 2001). In terpenoid flux measurements, PTR-MS can distinguish between VOCs of different molecular weights by using quadrupole or time of flight (TOF) mass filters. The TOF mass filter has the advantage of mass resolution as it allows the estimation of the molecular formula of the detected ions, though we cannot know whether the ions originate from molecular or fragment ions; in most cases they originate from both ion types, however we cannot be certain what percentage comes from molecular ions, which causes quantification and qualification uncertainties. Humidity affects the PTR-MS sensitivity and the fragment ion patterns of the proton-transfer-reaction products of monoterpenes (Tani *et al.*, 2004), and these effects should not be ignored in certain cases. A theoretically determined concentration does not always provide an accurate absolute value of VOC concentrations (Kato *et al.*, 2004) and requires correction using the known concentration of the target gas (Tani *et al.*, 2003). To overcome these uncertainties, a recent study tried to improve the data handling method of PTR-MS based flux measurements (Millet *et al.*, 2018).

The relaxed accumulation method (REA) coupled with the thermal desorption method and gas chromatography mass spectrometry (GCMS) can provide a more reliable identification of each compound and more accurate concentrations (e.g., Mochizuki *et al.*, 2014). The upward and downward airflows are separately accumulated into reservoirs and the determined concentrations of the two reservoirs are used for the flux calculation. The reservoir type is either canister or adsorbent tube.

The gradient method is also used for many trace gas species including terpenoids (Tani *et al.*, 2002). This method was used in the early years of trace gas flux measurements. However, it is still used if measurement devices with high-time resolution for EC measurement are unavailable and if the gas species cannot be accumulated into REA reservoirs owing to its unstable characteristics. The concentration of the target gas at two different heights within the boundary layer above the tree canopy is

measured and the difference between the two concentrations is divided by the height difference and multiplied by the diffusion coefficient of the target gas to determine its flux.

Other methods including the disjunct eddy sampling method (Rinne *et al.*, 2000) have been developed. Although several methods to measure trace gas fluxes are available, the EC method may be advantageous from a timesaving point of view if fast-response analytical instruments provide reliable data.

4.2 Terpenoid fluxes

Isoprene and monoterpene fluxes have been reported for various forest types including boreal, cool temperate, temperate, Mediterranean, tropical, and savanna forests (Table 2). Broadleaved forests mainly emit isoprene and coniferous forests mainly emit monoterpenes. The canopy flux of isoprene in boreal and cool temperate, temperate and Mediterranean, and tropical

Table 2. Isoprene and monoterpene fluxes for various vegetation types.

