

Trends in Plant Science

Volume 22 Number 9
September 2017
ISSN 1360-1385

Blue Haze Plant-Derived Secondary Organic Material in the Air and Ecosystems

CellPress
REVIEWS

September 2017
Volume 22, Issue 9

Biogenic secondary organic aerosol (SOA) and deposited secondary organic material (SOM) are formed by oxidation of volatile organic compounds (VOCs) emitted by plants. Many SOA compounds, sometimes visible as "blue haze", have much longer chemical lifetimes than the original VOC, and may accumulate on plant surfaces and in soil as SOM because of their low volatility. This suggests that they may have important and presently unrecognized roles in plant adaptation. On pages 744–753 Jarmo K. Holopainen and colleagues use reactive plant terpenoids as a model to propose a three-tier (atmosphere – vegetation – soil) framework to better understand the ecological and evolutionary functions of SOM. Image credits: Jarmo K. Holopainen. Cover design by Susanne C. Brink.

Opinion

Plant-derived Secondary Organic Material in the Air and Ecosystems

J.K. Holopainen,^{1,*} M. Kivimäenpää,¹ and S.A. Nizkorodov^{2,3}

Biogenic secondary organic aerosol (SOA) and deposited secondary organic material (SOM) are formed by oxidation of volatile organic compounds (VOCs) emitted by plants. Many SOA compounds have much longer chemical lifetimes than the original VOC, and may accumulate on plant surfaces and in soil as SOM because of their low volatility. This suggests that they may have important and presently unrecognized roles in plant adaptation. Using reactive plant terpenoids as a model we propose a three-tier (atmosphere–vegetation–soil) framework to better understand the ecological and evolutionary functions of SOM. In this framework, SOA in the atmosphere is known to affect solar radiation, SOM on the plant surfaces influences the interactive organisms, and wet and dry deposition of SOM on soil affects soil organisms.

Degradation of Plant Volatiles Leads to Secondary Organic Material

Plants represent the largest source of **volatile organic compounds (VOCs)** (see [Glossary](#)) into the atmosphere [1–3]. Plants use VOCs in many ways to reduce abiotic or biotic stress or communicate with other organisms [4–7]. Typically, plants utilize VOC blends with one or few key volatile compounds as signaling compounds to repel herbivores or to attract pollinators and natural enemies of herbivores [8]. Most of the VOCs emitted by plants have relatively short lifetimes in the atmosphere ranging from less than a minute to few hours depending on the atmospheric conditions [5]. The short lifetime, with a deep concentration gradient around the emission source might have evolved to keep the high signaling value of induced VOCs to guide other organisms [9]. Recently, high reactivity of plant VOCs in polluted atmosphere has been associated with loss of their ecological functions [10–13].

Our current knowledge of biogenic **secondary organic aerosol (SOA)** and **secondary organic material (SOM)** formation from plant volatiles is limited and most of the experimental evidence of the formation processes comes from atmospheric oxidation of VOC in reaction chambers, where they are exposed to natural atmospheric oxidants in controlled conditions [14,15] or from atmospheric measurements above forests [16]. Plant foliage is the most important source of biogenic VOCs in nature, but also represents an important sink by adsorption on leaves and uptake through stomata, representing in some cases over 40% of emitted VOCs [17,18]. However, **primary organic aerosol (POA)** such as fungal spores and carbon from fossil fuel combustion as well as inorganic aerosols may contribute VOC adsorption. Furthermore, microbiota on plant surfaces (phyllosphere) may also contribute to both VOC emission and adsorption [19]. The chemical behavior of VOCs and SOM in plant foliage is the key for understanding the role of secondary compounds for plant biology and ecosystem function. Some known first-stage volatile reaction products of VOCs such as gaseous methacrolein, which is produced by oxidation of isoprene, have been shown to affect plant species interaction [20]. The ecological effects of less volatile VOC oxidation products are

Trends

Oxidation of biogenic and anthropogenic VOCs in the atmosphere leads to formation of SOA particles which further grow and participate in cloud formation, and affect solar irradiation, temperature, and precipitation.

Part of the atmospheric SOA also accumulates as SOM on foliage of plants and deposits on soil surface.

Biogenic VOCs are emitted at high rates from plant foliage, but SOM formation under conditions found in the leaf boundary layer is unexplored.

The ecological and evolutionary effects of biogenic VOCs may persist even after the original VOCs are oxidized. SOM formed from plant VOCs are expected to have even stronger ecological effects than the parent VOCs as these oxidation products are decorated with a number of reactive functional groups (carbonyls, carboxyls, hydroxyls, peroxy, hemiacetal, etc.) which may affect, for example, sensory organs of herbivores.

¹Department of Environmental and Biological Sciences, University of Eastern Finland, FI-70211 Kuopio, Finland

²Department of Chemistry, 1102 Natural Sciences II, University of California, Irvine, CA 92697-2025, USA

³Department of Applied Physics, University of Eastern Finland, FI-70211 Kuopio, Finland

*Correspondence: jarmo.holopainen@uef.fi (J.K. Holopainen).

presently unknown, but can be expected to be stronger than for the parent VOCs, because these products are decorated with a number of reactive functional groups (carbonyls, carboxyls, hydroxyls, peroxy, hemiacetal, etc.), which may affect also gustatory sensors of herbivores [21]. Thus, the ecological functions of SOM formed from plant VOCs may have adaptive value for plants. Analyses of decaying plant litter of monoterpene-storing plant species have found SOM species known as early-stage products of atmospheric oxidation of monoterpenes [22]. Therefore, using reactive plant **terpenoids** as a model, we propose a three-tier (atmosphere, vegetation surfaces, soil) framework of SOM formation and deposition to better understand the ecological and evolutionary functions of SOM in the atmosphere and in ecosystems on individual plant and community level (Figure 1, Key Figure).

Formation and Aging of SOA in Atmosphere

The specific blend of VOCs emitted by a single plant is highly individual and strongly dependent on environmental conditions, including time of year, temperature, humidity, and presence of herbivores [5,23,24]. Furthermore, multiple plant species emit their own blends of VOCs at the same time resulting in a complex mixture of **primary VOCs**, which have variable atmospheric lifetimes. However, there are usually one or a few principal VOC compounds, such as isoprene or α -pinene, which dominates the emissions of volatiles and resulting SOA formation [24]. For the purpose of this opinion article, we will focus on the chemistry of α -pinene, which accounts for more than 30% of global monoterpene emissions, but similar considerations should apply to environments dominated by other types of VOCs. Reaction chamber experiments with real plant VOC emissions have indicated that SOA mass yields are generally lower, but within the same range as found in single precursor VOC experiments [25,26]. However, abiotic [14,27] and biotic [27–29] stressors cause plants to substantially increase VOC emissions and SOA yields.

