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ADEDAYO OLUDELE MOFIKOYA

**PROTECTIVE FUNCTIONS OF PLANT SEMI-VOLATILES AND
THEIR DEGRADATION PRODUCTS ON PLANT SURFACES**

Adedayo Oludele Mofikoya

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SURFACES

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Protective functions of plant semi-volatiles and their degradation products on plant surfaces

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ABSTRACT

Plants synthesize and emit a plethora of volatile and semi-volatile organic compounds (VOCs and SVOCs) as a means of interacting and adapting to their environment. These compounds play important roles in plant defence against biotic and abiotic stressors, plant interactions with other plants, pathogens and arthropods as well as atmospheric chemistry. Plants emit VOCs constitutively and in response to biotic and abiotic stressors. Once released, VOCs may serve as signalling molecules to other plant parts or neighbouring plants. They may also be used by plant pests and other insects as host location cues and by pollinators as foraging signals. In the atmosphere, VOCs serve as precursors for the formation of tropospheric ozone (O₃) – a secondary atmospheric pollutant – and may be oxidized by atmospheric pollutants to form secondary organic aerosol (SOA).

This thesis explores volatile-mediated plant-to-plant interactions in nature, it also considers the effect of tropospheric O₃ on volatile-mediated interactions. Additionally, it considers the effects of the products of reactions of VOCs with O₃ and other atmospheric oxidants on plant VOC emissions and their interactions with arthropods.

To address the question of volatile-mediated plant-to-plant interactions in nature, mountain birch, *Betula pubescens*, trees in a Finnish subarctic forest were grouped based on the density of naturally occurring *Rhododendron tomentosum* shrubs in their understorey. It was observed that VOCs and SVOCs emitted by *R. tomentosum* were passively adsorbed and re-emitted by *B. pubescens* branches growing above them. The density of *R. tomentosum* growing in the understorey as well as foliar glandular trichome density of both *R. tomentosum* and *B. pubescens*, affected their volatile emissions. To test the effects of O₃ on volatile-mediated interactions between plants and other organisms, a system comprising *R. tomentosum* as an emitter plant, white cabbage, *Brassica oleracea*, as a receiver plant and the specialist cruciferous

pest *Plutella xylostella* as a herbivore was utilised. VOCs and SVOCs emitted by *R. tomentosum* were passed through air with elevated ozone levels that reached a concentration of 100ppb before being exposed to the receiver *B. oleracea* plants. Ozone degraded some compounds, which resulted in the formation of reaction products and thus changed the blend of *R. tomentosum* VOCs. Ozone degradation also affected the blend of *R. tomentosum* volatiles adsorbed by cabbage, but did not alter the resistance to *P. xylostella* oviposition conferred on *B. oleracea* plants by exposure to *R. tomentosum* volatiles.

The degradation of VOCs by atmospheric oxidants leads to the formation of less volatile reaction products and SOA that may be deposited on plant surfaces, subsequently affecting plant chemistry and plant-insect interactions. To test the effects of VOC oxidation products and SOA on plant chemistry and plant-herbivore interactions, α -pinene, a ubiquitous monoterpene emitted by a wide range of plants was oxidized by O₃ and OH radicals in a flow tube and chamber system. The reaction products and SOA from these O₃- and OH-induced α -pinene oxidation were then passed into a 99L glass chamber containing cabbage, *B. oleracea*, plants. Exposure to α -pinene oxidation products and SOA altered the VOC emission of cabbage plants; exposed cabbage plants adsorbed and re-emitted gas-phase α -pinene oxidation products as part of their volatile bouquet. Exposure to SOA and α -pinene oxidation products also affected *P. xylostella* oviposition and reduced feeding by the polyphagous Indian stick insect, *Carausius morosus* on cabbage plants.

In conclusion, this thesis highlights the phenomenon of passive adsorption and re-emission of VOCs, SVOCs and VOC oxidation products by plants and their implications for plant-herbivore interactions.

Universal Decimal Classification: 574.2, 581.116, 581.573, 582.622.2, 582.683.211, 632.7

CAB Thesaurus: plants; plant ecology; plant interaction; volatile compounds; organic compounds; aerosols; atmosphere; ozone; oxidation; degradation; terpenoids; sesquiterpenoids; alpha-pinene; adsorption; deposition; Betula pubescens; Rhododendron tomentosum; Brassica oleracea var capitata; insect pests; herbivores; herbivory; oviposition; Plutella xylostella; Carausius morosus; repellents; leaves; epidermis; trichomes; Finland

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*To Layan, who always encouraged us to go a bit further, and Funke, who made
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Dayo Mofikoya