Site	Vegetation	Method	Isoprene	Monoterpenes	Period	References
Boreal and cool temperate						
Saskatchewan, Canada	<i>Picea mariana</i> <i>Populus tremuloides</i>	REA	5.6 nmol m⁻² s⁻¹ 10.6 nmol m⁻² s⁻¹		Midsummer 1994	Westberg <i>et al.</i> (2000)
Huhus, Finland	<i>Pinus sylvestris</i>	FG		1.8 nmol m⁻² s⁻¹	June–September 2003	Räsänen <i>et al.</i> (2009)
The Czech Republic	<i>Picea abies</i>	EC		1.3 nmol m ⁻² s ⁻¹	Summer 2010, 2011, and 2012	Juráň <i>et al.</i> (2017)
Tomakomai, Japan	<i>Larix kaempferi</i>	FG	0.5 nmol m ⁻² s ⁻¹	0.07 nmol m ⁻² s ⁻¹	September 2003	Ieda <i>et al.</i> (2006)
Yamanashi, Japan	<i>Larix kaempferi</i>	REA		1.3 nmol m⁻² s⁻¹	2011–2012	Mochizuki <i>et al.</i> (2014)
Temperate and Mediterranean						
Yamanashi, Japan	<i>Pinus densiflora</i> , <i>Quercus serrata</i>	REA	3.1 nmol m⁻² s⁻¹	1.2 nmol m⁻² s⁻¹	Summer 2012	Mochizuki <i>et al.</i> (2020)
Nagano, Japan	<i>Pinus densiflora</i>	FG		0.12–3.8 nmol m⁻² s⁻¹	May–November 2000	Tani <i>et al.</i> (2002)
New England, USA	Mixed forest (red oak, red maple, red pine)	EC	18.0 nmol m ⁻² s ⁻¹	0.4 nmol m ⁻² s ⁻¹	Summer 2007	McKinney <i>et al.</i> (2011)
California, USA	<i>Ponderosa pine</i>	EC		0.3 nmol m⁻² s⁻¹	June 2003–April 2004	Holzinger <i>et al.</i> (2006)
California, USA	<i>Ponderosa pine</i>	REA		2.5 nmol m⁻² s⁻¹	1999–2000	Bouvier-Brown <i>et al.</i> (2012)
Missouri, USA	Mixed forest (white oak, post oak, blank oak, sugar maple, red cedar)	DEC	58 nmol m ⁻² s ⁻¹	3.9 nmol m ⁻² s ⁻¹	May–November 2013	Seco <i>et al.</i> (2015)
Michigan, USA	Hardwood forest (aspen, beech)	EC	13.0–14.8 nmol m ⁻² s ⁻¹		May–September 1999–2002	Pressley <i>et al.</i> (2005)
Yatir, Israel (Edge of the desert)	<i>Pinus halepensis</i>	DEC		1.0–2.0 nmol m⁻² s⁻¹	Spring 2013	Seco <i>et al.</i> (2017)
Biryat, Israel (Mediterranean)	<i>Pinus halepensis</i>	DEC		0–2.7 nmol m⁻² s⁻¹	Spring 2013	Seco <i>et al.</i> (2017)
Vielsalm, Belgium	Mixed forest (<i>Pseudotsuga menziesii</i> , <i>Picea abies</i>)	DEC	8.2–9.0 nmol m⁻² s⁻¹	2.0–5.4 nmol m⁻² s⁻¹	July–September 2009	Laffineur <i>et al.</i> (2011)
Lochristi, Belgium	Poplar plantation	EC	0–6 nmol m ⁻² s ⁻¹		January–December 2015	Portillo-Estrada <i>et al.</i> (2018)
West of Cologne, Germany	Mixed deciduous forest (beech, birch and oak)	EC	35.3 nmol m⁻² s⁻¹	3.9 nmol m⁻² s⁻¹	July 2003	Spirig <i>et al.</i> (2005)
Zhejiang province, China	Bamboo (<i>Phyllostachys violascens</i>)	REA	13.5 nmol m⁻² s⁻¹	0.02 nmol m⁻² s⁻¹	July 2012	Bai <i>et al.</i> (2016)
Changbai Mountain, China	Deciduous broad-leaved and coniferous forest	REA	14 nmol m⁻² s⁻¹	0.72 nmol m⁻² s⁻¹	Summer 2011	Bai <i>et al.</i> (2015)
Mediterranean, France	Oak forest (<i>Quercus pubescens</i>)	DEC	30.2 nmol m⁻² s⁻¹		May–June 2012	Kalogridis <i>et al.</i> (2014)
Mediterranean, France	<i>Quercus pubescens</i> , <i>Acer monspessulanum</i>	DEC	22.1–41.2 nmol m ⁻² s ⁻¹		July–August 2010	Baghi <i>et al.</i> (2012)
Mediterranean, Italy	<i>Quercus ilex</i>	REA		5.9 nmol m⁻² s⁻¹	July 1997	Ciccioli <i>et al.</i> (2003)
Mediterranean, Italy	<i>Quercus ilex</i> and <i>Pinus pinea</i>	EC	2.5 nmol m⁻² s⁻¹	3.6 nmol m⁻² s⁻¹	September–October 2011	Fares <i>et al.</i> (2013)
Mediterranean, Spain	<i>Quercus ilex</i>	FG		2.2 nmol m⁻² s⁻¹	September–October 2000	Plaza <i>et al.</i> (2005)
Tropical and Savanna						
Sabah, Malaysia	Oil palm plantation	DEC	6.5 nmol m⁻² s⁻¹	0.9 nmol m⁻² s⁻¹	Spring–summer 2008	Langford <i>et al.</i> (2010)
Borneo, Malaysia	Oil palm plantation	EC	32 nmol m ⁻² s ⁻¹		May–June 2008	Misztal <i>et al.</i> (2011)
Yunnan province, China	Rubber tree	EC	4.1 nmol m ⁻² s ⁻¹ 0.6 nmol m ⁻² s ⁻¹		Wet season, 2002 Dry season, 2003	Baker <i>et al.</i> (2005)
Costa Rica	Tropical wet forests (<i>Mimosaceae</i> , <i>Arecaceae</i>)	REA	10.2 nmol m ⁻² s ⁻¹		October 1999	Geron <i>et al.</i> (2002)
Amazon, Brazil	Rainforest	DEA	9.8 nmol m⁻² s⁻¹	0.5 nmol m⁻² s⁻¹	July 2000 (rainy season)	Rinne <i>et al.</i> (2002)
Amazon, Brazil	Tropical forest	REA	9.7 nmol m ⁻² s ⁻¹	0.9 nmol m ⁻² s ⁻¹	Summer 2001	Kuhn <i>et al.</i> (2007)
Savanna, South Africa	Combretum, Acacia	REA	1.4 nmol m ⁻² s ⁻¹		February 2001	Harley <i>et al.</i> (2003)
Maun, Botswana	<i>Colophospermum mopane</i>	REA		~6.9 nmol m ⁻² s ⁻¹	January and February 2001	Greenberg <i>et al.</i> (2003)
Northern Congo	Mixed tropical forest	REA	2.1–6.5 nmol m ⁻² s ⁻¹		March and November 1996	Serca <i>et al.</i> (2001)