Box 1 illustrates a typical fate of α -pinene in a boreal forest atmosphere. Under representative atmospheric conditions, α -pinene is converted into its first-generation oxidation products, such as pinonaldehyde or *cis*-pinonic acid, on a timescale of few hours. The first-generation products of VOCs have considerably lower volatility than their precursor species [30] and are distributed between the gas and particle phases of SOA. Further oxidation produces progressively less volatile products, such as 10-hydroxypinonic acid and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) [31], which are found almost exclusively in the condensed (particle) phase of SOA. Furthermore, the monomeric oxidation products, which retain remnants of the initial molecular structure of α -pinene, can dimerize in the condensed phase resulting in larger dimer molecules with even lower vapor pressures. Such dimer compounds have been detected in both laboratory and field measurements [32–34].

The recent advances in high-resolution mass spectrometry suggest that the SOA particles are not only chemically complex [35], but also change their chemical composition over time as a result of various chemical and photoinitiated **aging** processes [36]. The same chemical processes are expected to affect SOM deposited on various surfaces, including vegetation. For example, exposure of biogenic or anthropogenic SOAs to sunlight was found to trigger photodegradation of organic compounds as well as release of small oxidized VOCs, such as formic acid and acetone, in the air [37]. Exposure of particles to common oxidants, such as OH, O₃, and NO₃, leads to heterogeneous reactions that modify both the surface and bulk composition of the particles [38].

Removal of SOA from the atmosphere involves dry and wet deposition in various ecosystems, with the SOA compounds ending up on various environmental surfaces as SOM. For example, accumulation of biogenic SOM deposition layers was detected in snow [39] and ice of high mountain glaciers [40]. Biogenic SOA and SOM can be recognized through unique tracer

Glossary

Aging: various chemical processes, often driven by sunlight, which slowly occur in SOM and change its chemical composition. Aging finally leads to full degradation of SOM and emissions of volatile products such as formic acid.

Cloud condensation nuclei

(CCNs): aerosol particles, typically over 100 nm in size, on which water vapor condenses to form cloud droplets.

Herbivore-induced plant volatiles

(HIPVs): a bouquet of plant volatiles emitted after plant tissue damage by a herbivore. Constitutively emitted VOCs are emitted at higher rates after the damage, and emissions of several other compounds are induced. Typical compounds are 6-carbon green leaf volatiles including aldehydes, esters, and alcohols released after mechanical damage to plant cell membranes.

Primary organic aerosol (POA):

primary organic aerosol represents organic particles emitted from biogenic (fungal spores, plant debris, wildfires) or anthropogenic (fossil fuel combustion, biomass burning) sources.

Secondary organic aerosol (SOA):

consisting of particulate matter and gaseous species produced by oxidation of various biogenic and anthropogenic VOCs in air.

Secondary organic material

(SOM): containing low volatility SOA compounds that accumulate in condensed phase including SOA particles and films on surfaces of plants and on other objects. (Not to be confused with soil organic matter, which has the same abbreviation in the current literature.)

Terpenoids: compounds derived

from one or more isoprene units (C₅H₈), including monoterpenes (C₁₀H₁₆), sesquiterpenes (C₁₅H₂₄), and their numerous derivatives. Many VOCs emitted by plants belong to the terpenoid family.