Kuopio, September, 2019

LIST OF ABBREVIATIONS

CCN	Cloud condensation nuclei
CH ₄	Methane
CO ₂	Carbon dioxide
DMAPP	Dimethylallyl pyrodiphosphate
DMNT	4,8-dimethylnona-1,3,7-triene
EFN	Extrafloral nectar
ELVOC	Extremely low volatility organic compounds
GC-MS	Gas chromatography – mass spectrometry
GLVs	Green leaf volatiles
HIPVs	Herbivore-induced plant volatiles
HPL	Hydroperoxide lyase
HO ₂	Hydroperoxy radical
HOM	Highly oxidized molecules
IPP	Isopentenyl diphosphate
IVOC	Intermediate volatility organic compounds
kPa	Kilopascal
LOX	Lipoxygenase
LVOC	Low volatility organic compounds
MAC	Methacrolein
MB	Mountain Birch
MEP	Methyerythritol phosphate
MVA	Mevalonic acid
MVK	Methyl vinyl ketone
NO	Nitric oxide
NO ₂	Nitrogen dioxide
NO ₃	Nitrate radical
NO _x	Oxides of nitrogen
NPF	New particle formation
O ₃	Ozone
OH	Hydroxyl radical
PET	Polyethylene terephthalate
ppb	Parts per billion
ROS	Reactive oxygen species
RO ₂	Alkyl peroxy radical
RT	<i>Rhododendron tomentosum</i>
SOA	Secondary organic aerosols
SVOCs	Semi-volatile organic compounds
TMTT	4,8,12-trimethyltrideca-1,3,7,11-tetraene
VOCs	Volatile organic compounds

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on data presented in the following articles, referred to by the Roman Numerals I-III.

- I Mofikoya AO, Miura K, Ghimire RP, Blande JD, Kivimäenpää M, Holopainen T, Holopainen JK (2018) Understorey *Rhododendron tomentosum* and Leaf Trichome Density Affect Mountain Birch VOC Emissions in the Subarctic. *Scientific reports*, 8: 13261.
- II Mofikoya AO, Kivimäenpää M, Blande JD, Holopainen JK (2018) Ozone disrupts adsorption of *Rhododendron tomentosum* volatiles to neighbouring plant surfaces, but does not disturb herbivore repellency. *Environmental Pollution* 240:775-780.
- III Mofikoya AO, Yli-Pirilä P, Kivimäenpää M, Blande JD, Virtanen A, Holopainen JK (2019) Deposition of oxidation products of α -pinene on plant surfaces affects plant VOC emission and herbivore feeding and oviposition. *Manuscript*.

AUTRHOR'S CONTRIBUTION

In chapter 2, AOM, KM and JKH designed the experiment; all listed authors participated in the field data collection. MK collected and analysed microscopy data for glandular trichome analysis, TH collected data on understorey plants and species description, AOM analysed VOC data. AOM and KM wrote the manuscript. RPG, JB, MK, TH and JKH revised and edited the manuscript; all authors checked and approved the final version of the manuscript.

In chapter 3, AOM, JB and JKH designed the experiment. MK provided statistical support. AOM collected and analysed VOC and herbivore data. AOM wrote the manuscript, JKH, JB and MK edited the manuscript. All authors checked and approved the final version of the manuscript.

In Chapter 4, AOM and JKH designed the experiment. PYP helped to construct the experimental setup. AOM collected and analysed VOC and herbivore data. AOM wrote the manuscript, JKH edited and revised the manuscript, JB, MK, AV and PYP edited the manuscript. All authors checked and approved the final version of the manuscript.

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1 INTRODUCTION

1.1 BACKGROUND

Plants interact and adapt to their natural environment by physical and chemical means; physical adaptation may involve leaf and flower colouration, leaf toughness as well as leaf surface properties such as epicuticular waxes and trichomes (Jetter et al., 2000; Werker, 2000; Hamilton and Brown, 2001; Lev-Yadun et al., 2004). Leaf colouration is important for light adsorption during photosynthesis as well as relieving light-related environmental stresses (Chalker-Scott, 1999; Nishio 2000). Floral colouration mainly serves in pollinator attraction (Chittka and Menzel 1992; Dyer et al., 2006). Leaf toughness and surface waxes and trichomes help protect plants against mechanical injury, insect movement and feeding as well as water loss and plant desiccation (Schoonhoven et al., 2005). Chemical adaptation on the other hand, involves the synthesis and use of plant primary and secondary metabolites. Plant secondary metabolites are products of plant primary metabolism that are not directly involved in plant growth, development and reproduction but rather in plant defence against biotic and abiotic stresses as well as plant signalling (Wink, 2003; Schoonhoven et al., 2005). Volatile organic compounds (VOCs) represent a distinct group of plant secondary metabolites synthesized and released by plants. VOCs are a diverse group of lipophilic compounds marked by high vapour pressure (above 0.01kPa) at ambient temperature (20 °C) (European VOC Solvents Directive 1999/13/EC; Dudareva et al., 2013).