Values in bold letters indicate the standard isoprene flux at the standard temperature (30 °C) and standard light intensity (1000 μmol m⁻² s⁻¹) or the standard monoterpene flux at the standard temperature (30 °C).

FG: flux gradient method

EC: eddy covariance method

REA: relaxed eddy accumulation method

DEC: disjunct eddy covariance method

DEA: disjunct eddy accumulation method

forests ranges from 0.5–10.6 nmol m⁻² s⁻¹, 0–58 nmol m⁻² s⁻¹, and 1.4–32 nmol m⁻² s⁻¹, respectively. Bamboo forests also emit isoprene (average flux = 13.5 nmol m⁻² s⁻¹). The canopy flux of monoterpene in boreal and cool temperate, temperate and Mediterranean, and tropical forests ranges from 0.07–1.8 nmol m⁻² s⁻¹, 0.02–5.9 nmol m⁻² s⁻¹, and 0.5–6.9 nmol m⁻² s⁻¹, respectively. Relatively high monoterpene fluxes were observed in Mediterranean broadleaved forests and in savanna woodland areas (broadleaved trees) compared with coniferous forests. Overall, the canopy flux of isoprene is higher than that of monoterpenes.

Isoprene and monoterpenes include 5 and 10 carbon atoms, respectively, in each molecule. The emission of isoprene and monoterpenes is the loss of carbon fixed by photosynthesis. The annual carbon emissions as monoterpenes from a *L. kaempferi* forest (Mochizuki *et al.*, 2014) and a *P. ponderosa* forest (Bouvier-Brown *et al.*, 2012) was reported to account for 0.9% and 0.5%, respectively, of the net ecosystem exchange of carbon (NEE). The annual carbon emission as isoprene from poplar plantations accounts for 0.3% of the NEE (Portillo-Estrada *et al.*, 2018). Ignoring the loss of carbon emitted by isoprene and monoterpenes may result in an overestimation of the carbon stored in the forest ecosystem.

4.3 Factors affecting ecosystem-level exchange of biogenic VOCs

Generally, canopy-scale isoprene and monoterpene emissions start to increase in the morning and reach a peak around noon or in the afternoon, as they are affected by ambient air temperature and light intensity (Laffineur *et al.*, 2011; Mochizuki *et al.*, 2014; Seco *et al.*, 2015; Mochizuki *et al.*, 2020). However, higher monoterpene fluxes were observed in the morning than in the afternoon (Tani *et al.*, 2002). This is because of the so-called storage effect.