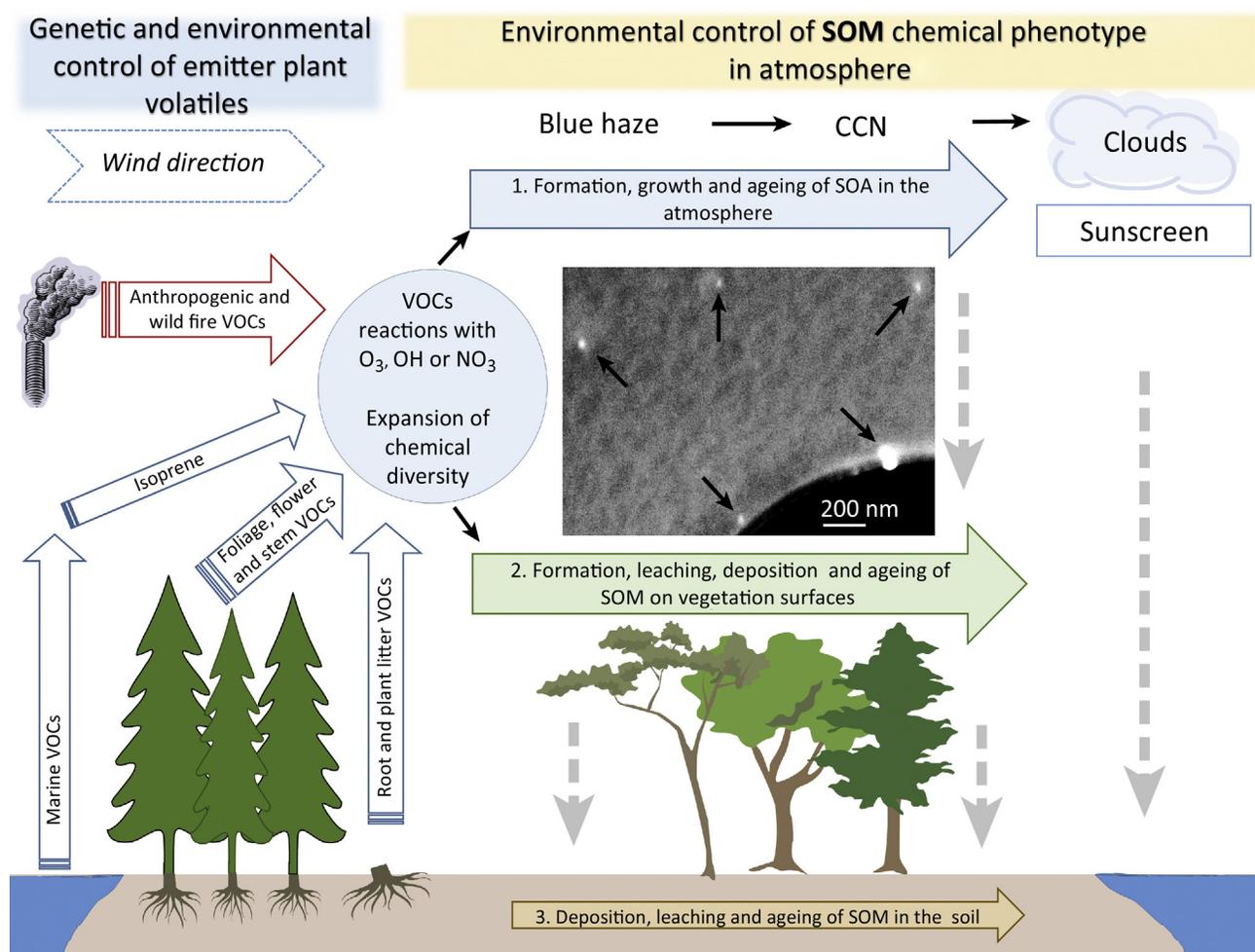
Volatile organic compounds

(VOCs): emitted from biogenic (plants, animals, microbes) or anthropogenic (fossil fuel production and use, biomass burning) sources. VOCs synthesized by plants have various functions in plant physiology, and when emitted, they have various ecological purposes, for example, to repel herbivores or attract pollinators.

compounds formed from biogenic VOCs by atmospheric photooxidation (Table 1). It has been estimated that global biogenic and anthropogenic VOC emissions add up to 1350 TgC/y [15]. Of this amount, ~150 TgC/y is estimated to become deposited as particles and ~800 TgC/y as organic vapors to various ecosystems [15,41], becoming SOM. Based on the large amounts of deposited SOM, and based on the expectation that SOM molecules have higher biological activity compared to VOCs, we can conclude that the global ecological effects of deposited SOM may be comparable those of their parent VOCs.

Key Figure

A Conceptual Model of VOC Degradation, SOA and SOM Formation and SOM Aging in Atmosphere, Surfaces of Vegetation and in Soil of Terrestrial Ecosystems



Trends in Plant Science

Figure 1. Most atmospheric VOCs are emitted by living plants and decaying plants in soils. In addition, marine phytoplankton is a significant emission source of VOCs, such as isoprene, at lower latitudes [74]. A significant fraction of the emitted VOCs ends up in SOA. There is deposition of SOA from atmosphere and leaching of SOM from vegetation and soil to aquatic ecosystems. Unbroken arrows indicate the direction of VOC release and chemical evolution of VOCs and release of degradation VOCs from SOM. Broken arrows indicate the direction of SOM deposition and leaching. Potential feedback routes and other effects of VOC and SOM on the VOC emitting and storing plants are not indicated to simplify the three-tier framework. *Tier 1: SOA in the Atmosphere.* Feedback effects on the first tier in the atmosphere are always on ecosystem scale and may influence vegetation at several hundred kilometers distances from the emitter plants depending on the prevailing winds. SOA in

(See figure legend on the bottom of the next page.)

SOM on Plant Surfaces

Leaf surface has an important role as a VOC emitter, but it may also serve as a SOM sink and substrate for further SOM aging chemistry. Both SOA particles and semivolatile molecules will readily deposit on surfaces of emitter and nonemitter plants forming a film of SOM that includes a variety of organic compounds (peroxides, carbonyls, carboxylic acids, alcohols, esters, hemiacetals, etc.).

There could be shortcuts that form SOM on plant surfaces without the intermediary of SOA. In the leaf boundary layer, the atmospheric concentrations of VOCs are elevated before their dilution during emissions. Therefore, VOC oxidation products may form faster and be deposited directly on surfaces of the emitting plants. Isoprene, the most abundant biogenic VOC emitted by vascular plants, and its first-generation oxidation products methyl vinyl ketone (MVK) and methacrolein are common in leaf headspace [42]. It has been shown that there is a bidirectional flux of these compounds from/to leaves and uptake by leaves from the atmosphere [43], but earlier ecosystem level analysis suggested that deposition on plant surfaces is dominant [44]. It has also been proposed that the primary VOCs can be oligomerized directly on the surfaces of vegetation [45], producing SOM. In addition, photosensitized processes have been suggested as a potential route for direct oxidation of VOCs into SOM on surfaces [45,46]. Thin, mildly acidic water films on surfaces of plant foliage at night time create an environment for the reactive uptake of gaseous isoprene and converting it into less volatile oligomeric products [45].

Plant leaves are known to act as an important sink of hygroscopic aerosol particles [47]. Particles smaller than 300 nm can even penetrate into the intercellular space of the leaf via stomata [48,49]. In the case of SOA, experimental evidence of particle deposition directly on plant leaves is still lacking, but it is reasonable to assume that the particles readily stick to the leaf surfaces. While SOA particles remain in air for just a few days, SOM can remain on surfaces of plants considerably longer especially for hydrophobic compounds that cannot be efficiently washed away by dew condensation on surfaces or rain. Therefore, the aging processes mentioned above in the context of SOA particles may be much more extensive in the SOM material deposited on plant surfaces.

Monoterpenes emitted from forest rapidly become semivolatile and low-volatility compounds and condense on surfaces of existing aerosol particles [16]. Some of the early-generation SOM species may behave similarly to the semivolatile sesquiterpene alcohols ledol and palustrol. These compounds are emitted by *Rhododendron tomentosum* and were detected in atmospheric SOA particles [50] and found on the surfaces of other plant species [51]. These compounds, which are common only in one emitter plant species in boreal and subarctic ecosystems, might offer a model system to better understand the ecological functions and biological effects of plant-derived SOM. Ledol and palustrol, when deposited on the surfaces of neighboring plants, reduced specialist moth oviposition on foliage [52]. Similarly moth larvae avoided surfaces of filters exposed to O₃-transformed damaged host plant VOCs at 100 ppb