Plant VOCs play important roles in atmospheric chemistry and plant ecology; their synthesis and emission may be constitutive or induced by biotic and abiotic stress factors (Holopainen, 2004; Dicke and Baldwin, 2010). In the atmosphere, plant VOCs along with oxides of nitrogen(NO_x) serve as precursors in the formation of tropospheric ozone (Holopainen and Blande, 2013). VOCs may also react with ozone (O_3), hydroxyl (OH) and nitrate (NO_3) radicals in the atmosphere to form secondary organic aerosol (SOA) particles (Hallquist et al., 2009; Seinfeld and Pandis, 2012). VOC oxidation in the atmosphere also play important roles in new particle formation (NPF). Atmospheric oxidation of monoterpenes such as alpha-pine via autooxidation processes lead to the formation of highly oxygenated molecules (HOMs) and extremely low-volatility organic compounds (ELVOCs) (Crouse et al., 2013; Ehn et al, 2014). These HOMs and ELVOCs

may nucleate and initiate NPF and also contribute to particle growth (Kulmala et al., 2013a; Kirkby et al., 2016). Atmospheric transformation of biogenic VOCs are critical for atmospheric processes including cloud formation, radiation absorbance and scattering, processes that potentially have important climatic effects (Virtanen et al., 2010; Kulmala et al., 2013b; Dunne et al., 2016).

Ecologically, plant VOCs function as plant defence compounds as well as mediators of plant interactions across trophic levels (Holopainen, 2004; Dicke and Baldwin, 2010). VOCs are released by plants in response to herbivore feeding or oviposition and may subsequently deter feeding and oviposition by herbivores (Kessler and Baldwin, 2001; Heil, 2004) in a process known as direct defence. In indirect defence, these compounds attract herbivore enemies in forms of predators and parasitoids that attack and reduce herbivore populations (Turlings et al., 1990; Kessler and Baldwin, 2001). Apart from their role in plant defence, VOCs also function as host location cues for foraging insects, pollinators and gravid female insects looking for oviposition sites (Bruce et al., 2005; Schiestl, 2010; Tasin et al., 2011). Abiotic stresses like temperature increase, altered light intensity, drought and oxidative stress may also induce or reduce VOC emissions in plants (Holopainen and Gershenson, 2010; Loreto and Schnitzler, 2010).

Another ecological process mediated by VOCs is plant-to-plant interactions. These interactions may be between different parts of the same individual plant (within-plant signalling) or two individual plants (between plant signalling) (Heil and Karban, 2010). Volatile-mediated plant-to-plant interactions are marked by the release of a volatile or blend of volatile compounds by a damaged (Girón-Calva et al., 2014) or intact emitter plant (Glinwood et al., 2004, 2011) that is subsequently sensed by a neighbouring plant or different plant part and elicits a response (Heil and Karban, 2010). Between and within plant signalling may result in increased herbivore resistance in receiver plants or plant parts. This resistance may be marked by priming – an increased physiological preparedness to resist future biotic and abiotic stresses or the release of extra floral nectar (EFN) to attract natural herbivore enemies (Heil and Kost, 2006; Frost et al., 2008; Heil and Karban, 2010). The mechanisms of volatile-mediated plant-to-plant interactions may be either active or passive. In active plant-to-plant interactions, volatiles released by the emitter plant elicit a physiological response in the receiver (Heil and Kost, 2006; Kost and Heil, 2006), while passive interactions involve the adsorption of volatile compounds released by the emitter plant to the

surface of receiver plants (Himanen et al., 2010; Li and Blande, 2015). Both these processes may alter the receiver plants' response to herbivory (Choh et al., 2004).

Once released into the atmosphere, VOCs are subject to atmospheric conditions that may undermine the success of their ecological functions (Pinto et al., 2007a, 2010). VOCs also serve as precursors for the formation of secondary atmospheric pollutants like O₃ (Holopainen and Blande, 2013). In the atmosphere, VOCs are subject to dilution, air turbulence and wind direction (Koehl, 2005). They may also react with atmospheric oxidants, which results in the degradation of reactive compounds and a change of the VOC blend (Pinto et al., 2010). These reactions between VOCs and atmospheric oxidants produce less volatile or semi-volatile reaction products, which are further oxidized and condensed to form SOA particles that play important roles in atmospheric chemistry (Seinfeld and Pandis, 2012) and possibly in plant ecology (Holopainen et al., 2017).