A relatively high isoprene flux was observed in broadleaved mixed forests in the summer (Seco *et al.*, 2015). The monoterpene fluxes of *L. kaempferi* and *P. ponderosa* forests are significantly higher in summer than in winter (Mochizuki *et al.*, 2014; Holzinger *et al.*, 2006). The seasonal variation in isoprene and monoterpene fluxes above the forest is not only linked to ambient air temperature variations, but is also involved in emission capacity changes caused by enzymatic activity. The monoterpene flux standardized to 30 °C is highest in early summer (June) in a *P. densiflora* forest (Tani *et al.*, 2002).

High monoterpene flux in a *P. ponderosa* forest (Holzinger *et al.*, 2006) and a *L. kaempferi* forest (Mochizuki *et al.*, 2014) has been observed after rain events. Mochizuki *et al.* (2014) also reported that standardized monoterpene fluxes had a strong positive correlation with the volumetric soil water content, suggesting that rainfall enhances monoterpene emissions from larch forest ecosystems, including soils. In contrast, drought conditions had no impact on the isoprene flux of broadleaved mixed forests (Seco *et al.*, 2015) and the monoterpene flux of Mediterranean pine forests (Seco *et al.*, 2017), even though the net CO₂ assimilation rate decreased.

When comparing the terpenoid emissions from the forest floor (E_{floor}) with canopy scale terpenoid fluxes (E_{canopy}), the ratio of $E_{\text{floor}}/E_{\text{canopy}}$ in a *P. sylvestris* forest in autumn (Aaltonen *et al.*,

2011) and a *P. ponderosa* forest (Greenberg *et al.*, 2012) in the summer was 10% and 1%, respectively. Janson (1993) observed a higher $E_{\text{floor}}/E_{\text{canopy}}$ ratio (20–40%) under wet conditions. The soil and the forest floor may be important terpenoid emission sources from forest ecosystems, but their importance depends on the vegetation type, season, and environmental conditions. In particular, wet conditions may enhance monoterpene emissions from the soil and litter.

Long-term flux measurements may provide insight into the response of terrestrial ecosystems' terpenoid emissions to complex climate change. However, continuous or intermittent measurements of terpenoid fluxes for years have not been conducted. Compared with CO₂ and H₂O fluxes, it is difficult to operate the measurement devices automatically in order to measure the terpenoid concentrations. Only PTR-MS may be a candidate, but it requires careful operation and frequent maintenance. A limited number of researchers use PTR-MS for such exclusive monitoring for years.

5. Combined effect analyses to address climate change effects

Recent studies have focused on the combined effects of two or more environmental parameters on plant terpenoid emissions, in order to estimate the impact of ongoing climate change on terpenoid-related atmospheric chemistry and climate. For this study, leaf, branch, and individual tree measurements were conducted.

A combined experiment of long-term CO₂ and O₃ exposure was conducted by Calfapietra *et al.* (2008), the results of which suggest that the decline of isoprene emission under elevated CO₂ and elevated O₃ may be exacerbated by a combination of substrate (CO₂ effect) and enzyme limitations (O₃ effect). The effects of CO₂ and O₃ on monoterpene emissions from *B. pendula* (Vuorinen *et al.*, 2005) and *P. sylvestris* (Sallas *et al.*, 2001) differed by season and monoterpene compounds.

The inhibition of isoprene production under elevated CO₂ has been reported to be mitigated by high temperatures (Loreto and Sharkey, 1990; Sun *et al.*, 2013; Potosnak *et al.*, 2014). However, these experimental results are based on relatively short-term experiments and are not enough to provide an understanding of the mechanism responsible for the plants acclimated to elevated CO₂ or high temperature.

Mochizuki *et al.* (2018) measured the monoterpene emission rate of *C. japonica* clone saplings grown at elevated CO₂ conditions in an open-top chamber. The normalized monoterpene emission rates were positively and linearly correlated with soil water content (SWC) under both the control and elevated CO₂ conditions, but the slope of the regression line between them was significantly higher under the elevated CO₂ conditions, indicating that the monoterpene emissions from plants grown under elevated CO₂ conditions are more sensitive to SWC.