atmosphere affects light dispersion into tree canopies, further particle growth to CCN leads to cloud formation and sun-screening effects (negative radiative climate effect). These effects have important role in adaptation of vegetation to changing climate [75] on biome scale. *Tier 2: SOM in the Vegetation.* SOM formation and deposition on the green and protecting surfaces of vascular plants have important effects on community level in the ecosystem where the emitting plant grows. VOC reaction products in SOM may improve fitness of the emitting individual, but also fitness of other individuals of the same plant species and fitness of individuals of other plant species [76]. For example, SOM products on the plant foliage affect species interactions and may reduce herbivore pressure [53]. Scanning electron microscope image shows SOA particles (arrows) formed in α -pinene and ozone reactions in a reaction chamber. These sub-100 nm (ultrafine) particles were deposited on the surface of a copper grid covered by perforated carbon film in a 99-l glass chamber connected to the outlet of the reaction chamber. *Tier 3: SOM in the Soil.* In soil ecosystem, there are two distinctively different SOM forming plant VOC sources, plant rhizosphere and VOC-storing dead plant material accumulating on soil. Mechanisms of SOM formation in soil are poorly known. Deposition of SOM from atmosphere on soil can be a result of long-range transport of SOA. Leaching of SOM from plant surfaces might lead to accumulation of SOM, for example, under tall trees. Microbial activity may have important role in degradation of stored VOC compounds in dead plant material, but also in breakdown of deposited SOM. Abbreviations: CCN, cloud condensation nuclei; SOA, secondary organic aerosol; SOM, secondary organic material; VOC, volatile organic compound.

Box 1. Formation of SOM in Oxidation of Primary VOC Emissions

Once emitted by vegetation and soils, the primary VOCs are converted into various photooxidation products by reactions with photochemically created gas-phase oxidants (Figure 1). Continued photooxidation and particle-phase accretion reactions create progressively less volatile compounds, which eventually deposit into aerosol particles or on various surfaces, including surfaces of plants. Effective lifetimes (τ) with respect to gas-phase reactions with OH, O₃, and NO₃ and with respect to photolysis (denoted by subscript hv) are calculated (Table 1), assuming constant oxidant concentrations fixed at the typical ambient values of daytime [OH] = 2×10^6 molecules/cm³, daytime [O₃] = 1.2×10^{12} molecules/cm³ (about 50 ppb), and nocturnal [NO₃] = 2.5×10^8 molecules/cm³ (about 10 ppt). Rate constants and peak photolysis rates for α -pinene, pinonaldehyde, *cis*-pinonic acid, and 10-hydroxypinonic acid are taken from recommendations in [77–79]. Parameters for verbenone and other compounds are estimated from values found for structurally related compounds that exist in the Master Chemical Mechanism for VOC photooxidation [77–79] (e.g., the photolysis rate for the carbonyl group in the 368-dimer is taken to be the same as that for *cis*-pinonic acid). If the rate is missing it means the reaction is expected to be much too slow to contribute to the removal of the compound. For example, ozone reactions are only significant for compounds containing unsaturated C=C bonds, NO₃ reactions are significant for the unsaturated compounds and aldehydes, and photolysis is only significant for carbonyls and peroxides.

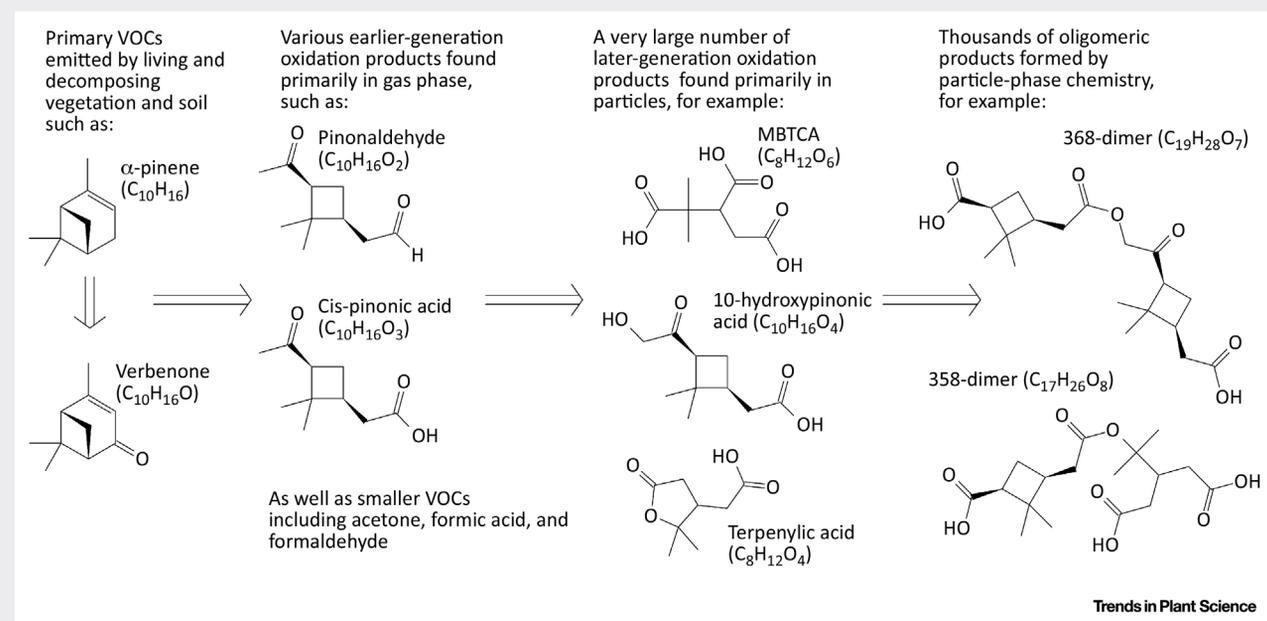


Figure 1. Conversion of Primary VOCs into Various Photooxidation Products. Abbreviations: MBTCA, 3-methyl-1,2,3-butanetricarboxylic acid; VOC, volatile organic compound.

Table 1. Effective Lifetimes (τ) of Primary VOCs and Various Photooxidation Products

	Primary VOC		Earlier-generation oxidation products		Later-generation oxidation products		
Common name	α -Pinene	Verbenone	Pinonaldehyde	<i>cis</i> -Pinonic acid	10-Hydroxypinonic acid	3-Methyl-1,2,3-butanetricarboxylic acid (MBTCA)	The '368-dimer' (and similar numerous oligomeric products)
Primarily in	Gas phase	Gas phase	Gas phase	Particle and gas phases	Particle phase	Particle phase	Particle phase
τ_{OH} (hours)	2.6	2.3	3.3	21	24	23	17
τ_{O_3} (hours)	2.6	1.5	–	–	–	–	–
τ_{NO_3} (hours)	0.18	0.12	56	–	–	–	–
τ_{hv} (hours)	–	10	14	69	69	–	69

ozone and spent less time searching on them compared to filters exposed to host plant VOCs in filtered air [53]. This is the first evidence that SOM formed on surfaces of plants other than emitter plants may have effects on species interaction. Reduced fitness of moth on plants with SOM deposition originating from metabolome of neighboring plant typically represents an extended phenotype effect [54,55] of emitter plant. It also demonstrates potential community effects [56,57] of SOM compounds from specific genotypes of living plants.