Semi-volatile compounds typically have lower vapour pressures (< 0.005 kPa at 25 °C) and higher boiling points (240 – 400 °C) compared to VOCs (Copolovici and Niinenmets 2015; Lucattini et al., 2018). A common group of semi-volatile organic compounds (SVOCs) emitted by plants are sesquiterpenes (Copolovici and Niinenmets, 2015) and their emission by plants may be stress induced (Niinenmets, 2010; Li and Blande 2015) or constitutive (Himanen et al., 2010, 2015). Semivolatile compounds may also be formed as the less volatile reaction products of VOC oxidation (Presto and Donahue, 2006). In spite of their relatively low volatility, some SVOCs are very reactive and are degraded easily upon release into the atmosphere (Atkinson and Arey, 2003a); however, other saturated semivolatile compounds are less prone to atmospheric oxidation and may persist on leaf surfaces (Helmig et al., 2004; Himanen et al., 2010, 2015). In the atmosphere, semivolatile compounds condense to form SOA particles (Helmig et al., 2006; Seinfeld and Pandis, 2012; Holopainen et al., 2017). These SOA particles and other reaction products of VOC and SVOC oxidation in the atmosphere are readily redeposited on vegetation (Karl et al., 2005, 2010; Holopainen et al., 2017).

This thesis discusses volatile-mediated passive plant-to-plant interactions mediated by VOCs and SVOCs emitted by the perennial evergreen shrub, *Rhododendron tomentosum*. It examines the phenomenon of passive volatile adsorption between naturally occurring *R. tomentosum* and *Betula pubescens* trees in a subarctic climate. It also considers the effects of ozone on the process of passive volatile adsorption and the herbivore resistance it may confer.

Finally, the effects of the deposition of SOA and reaction products of VOC oxidation on plant surfaces and their corresponding effects on insect feeding and oviposition were tested and discussed.

1.2 BIOGENIC VOLATILE ORGANIC COMPOUNDS

1.2.1 Biosynthesis of volatile organic compounds

Plant VOCs can be broadly categorized as terpenoids, benzenoids and phenylpropanoids, fatty acid derivatives and nitrogen and sulphur containing compounds. Terpenoids are the largest and most diverse group of plant secondary metabolites. Originating from a five carbon (C5) precursor, they include hemiterpenes (C5), monoterpenes (C10), sesquiterpenes (C15), diterpenes (C20) and homoterpenes (C11 and C16) (Dudareva et al., 2004).

All terpenoids are derived from the universal C5 precursors isopentenyl diphosphate (IPP) or dimethylallyl diphosphate (DMAPP). These precursors are formed from acetyl-CoA, pyruvate and glyceraldehyde-3-phosphate via the mevalonic acid (MVA) pathway in the cytosol and the methyerythritol phosphate (MEP) pathway in the plastids (Dudareva et al., 2013). The MEP pathway provides C5 units for the synthesis of hemiterpenes, monoterpenes and diterpenes while the MVA pathway results mostly in sesquiterpene and homoterpene synthesis. The huge diversity of terpenoids is due to the actions of terpene synthase enzymes that are able to synthesize multiple products from a single substrate (Dudareva et al., 2004). Other chemical reactions, such as oxidation, dehydrogenation and acylation may also result in the formation of terpenes without the use of terpene synthases (Dudareva et al., 2006; Maffei, 2010). Homoterpenes are irregular acyclic terpenoids such as the (C11), 4,8-dimethylnona-1,3,7-triene (DMNT) and (C16), 4,8,12-trimethyltrideca-1,3,7,11-tetraene (TMTT), they are typically derived from the oxidative degradation of a (C15) and (C20) compound respectively (Dudareva et al., 2006).

Another large group of plant VOCs are the fatty acid derivatives; they are generally termed oxylipins and include green leaf volatiles and jasmonic acid and its derivatives (Mwenda and Matsui 2014). Oxylipins are synthesised from C18 fatty acids that undergo dioxygenation catalysed by the lipoxygenase (LOX) enzyme (Dudareva et al., 2006). These oxidation reactions may occur at the C9 or C13 positions and produce two compound groups – the 9-hydroperoxy and the 13-hydroperoxy derivatives of polyenoic fatty acids (Gigot et al., 2010). Subsequent reactions catalysed by the allene

oxidase synthase results in the synthesis of jasmonic acid and methyl jasmonate. Another enzyme, the hydroperoxide lyase (HPL) leads to the formation of C6 and C9 aldehydes, which are often reduced to alcohols and esters that make up plant green leaf volatiles (GLVs) (Dudareva et al., 2013; Maffei, 2010). Benzenoids, phenylpropanoids and sulphur and nitrogen containing compounds are typically derived from plant amino acids and synthesized in the plastids (Dudareva et al., 2006; Pichersky et al., 2006).