The combined effects of O₃ and nitrogen on plant terpenoid emissions have been investigated (Llusià *et al.*, 2014; Carriero *et al.*, 2016; Yuan *et al.*, 2017). The results of these studies suggest that the effects of O₃ and N on terpenoid emission from plants are additive and not interactive. More complicated effects of elevated CO₂ and O₃ and high temperature on herbivore-induced terpenoid emissions

were addressed by Kivimäenpää *et al.* (2016) and Ghimire *et al.* (2017). They showed a dramatic increase in total sesquiterpene emissions from the fed shoots of *B. pendula* and *P. sylvestris* in combination with high temperature and elevated ozone.

6. Model estimates and satellite measurements to address climate change effects

Based on the findings of leaf, branch, and individual tree measurements, several process-based models have been developed to estimate global and local terpenoid emissions (Arneth *et al.*, 2008). Most of the models employ the G93 algorithm (i.e., the MEGAN model by Guenther *et al.* (2006)), while others include a model based on energetic requirements for isoprene synthesis (Niinemets *et al.*, 1999). Using the process-based models, coupled with leaf area index (LAI), land cover data, vegetation lists classified as terpenoid emission type, and climate data, terpenoid emissions on global (Pacífico *et al.*, 2012; Sindelarova *et al.*, 2014) and regional (Ren *et al.*, 2014; 2017; Bauwens *et al.*, 2018) scales have been estimated for the past, present, and future. The resolution of climate data (Ashworth *et al.*, 2010) and plant classification (Arneth *et al.*, 2013) has been suggested to affect the accuracy of the terpenoid emission estimates. The tower-flux measurement data from a very limited number of vegetation types were compared with the model estimates for the sites to investigate the validity of the models (Sindelarova *et al.*, 2014; Bauwens *et al.*, 2018). Because of the limited number of flux data at individual sites, the comparisons showed fair agreement. Future estimates of global isoprene emissions based on climate change scenarios indicate that the isoprene emission may increase because of global warming, but this could be inhibited by a CO₂ increase. The degree of change in global isoprene emission estimates depends on the model characteristics, vegetation data, and future scenarios (Pacífico *et al.*, 2012; Bauwens *et al.*, 2018). Ozone and SOA formations have been estimated according to the global warming scenario with a process-based isoprene emission model coupled with an atmospheric chemistry model. Pacífico *et al.* (2012) suggest that the ozone and SOA burden into the atmosphere may increase by 15% and two-fold, respectively, in the future (2100–2109) compared with the present levels.

Top-down isoprene emission models have also been developed using space-based formaldehyde (HCHO) vertical columns, as observed by the ozone monitoring instrument (OMI) (Levelt *et al.*, 2006) and scanning imaging absorption spectrometer for atmospheric chartography (SCIAMACHY) (Bovensmann *et al.*, 1999). As HCHO is an oxidation product of most VOCs emitted by biomass burning, vegetation, and anthropogenic activities, satellite observations of HCHO may provide information on the underlying VOC sources. Barkley *et al.* (2013) showed that the annual isoprene emission over tropical South America estimated by the SCIAMACHY column was two times higher than that estimated by the OMI column, the reason of which could not be explained by sampling time of sensors and cloud products by the air-mass factor (AMF) calculation. Bauwens *et al.* (2016) compared the inverse analysis using the HCHO vertical column with the MEGAN bottom-up model and discussed the reason for the difference in isoprene emission estimates. Recently, Fu

et al. (2019) showed the possibility of the direct measurement of isoprene columns from space using the satellite-borne cross-track infrared sounder (CrIS). If the model based on the isoprene column is verified by ground truth data at multiple sites, the approach has the potential to become a more reliable method to estimate isoprene emission sources and their strength from space.

To validate the global and local terpenoid emissions estimated from bottom-up process-based models and top-down satellite estimates, a comparison between the two different methods may not lead to realistic results. To validate the accuracy and precision of the models, much more in-situ ground truth data, such as long-term flux and concentration measurement data at various sites, are required. As accumulated in-situ flux data may indicate a good relationship between the measured flux and environmental factors (e.g., Mochizuki *et al.*, 2014), the data can be used to validate the developed models. Otherwise, these models may still leave large uncertainties compared with global carbon exchange models that can be validated with a large number of ground truth flux data.

7. Acknowledgements

This work was supported by MEXT KAKENHI Grant Number No. 19H04257, 19H05666 and 18K18181.

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