Table 1. Examples of Tracer Compounds of Biogenic SOA/SOM Originating from Ozonolysis and OH Reactions of Isoprene, Monoterpenes α -Pinene and β -Pinene or Sesquiterpene β -Caryophyllene

Isoprene tracers	α / β -Pinene tracers	β -Caryophyllene tracers
2-Methylglyceric acid [40,80]	Norpinic acid [81]	β -Caryophyllinic acid [80]
2-Methylthreitol [40,80]	10-Hydroxypinonic acid [81]	β -Caryophyllene aldehyde [82]
2-Methylerythritol [40,80]	Diterpenylic acid acetate [81]	β -Nocaryophyllone aldehyde [82]
<i>cis</i> -2-Methyl-1,3,4-trihydroxy-1-butene [40,80]	Dinorpinic acid [81]	β -Nocaryophyllon aldehyde [83]
<i>trans</i> -2-Methyl-1,3,4-trihydroxy-1-butene [40,80]	8-Hydroxypinonic acid [81]	β -Hydroxynocaryophyllon aldehyde [83]
3-Methyl-2,3,4-trihydroxy-1-butene [40,80]	3-Hydroxyglutaric acid [40,80]	β -Dihydroxynocaryophyllon aldehyde [83]
	<i>cis</i> -Pinonic acid [40,80]	
	Pinic acid [40,80]	
	3-Methyl-1,2,3-butanetricarboxylic acid (MBTCA) [31,80]	

SOM in Soil

Soil is an important source of biogenic VOCs released by living plant roots and other organisms such as fungi and bacteria, but it may also act as a sink of VOCs [58]. Dead plant material, such as wood [59] and needle litter [60] of terpene-storing plant species, is a significant source of soil VOCs and possibly they form SOM by both biotic and abiotic pathways. (We should note that abbreviation 'SOM' is often used in the soil literature for 'soil organic matter', which is a larger pool of organics and includes the secondary organic material from VOC oxidation that discussed in this paper.) For instance, there was substantial reduction in monoterpene content of Scots pine needle litter during 19 months of natural decomposition, and at the same time concentration of several monoterpene oxidation products including α -pinene-derived verbenone, verbenol, and myrtenal increased in litter [22]. These secondary compounds in litter are believed to be fungal conversion products of α -pinene [61]. However, verbenone [62] has been found in organic aerosols above forests, and myrtenal is an important early-stage α -pinene oxidation product, which after further oxidation leads to formation of terebic acid and pinic acid, important α -pinene tracers in SOA [63]. Biogenic SOM in the soil may originate directly from oxidation of dead plant material, leached from surfaces of living plants or deposited directly to soil from atmosphere. The SOM accumulated in the soil may have long lifetimes, and SOM effects on soil organisms can be ecologically considered as afterlife effects of plants [56], that is, the original producer of VOCs and SOM might not be alive any longer.

As previously described, snow [39] and ice covers [40] accumulate atmospheric SOM, but snow surface possibly lack biotic production of SOM. Snow and ice depositions could potentially be used to distinguish between deposited SOA and SOM formed in soil processes. So far, no analysis of biogenic SOA/SOM deposited directly or leached to soil layers has been done.

Ecological and Co-evolutionary Considerations of SOM

Plant VOC emissions are typically divided into constitutive and induced. Constitutive VOCs are normally used as orientation cues by specialist herbivores of the host plant. Polyphagous herbivores and specialist herbivores of other plant species are usually repelled by these emissions [5]. The induced VOCs that are emitted after herbivore feeding have a much more diverse blend of VOCs, and typically attract enemies of herbivores. The **herbivore-induced plant volatiles (HIPV)** are often dominated by compounds such as sesquiterpenes and homoterpenes, which are more reactive towards oxidants than constitutive emission VOC blends [64], and are efficiently converted into SOA.

Abiotic and biotic stressors affect not only the VOC emissions but also the properties of resulting SOA. SOA particles formed from herbivore-induced VOCs have higher hygroscopicity; the particles grow faster and show improved potential to act as **cloud condensation nuclei (CCN)** [65]. Does the improved CCN formation from stressed terrestrial plants imply feedback

between plants and local climate [66,67]? In natural ecosystems, wind stimulates VOC emissions from plants [68] and prevailing winds may result in SOA particle formation visible as 'blue haze', to take place downwind from the emitting forest stand [67]. In this case, the light scattering effect of SOA [69] may only partly affect the VOC emitting population by the improved diffusion of solar light within the canopy [67]. SOA taken by air currents to cloud base (1 km altitude) may affect formation of CCN and have atmospheric feedback to ecosystems even hundreds of kilometers from the emission site [28]. This suggests the plant-SOA-dependent feedback in climatic conditions takes place in regional scale in large ecosystems, called biomes.

At the plant foliage level, chemical properties of SOM might be most important to affect biotic interactions on plants. High reactivity of induced VOCs and rapid formation of SOM in the headspace of the herbivore-damaged *Brassica* plants have been demonstrated [53]. Herbivorous diamond back moth (*Plutella xylostella*) larvae avoided filters exposed to O₃-transformed *Brassica* VOCs and spent less time searching on them compared to filters exposed to original *Brassica* VOCs in filtered air. This served as evidence that SOM formed in ozonolysis reactions and accumulated on simulated leaf surfaces has repellent properties [53]. Avoidance of SOM-containing surfaces by herbivore larvae may reduce feeding damage and eventually improve plant fitness. Another study [70] with *P. xylostella* adults and artificial leaves (microscope slides covered with broccoli leaf wax) showed that herbivore-induced VOCs were adsorbed on artificial leaves in filtered air and the leaves released 24 h and 48 h afterwards adsorbed sesquiterpenes. Artificial leaves were preferred for egg-laying by *P. xylostella*, but if leaves were exposed to herbivore induced VOCs at air with 80 nmol mol⁻¹ ozone, artificial leaves did not release sesquiterpenes anymore and lower numbers of eggs were laid on them. Surface chemistry was not analyzed, but it can be speculated that the loss of sesquiterpenes led to formation of SOM on artificial leaves, and SOM might have partly affected the egg-laying rate.