VOC synthesis and emission may be *de novo* in damaged or undamaged tissues, where the processes may be spatially, temporally and developmentally regulated. They may also be accumulated in storage organs like resin ducts and glandular trichomes from where they can be released upon disturbance (Dudareva et al., 2006; Maffei, 2010). Biotic and abiotic stressors may also trigger the synthesis and emission of VOCs (Holopainen and Gershenzon, 2010; Loreto and Schnitzler, 2010).

1.2.2 Plant semi-volatile organic compounds (SVOCs)

Plant semi-volatile organic compounds (SVOCs) are secondary metabolites marked by relatively low volatility compared to other plant VOC groups such as monoterpenes and GLVs; they have a vapour pressure lower than 0.005 kPa at 25 °C, and include sesquiterpenoids and diterpenoids emitted by plants (Hoskovec et al., 2005; Copolovici and Niinemets, 2015; Jud et al., 2016). They are constitutively emitted by flowers and some aromatic plants and can be induced in other plants by abiotic and biotic stresses (Klimankova et al., 2008; Holopainen and Gershenzon, 2010; Muhlemann et al., 2014). They play important ecological roles in pollinator attraction due to their long distance signalling capacity (Muhlemann et al., 2014). The synthesis and emission as well as the physicochemical state of plant SVOCs are temperature dependent (Copolovici and Niinemets, 2015). In nature, SVOCs emitted by a plant species have the capacity to condensate on the surfaces of neighbouring plants at low night-time temperatures (Holopainen et al., 2017). Plant emitted semi-volatile sesquiterpenes have been shown to be mediators of passive plant-to-plant interactions (Himanen et al., 2010; Li and Blande, 2015). SVOCs may also react with oxidants in the atmosphere and play appreciable roles in secondary organic aerosol (SOA) formation and atmospheric chemistry (Helmig et al., 2006; Holopainen et al., 2017).

VOC and SVOC reactions with atmospheric oxidants lead to the formation of highly oxidized compounds with different volatility classes. Donahue et al. (2003) classified reaction products based on their decreasing saturation

vapour pressures as intermediate volatility organic compounds (IVOC), SVOC, low volatility organic compounds (LVOC) and extremely low volatility organic compounds (ELVOC). The less volatile ELVOC and LVOC classes tend to condense easily to form organic aerosols compared SVOCs, IVOCs and VOCs (Donahue et al., 2003)

1.3 ECOLOGICAL ROLES OF VOLATILE ORGANIC COMPOUNDS

1.3.1 Plant defence against abiotic stress

Plant VOCs play important ecological roles in plant defence against abiotic stresses. Changes in temperature and light intensity as well as drought and oxidative stress alter plant VOC emission (Holopainen and Gershenzon, 2010; Loreto and Schnitzler, 2010). Abiotic stresses may reduce or induce plant VOC emissions depending on the intensity and duration of the stress (Loreto and Schnitzler, 2010). Within plant tissues, VOCs move from their site of synthesis through subcellular barriers and are released via the stomata. They may also be released due to mechanical disturbance or via the cuticle (Niinemets et al., 2002; Widhalm et al., 2015). Abiotic stresses may inhibit photosynthesis and subsequently reduce photosynthetically fixed carbon that may be required for VOC synthesis (Loreto et al., 1996; Loreto and Schnitzler, 2010), thus resulting in reduced VOC emissions. Alternatively, plants may synthesize and increase emission of VOCs in response to abiotic stresses (Loreto and Schnitzler, 2010). In the case that photosynthetic carbon is absent or reduced in abundance, VOCs may be synthesized from alternative carbon sources, such as starch from leaf internal carbon pools and extra-chloroplastic sources, such as xylem-transported carbohydrates (Karl et al., 2002; Kreuzwieser et al., 2002; Schnitzler et al., 2004).

An increase in temperature generally tends to increase the emission of terpenes emitted from storage structures and via *de novo* synthesis by increasing diffusion and enzymatic activity, respectively (Loreto and Schnitzler, 2010; Copolovici and Niinemets, 2016). Plants release isoprene and monoterpenes in response to short term and longer-term temperature increase (Niinemets, 2010; Copolovici and Niinemets, 2016). Sesquiterpene and GLV emissions were also increased by long term temperature increase (Hartikainen et al., 2012; Kivimäenpää et al., 2016). In cases where temperature goes above the optimum for enzymatic activity, terpene emissions are reduced due to the denaturation of enzymes, whereas the

emission of VOCs like GLVs and methanol, which are related to cell membrane and cell wall damage, increase (Loreto et al., 2006). There is evidence that emissions of isoprene and monoterpenes protect plant photosynthetic apparatus against damage caused by high temperature (Loreto and Schnitzler, 2010; Niinemets and Keenan, 2014). The increased concentration of monoterpenes in leaf tissues protects foliage from heat flecks (Niinemets et al., 2010; Copolovici and Niinemets, 2016). Plants fumigated with isoprene and other monoterpenes prior to exposure to heat stress showed a quicker recovery time compared to controls in terms of the restoration of photosynthesis rate (Copolovici et al., 2005).