Various derivatives of the same plant volatile compound might have very different ecological functions. Monoterpene α -pinene emitted by host trees is an attractant for the females and males of the mountain beetle *Dendroctonus ponderosae* [71]. Derivatives (*cis*-verbenol and *trans*-verbenol) of dietary α -pinene produced in fat body tissue of these bark beetles act as aggregation pheromones, but under high population density beetle-repelling verbenone is produced. Verbenone also exists in pine emissions and it is found in natural SOA [62], but under sunny conditions, this compound is photoisomerized to chrysanthenone, a compound with no known effects on bark beetle behavior [71]. However, chrysanthenone acts as an attractant for females of xylem feeding Cerambycid beetles [72]. We may expect SOM formed from plant terpenes to have diverse ecological functions depending on the type of SOM formation process and aging.

It is obvious that at least part of the SOM formed from plant VOC emission in the headspace of foliage can be deposited on other plants. Given that it takes a few hours to oxidize VOC into SOM (Box 1), the air mass can travel many kilometers (assuming average wind speeds of ~10 km/h) before VOCs are oxidized and deposited as SOM. Does this have any ecological relevance? We might expect that ecological information can be the same at 1 m and 100 km distance, if the vegetation type and ecosystem structure is the same. For example, if SOM formed from pine VOCs can act as a repellent for pine-feeding beetles it should act as a feeding repellent to the same herbivore on all pine trees downwind of the emission site.

We may expect that ecologically effective distance of SOM is therefore longer than the 1-m [9] distance that was found to be effective in plant-plant communication by induced plant VOCs. By contrast, deposition of species-specific semivolatile VOCs of emitting neighboring plants have been detected on birch foliage at a 5-m distance from emitter plant [51]. This suggests

that also semivolatile reaction products of plant VOC in the early stage of SOM formation process can stick on surfaces of neighboring plants. So far, we cannot detect SOM from plant foliage and evaluate the proportions of SOM from self-emitted VOC and deposited SOM originating from other plants.

Concluding Remarks and Future Perspectives

In this opinion paper, we propose that both the SOM made of early-generation VOC oxidation products and the complex mixture of products of further SOM aging can significantly affect the plant–plant interactions and plant interactions with other organisms [53] and also have wide-ranging ecosystem level effects. Better knowledge of the chemical fate and effects of biogenic SOM might improve identification and quantification of chemical signatures of stress at the ecosystem scale [73] and help reveal how ecosystems will respond and adapt to future climate change (see Outstanding Questions). The plant scientists and ecologists should look beyond the effects of the initially emitted VOCs and start doing laboratory experiments and field measurements on various biological effects of SOM as well as gaseous VOC oxidation products. Better knowledge of the biological effects of plant VOC oxidation products may allow development of future SOM-based applications in plant resistance breeding and biological control.

Author Contributions

Authors developed the hypothesis together, J.K.H. drafted the manuscript, and all authors gave critical input in the final version of the manuscript.

Acknowledgments

J.K.H and M.K. acknowledge the financial support from the Academy of Finland (project no. 278424). S.N. acknowledges Fulbright Finland Foundation and the Saastamoinen Foundation that funded his visit to the University of Eastern Finland.

References

- Guenther, A. *et al.* (1995) A global model of natural volatile organic compound emissions. *J. Geophys. Res. Atmos.* 100, 8873–8892
- Sindelarova, K. *et al.* (2014) Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years. *Atmos. Chem. Phys.* 14, 9317–9341
- Laothawornkitkul, J. *et al.* (2009) Biogenic volatile organic compounds in the Earth system. *New Phytol.* 183, 27–51
- Loreto, F. and Schnitzler, J.P. (2010) Abiotic stresses and induced BVOCs. *Trends Plant Sci.* 15, 154–166
- Blande, J.D. *et al.* (2014) Plant volatiles in polluted atmospheres: stress responses and signal degradation. *Plant Cell Environ.* 37, 1892–1904
- Loreto, F. *et al.* (2014) Plant volatiles and the environment. *Plant Cell Environ.* 37, 1905–1908
- Kask, K. *et al.* (2016) How specialized volatiles respond to chronic and short-term physiological and shock heat stress in *Brassica nigra*. *Plant Cell Environ.* 39, 2027–2042
- Junker, R.R. *et al.* (2017) Covariation and phenotypic integration in chemical communication displays: biosynthetic constraints and eco-evolutionary implications. *New Phytol.* Published online March 3, 2017. <http://dx.doi.org/10.1111/nph.14505>
- Heil, M. and Karban, R. (2010) Explaining evolution of plant communication by airborne signals. *Trends Ecol. Evol.* 25, 137–144
- Himanen, S.J. *et al.* (2009) Effects of elevated carbon dioxide and ozone on volatile terpenoid emissions and multitrophic communication of transgenic insecticidal oilseed rape (*Brassica napus*). *New Phytol.* 181, 174–186
- Blande, J.D. *et al.* (2010) Air pollution impedes plant-to-plant communication by volatiles. *Ecol. Lett.* 13, 1172–1181
- Fuentes, J.D. *et al.* (2013) Ozone impedes the ability of a herbivore to find its host. *Environ. Res. Lett.* 8, 014048
- Farre-Armengol, G. *et al.* (2016) Ozone degrades floral scent and reduces pollinator attraction to flowers. *New Phytol.* 209, 152–160
- Kourtchev, I. *et al.* (2016) Enhanced volatile organic compounds emissions and organic aerosol mass increase the oligomer content of atmospheric aerosols. *Sci. Rep.* 6, 35038
- Hallquist, M. *et al.* (2009) The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* 9, 5155–5236
- Ehn, M. *et al.* (2014) A large source of low-volatility secondary organic aerosol. *Nature* 506, 476–479
- Matsui, K. (2016) A portion of plant airborne communication is endorsed by uptake and metabolism of volatile organic compounds. *Curr. Opin. Plant Biol.* 32, 24–30
- Noe, S.M. *et al.* (2008) Foliar limonene uptake scales positively with leaf lipid content: 'non-emitting' species absorb and release monoterpenes. *Plant Biol.* 10, 129–137
- Bringel, F. and Couee, I. (2015) Pivotal roles of phyllosphere microorganisms at the interface between plant functioning and atmospheric trace gas dynamics. *Front. Microbiol.* 6, 486
- Kessler, A. *et al.* (2006) Priming of plant defense responses in nature by airborne signaling between *Artemisia tridentata* and *Nicotiana attenuata*. *Oecologia* 148, 280–292
- Kim, J. and Mullin, C. (1998) Structure-phagostimulatory relationships for amino acids in adult western corn rootworm, *Diabrotica virgifera virgifera*. *J. Chem. Ecol.* 24, 1499–1511
- Kainulainen, P. and Holopainen, J. (2002) Concentrations of secondary compounds in Scots pine needles at different stages of decomposition. *Soil Biol. Biochem.* 34, 37–42
- Carlton, A.G. *et al.* (2009) A review of secondary organic aerosol (SOA) formation from isoprene. *Atmos. Chem. Phys.* 9, 4987–5005

Outstanding Questions

What mass fraction of emitted biogenic VOCs ends up being deposited as SOM on vegetation and soil?

What is a typical lifetime of SOM compounds on plant surfaces with respect to photochemical aging and physical washout?

Can the products of the photochemical aging of SOM on plant surfaces affect plant–plant communication?

How are the plant–herbivore and plant–pollinator interactions affected by the presence of different kinds of SOM on plant surfaces?

Can we develop biological control methods based on SOM derived from natural plant VOCs?

24. Henze, D.K. *et al.* (2008) Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: high- vs. low-yield pathways. *Atmos. Chem. Phys.* 8, 2405–2420
25. Hao, L.Q. *et al.* (2011) Mass yields of secondary organic aerosols from the oxidation of α -pinene and real plant emissions. *Atmos. Chem. Phys.* 11, 1367–1378
26. Wyche, K.P. *et al.* (2014) Emissions of biogenic volatile organic compounds and subsequent photochemical production of secondary organic aerosol in mesocosm studies of temperate and tropical plant species. *Atmos. Chem. Phys.* 14, 12781–12801
27. Mentel, T.F. *et al.* (2013) Secondary aerosol formation from stress-induced biogenic emissions and possible climate feedbacks. *Atmos. Chem. Phys.* 13, 8755–8770
28. Joutsensaari, J. *et al.* (2015) Biotic stress accelerates formation of climate-relevant aerosols in boreal forests. *Atmos. Chem. Phys.* 15, 12139–12157
29. Yi-Pirila, P. *et al.* (2016) Herbivory by an outbreaking moth increases emissions of biogenic volatiles and leads to enhanced secondary organic aerosol formation capacity. *Environ. Sci. Technol.* 50, 11501–11510
30. Troestl, J. *et al.* (2016) The role of low-volatility organic compounds in initial particle growth in the atmosphere. *Nature* 533, 527–531
31. Szmigielski, R. *et al.* (2007) 3-Methyl-1,2,3-butanetricarboxylic acid: an atmospheric tracer for terpene secondary organic aerosol. *Geophys. Res. Lett.* 34, L24811
32. Beck, M. and Hoffmann, T. (2016) A detailed MSn study for the molecular identification of a dimer formed from oxidation of pinene. *Atmos. Environ.* 130, 120–126
33. Kristensen, K. *et al.* (2016) High-molecular weight dimer esters are major products in aerosols from α -pinene ozonolysis and the boreal forest. *Environ. Sci. Technol. Lett.* 3, 280–285
34. Kristensen, K. *et al.* (2013) Formation and occurrence of dimer esters of pinene oxidation products in atmospheric aerosols. *Atmos. Chem. Phys.* 13, 3763–3776
35. Nizkorodov, S.A. *et al.* (2011) Molecular chemistry of organic aerosols through the application of high resolution mass spectrometry. *Phys. Chem. Chem. Phys.* 13, 3612–3629
36. George, C. *et al.* (2015) Heterogeneous photochemistry in the atmosphere. *Chem. Rev.* 115, 4218–4258
37. Malecha, K.T. and Nizkorodov, S.A. (2016) Photodegradation of secondary organic aerosol particles as a source of small, oxygenated volatile organic compounds. *Environ. Sci. Technol.* 50, 9990–9997
38. Rudich, Y. *et al.* (2007) Aging of organic aerosol: bridging the gap between laboratory and field studies. *Annu. Rev. Phys. Chem.* 58, 321–352
39. Kippenberger, M. *et al.* (2008) Determination of higher carboxylic acids in snow samples using solid-phase extraction and LC/MS-TOF. *Anal. Bioanal. Chem.* 392, 1459–1470
40. Pokhrel, A. *et al.* (2016) Ice core records of monoterpene- and isoprene-SOA tracers from Aurora Peak in Alaska since 1660: implication for climate change variability in the North Pacific Rim. *Atmos. Environ.* 130, 105–112
41. Goldstein, A.H. and Galbally, I.E. (2007) Known and unexplored organic constituents in the earth's atmosphere. *Environ. Sci. Technol.* 41, 1514–1521
42. Brill, F. *et al.* (2016) Rapid leaf development drives the seasonal pattern of volatile organic compound (VOC) fluxes in a 'coppiced' bioenergy poplar plantation. *Plant Cell Environ.* 39, 539–555
43. Fares, S. *et al.* (2015) Bidirectional flux of methyl vinyl ketone and methacrolein in trees with different isoprenoid emission under realistic ambient concentrations. *Environ. Sci. Technol.* 49, 7735–7742
44. Park, J.H. *et al.* (2013) Active atmosphere-ecosystem exchange of the vast majority of detected volatile organic compounds. *Science* 341, 643–647
45. Enami, S. *et al.* (2012) Protonation and oligomerization of gaseous isoprene on mildly acidic surfaces: implications for atmospheric chemistry. *J. Phys. Chem. A* 116, 6027–6032
46. Monge, M.E. *et al.* (2012) Alternative pathway for atmospheric particles growth. *Proc. Natl. Acad. Sci. U. S. A.* 109, 6840–6844
47. Burkhardt, J. (2010) Hygroscopic particles on leaves: nutrients or desiccants? *Ecol. Monogr.* 80, 369–399
48. Räsänen, J.V. *et al.* (2017) Titanium dioxide (TiO₂) fine particle capture and BVOC emissions of *Betula pendula* and *Betula pubescens* at different wind speeds. *Atmos. Environ.* 152, 345–353
49. Eichert, T. *et al.* (2008) Size exclusion limits and lateral heterogeneity of the stomatal foliar uptake pathway for aqueous solutes and water-suspended nanoparticles. *Physiol. Plant.* 134, 151–160
50. Rissanen, T. *et al.* (2006) Characterization of organic compounds in aerosol particles from a coniferous forest by GC-MS. *Chemosphere* 64, 1185–1195
51. Himanen, S.J. *et al.* (2010) Birch (*Betula* spp.) leaves adsorb and re-release volatiles specific to neighbouring plants – a mechanism for associational herbivore resistance? *New Phytol.* 186, 722–732
52. Himanen, S.J. *et al.* (2015) Utilizing associational resistance for biocontrol: impacted by temperature, supported by indirect defence. *BMC Ecol.* 15, 16
53. Li, T. *et al.* (2016) Atmospheric transformation of plant volatiles disrupts host plant finding. *Sci. Rep.* 6, 33851
54. Pakeman, R. *et al.* (2006) The extended phenotype of Scots pine *Pinus sylvestris* structures the understorey assemblage. *Ecography* 29, 451–457
55. Gossner, M.M. *et al.* (2015) Where is the extended phenotype in the wild? The community composition of arthropods on mature oak trees does not depend on the oak genotype. *PLoS One* 10, e0115733
56. Whitham, T.G. *et al.* (2012) Community specificity: life and afterlife effects of genes. *Trends Plant Sci.* 17, 271–281
57. Tack, A.J.M. *et al.* (2012) Sizing up community genetics: it's a matter of scale. *Oikos* 121, 481–488
58. Penuelas, J. *et al.* (2014) Biogenic volatile emissions from the soil. *Plant Cell Environ.* 37, 1866–1891
59. Kivimaenpää, M. *et al.* (2012) Influence of tree provenance on biogenic VOC emissions of Scots pine (*Pinus sylvestris*) stumps. *Atmos. Environ.* 60, 477–485
60. Aaltonen, H. *et al.* (2011) Boreal pine forest floor biogenic volatile organic compound emissions peak in early summer and autumn. *Agric. Forest Meteorol.* 151, 682–691
61. van Dyk, M. *et al.* (1998) Hydroxylation of (+)limonene, (–)- α -pinene and (–)- β -pinene by a *Hormonema* sp. *Biotechnol. Lett.* 20, 431–436
62. Anttila, P. *et al.* (2005) Organic compounds in atmospheric aerosols from a Finnish coniferous forest. *Boreal Environ. Res.* 10, 371–384
63. Mutzel, A. *et al.* (2016) Monoterpene SOA – contribution of first-generation oxidation products to formation and chemical composition. *Atmos. Environ.* 130, 136–144
64. Pinto, D.M. *et al.* (2007) Ozone degrades common herbivore-induced plant volatiles: does this affect herbivore prey location by predators and parasitoids? *J. Chem. Ecol.* 33, 683–694
65. Zhao, D.F. *et al.* (2017) Environmental conditions regulate the impact of plants on cloud formation. *Nat. Commun.* 8, 14067
66. Penuelas, J. and Llusia, J. (2003) BVOCs: plant defense against climate warming? *Trends Plant Sci.* 8, 105–109
67. Holopainen, J.K. (2011) Can forest trees compensate for stress-generated growth losses by induced production of volatile compounds? *Tree Physiol.* 31, 1356–1377
68. Bourtsoukidis, E. *et al.* (2014) On-line field measurements of BVOC emissions from Norway spruce (*Picea abies*) at the hemiboreal SMEAR-Estonia site under autumn conditions. *Boreal Environ. Res.* 19, 153–167
69. Harvey, R.M. *et al.* (2016) Optical properties of secondary organic aerosol from *cis*-3-hexenol and *cis*-3-hexenyl acetate: effect of chemical composition, humidity, and phase. *Environ. Sci. Technol.* 50, 4997–5006