VOC emissions from stressed plants may also be associated with stress-induced stomatal action; high temperatures may affect stomatal behaviour as a single stress or in association with drought (Loreto and Schnitzler, 2010). Severe drought stress may inhibit or increase terpene emissions due to reduced photosynthesis or increased enzyme activity in association with increasing temperature (Llusià and Peñuelas, 1998, 2000). The increased emissions of terpenes as a response to drought stress may help plants to maintain membrane fluidity and stability (Peñuelas and Llusià 2002). Volatile terpene emissions, especially by emitters without VOC-storage organs, is light dependent and linked to photosynthesis (Staudt and Seufert, 1995). However, high light intensities may lead to the emission of C-6 compounds that are linked to extensive membrane damage (Loreto et al., 2006).

Some plant VOCs, especially isoprene and monoterpenes, are highly reactive with ozone and have been suggested to serve as ozone-quenching compounds within the leaves, and consequently reducing oxidative stress to the plants (Loreto and Velikova, 2001; Loreto et al., 2001, 2004). However, the ozone-quenching properties of isoprene are debatable due to their high volatility and high atmospheric lifetime (Atkinson et al, 2000). Monoterpenes and sesquiterpenes of shorter atmospheric lifetimes and lower volatility compared to isoprene (Atkinson et al., 2000) are physicochemically more likely compounds to be involved in ozone quenching within leaves (Loreto et al., 2004; Palmer-Young et al., 2015). These foliar ozone-scavenging reactions could also occur as a result of reaction with semivolatile compounds at leaf surfaces (Jud et al., 2016; Acton et al., 2018). These surface semi-volatile-mediated ozone quenching reactions may however not always reduce oxidative stress or improve plant fitness (Palmer-Young et al., 2015). Taken together, endogenously synthesized as well as exogenously acquired terpenes can be useful for plants in the resistance to various abiotic stresses.

1.3.2 Plant defence against biotic stress

Plant VOC emissions elicited by pathogen infection, herbivore-feeding and oviposition play important roles in plant defence; the mechanism of defence may be by direct repellence or deterrence or by indirect recruitment of natural enemies (Holopainen, 2004; Maffei, 2010). The blend of GLVs and terpenes produced by tomato, *Lycopersicon esculentum*, plants upon infestation by *Botrytis cinerea* showed strong inhibitory effects against the pathogen (He et al., 2006). Exposing *Arabidopsis* plants to (Z)-3-hexenal also effectively reduced the lesions of *B. cinerea* infection on the plant (Shiojiri et al., 2006). VOCs emitted by tobacco, *Nicotiana tabacum*, plants upon damage by the tobacco budworm, *Heliothis virescens*, larvae were repellent to gravid *H. virescens* female adults searching for oviposition sites (De Moraes et al., 2001). Kessler and Baldwin (2001) also showed that herbivore-induced VOCs of *Nicotiana attenuata* plants repelled ovipositing *Manduca sexta* females. The volatile blend released by herbivore damaged *N. attenuata* in this case also served in recruiting predators that fed on *M. sexta* eggs in a case of indirect defence across multiple trophic levels. Lima bean, *Phaseolus lunatus*, plants infested by spider mites release a VOC blend that attracts the predatory mites that prey on spider mites (Takabayashi and Dicke, 1996). Volatile-mediated indirect defence is not limited to combatting larval feeding; egg deposition by the pine sawfly, *Diprion pini*, on twigs of Scots pine, *Pinus sylvestris*, induces VOC emissions that attract the egg parasitoid *Chrysonotomyia ruforum* (Hilker et al., 2002). The recruitment of natural enemies and egg parasitoids as a result of volatiles induced by egg deposition has been reported in a number of plant species (Fatouros et al., 2016 and references therein).