70. Li, T. and Blande, J.D. (2015) Associational susceptibility in broccoli: mediated by plant volatiles, impeded by ozone. *Global Change Biol.* 21, 1993–2004
71. Progar, R.A. *et al.* (2014) Applied chemical ecology of the mountain pine beetle. *For. Sci.* 60, 414–433
72. Zhang, Y. *et al.* (2015) Identification of *Caragana* plant volatiles, overlapping profiles, and olfactory attraction to *Chlorophorus caragana* in the laboratory. *J. Plant Interact.* 10, 41–50
73. Kravitz, B. *et al.* (2016) A new paradigm of quantifying ecosystem stress through chemical signatures. *Ecosphere* 7, e01559
74. Dani, K.G.S. and Loreto, F. (2017) Trade-off between dimethyl sulfide and isoprene emissions from marine phytoplankton. *Trends Plant Sci.* 22 (5), 361–372
75. Ameth, A. *et al.* (2016) Future vegetation–climate interactions in Eastern Siberia: an assessment of the competing effects of CO₂ and secondary organic aerosols. *Atmos. Chem. Phys.* 16, 5243–5262
76. Whitham, T.G. *et al.* (2006) A framework for community and ecosystem genetics: from genes to ecosystems. *Nat. Rev. Genet.* 7, 510–523
77. Jenkin, M. *et al.* (1997) The tropospheric degradation of volatile organic compounds: a protocol for mechanism development. *Atmos. Environ.* 31, 81–104
78. Saunders, S. *et al.* (2003) Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds. *Atmos. Chem. Phys.* 3, 161–180
79. Atkinson, R. *et al.* (2006) Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – Gas phase reactions of organic species. *Atmos. Chem. Phys.* 6, 3625–4055
80. Haque, M.M. *et al.* (2016) Seasonal variations of biogenic secondary organic aerosol tracers in ambient aerosols from Alaska. *Atmos. Environ.* 130, 95–104
81. Yasmeen, F. *et al.* (2012) Characterisation of tracers for aging of α -pinene secondary organic aerosol using liquid chromatography/negative ion electrospray ionisation mass spectrometry. *Environ. Chem.* 9, 236–246
82. Parshintsev, J. *et al.* (2008) Preparation of α -caryophyllene oxidation products and their determination in ambient aerosol samples. *Anal. Bioanal. Chem.* 390, 913–919
83. Chan, M.N. *et al.* (2011) Influence of aerosol acidity on the chemical composition of secondary organic aerosol from α -caryophyllene. *Atmos. Chem. Phys.* 11, 1735–1751