1.3.3 Plant-arthropod interactions

VOCs emitted by flowering parts of plants provide species-specific cues for pollinator attraction. Although pollinators also use flower shape and colour in plant selection, the large diversity of VOCs mean that floral scents can be specific to a plant species (Schiestl, 2010; Muhlemann et al., 2014; Maffei, 2010). Constitutively emitted VOCs by plant vegetative parts are used by herbivores as host selection cues (Bruce et al., 2005). Feeding by herbivores may increase plant VOC emissions or induce the emission of new herbivore-induced plant volatiles (HIPVs). These compounds may serve as herbivore deterrents or recruit natural herbivore enemies (Holopainen and

Gershenzon, 2010; Schuman and Baldwin, 2012). HIPVs may also increase the apparency of plants to generalist herbivores and non-beneficial natural enemies. Application of methyl salicylate, an HIPV, increased the population of the leaf mining pest *Scaptomyza flava* on *Brassica rapa* plants (Orre et al., 2010). Small potato plants infested by larvae of the beet armyworm, *Spodoptera exigua*, release VOCs that are attractive to the Colorado potato beetle, *Leptinotarsa decemlineata* (Bolter et al., 1997). Finally, VOCs can also mediate interactions with the third trophic level by attracting parasitoids and predators of herbivores as part of an indirect defence mechanism (Kessler and Baldwin, 2001).

1.3.4 Plant-to-plant interactions

The earliest evidence of volatile mediated plant-to-plant interactions came in the 1980s, when Baldwin and Schultz (1983) proposed that airborne signals from damaged sugar maple, *Acer saccharum*, and Poplar, *Populus euroamericana*, caused an increased level of resistance-related compounds in undamaged neighbouring conspecifics. Another study by Rhoades (1983) proposed that the increased level of herbivore resistance expressed by willow, *Salix sitchensis*, trees growing close to herbivore-damaged neighbours was due to airborne volatiles. Although both these experiments were criticized for flaws in statistical design and unsatisfactory evidence (Fowler and Lawton, 1985), there is a substantial body of work today to support the phenomenon of volatile-mediated plant-to-plant interactions (e.g. Farmer and Ryan, 1990; Arimura et al., 2000; Karban et al., 2000). The phenomenon of volatile mediated interactions between plants has been referred to as communication (De Moraes and Mescher, 2006), signalling (Kost and Heil, 2006) and eavesdropping (Karbon et al., 2004). Ideally, the term 'plant communication' should convey a two-way benefit for both emitter and receiver plants, however the weight of evidence from much of the study of the phenomenon has shown benefits for the receiver with little known on the effects on the emitter (Heil and Karban, 2010). This gave rise to the term 'eavesdropping', which connotes the duplicitous use of a signal evolved to elicit a response in an alternative recipient (Heil and Karban, 2010). Thirdly, 'plant-to-plant signalling' has been used widely because it refers to the plastic emission of a VOC signal that elicits quick responses in a receiver plant (Heil and Karban, 2010). All of these terms however only cover cases of active plant-to-plant interactions, when there are physiological changes in a receiver plant, marked by induction or a primed response due to exposure to

induced plant volatiles. In cases where exogenous volatiles adhere to the surface of neighbouring plants without necessarily triggering a physiological response, the interactions cannot be said to be signalling or eavesdropping. Consequently, the term “passive” plant-to-plant interactions has been used (Choh et al., 2004; Himanen et al., 2010; Li and Blande 2015). In this thesis, all plant VOC-mediated interactions and the effects they elicit are broadly termed plant volatile-mediated interactions.

To demonstrate the signalling role of VOCs between parts of the same individual plant, Heil and Silva-Bueno (2007) exposed undamaged leaves of Lima bean, *P. lunatus*, to induced VOCs from damaged leaves of the same plant, this increased the secretion of EFN in the undamaged receiver leaves. Similarly, Frost et al. (2007) showed that undamaged leaves of hybrid poplar, *Populus deltoides* x *nigra*, exposed to HIPVs from damaged leaves of the same individual had increased defences against feeding by gypsy moth larvae, *Lymantria dispar*, compared to leaves that did not receive the VOCs. Exposure to herbivore-damaged leaf volatiles led to a systemic induction of sesquiterpenes and priming for GLV emissions in undamaged leaves of silver birch, *Betula pendula* (Girón-Calva et al., 2014). The use of plant volatiles for signalling within plants may be faster than vascular signals, especially between parts with limited vascular connections (Heil and Karban, 2010). Indeed, it has been proposed that signalling between plants arose from within-plant signalling, in which VOCs are emitted to prepare the not yet attacked organs of a plant for the upcoming attack (Heil and Karban, 2010).

In between-plant interactions, VOCs emitted by a damaged plant may prime neighbouring undamaged plants; preparing them for a stronger and quicker response if attacked. Lima bean plants exposed to herbivore-induced VOCs from insect-damaged conspecifics, responded to subsequent damage by increased secretion of EFN (Heil and Kost, 2006). Undamaged neighbouring silver birch seedlings exposed to volatiles from insect damaged neighbours were also primed for increased terpenoid and GLV emissions during subsequent feeding damage (Girón-Calva et al., 2014). Passive plant-to-plant interactions have been shown to be mediated by sesquiterpenes, their semivolatile property enables the compounds to adhere to and be re-emitted from neighbouring plant surfaces (Himanen et al., 2010, 2015; Li and Blande 2015). Birch seedlings growing close to *Rhododendron tomentosum* shrubs in a boreal ecosystem adsorbed and re-emitted *R. tomentosum* sesquiterpenoids; compared to unexposed controls, the exposed birch trees were repellent to the green leaf weevil, *Polydrusus flavipes* (Himanen et al.,

2010). Broccoli, *Brassica oleracea*, plants also showed increased resistance to *Plutella xylostella* oviposition after a 24-hour exposure to *R. tomentosum* plants (Himanen et al., 2015). Sesquiterpenes induced by herbivore-feeding on broccoli plants have also been shown to be passively adsorbed on neighbouring plant surfaces, subsequently increasing their susceptibility to oviposition by *P. xylostella* (Li and Blande, 2015). Both active and passive processes mediate plant-to-plant interactions and may have effects on plant herbivores and herbivore natural enemies (Choh et al., 2004). However, in cases where both emitter and receiver plants synthesize and emit the compounds that mediate passive interactions in nature, it becomes difficult to determine which compounds are adsorbed and re-emitted and which the receiver plants synthesize and emit themselves.

1.3.5 Foliar uptake and adsorption of VOCs and SVOCs

Volatile mediated plant-to-plant interactions are dependent on receiver plant foliage being exposed to emitter-plant volatiles; exposure to volatiles may result in uptake through the stomata and/or the adsorption of the VOCs within the cuticle. These processes have far-reaching consequences for plant chemistry and herbivore responses (Niinemets et al., 2014). Foliar uptake of VOCs from the atmosphere by plants is dependent on the concentration of the compound in the atmosphere and follows a diffusion flux pattern (Noe et al., 2007; Niinemets et al., 2014). Uptake occurs when ambient air concentration is higher than within leaf concentration until a compensation point is reached when both concentrations are in equilibrium. When atmospheric concentrations drop, VOCs are emitted back into the atmosphere (Niinemets et al., 2004; Niinemets et al., 2014).

The distance between emitter and receiver plants as well as wind speed and direction also affect foliar volatile uptake (Müller and Riederer, 2005). VOCs are dispersed in the air via diffusion and turbulent motion and may be diluted and rendered ineffective over longer distances. Induced resistance in *N. attenuata* plants via exposure to clipped sagebrush, *Artemisia tridentata* volatiles was observed only within a 15 cm distance and up to 60 cm between paired sagebrush plants (Karban, 2001; Karban et al., 2006). The presence of secondary organic pollutants in the atmosphere may further decrease VOC atmospheric lifetimes and shorten the effective distances for volatile mediated plant-to-plant interactions (Blande et al., 2010; Li et al., 2016). Due to their low vapour pressure and lipophilicity, semivolatile sesquiterpenoids are typical mediators of passive plant-to-plant interactions (Himanen et al.,

2010; Himanen et al., 2015, Li and Blande 2015). Oxygenated sesquiterpenoids are less prone to oxidation reactions in the atmosphere compared to sesquiterpenes and monoterpenes and may persist for a longer period in the atmosphere or on plant surfaces (Pinto et al., 2007b; Helmig et al., 2004; Himanen et al., 2010). Highly volatile monoterpenes not taken up through the stomata may also be adsorbed on plant surface from surrounding air. Thirteen emitting and non-emitting plant species fumigated with limonene, adsorbed and re-emitted the monoterpene (Noe et al., 2007).

Within plants, VOCs taken up from the atmosphere may undergo hydrolysis or glycosylation where they are converted to other compounds that may be protective to the plant (Sugimoto et al., 2016). Exogenously applied methyl jasmonate was hydrolysed within tobacco, *N. attenuata*, plants and later released as jasmonic acid (Wu et al., 2008). Intact *Arabidopsis thaliana* plants exposed to a labelled GLV, (Z)-3-hexenal, re-emitted labelled (Z)-3-hexenol and (Z)-3-hexenyl acetate, confirming the conversion of the compound within the plant and subsequent re-emission (Matsui et al., 2012).

Field examples of volatile monoterpene and GLV uptake and re-emission are difficult to measure due to the high vapour pressures of the compounds as well as their proneness to atmospheric oxidation (Atkinson and Arey, 1998). In addition, the ubiquity of GLVs and monoterpene emissions among many plants may also mask passive adsorption and re-emission of VOCs and SVOCs in nature. VOCs and SVOCs collected from plants in nature may originate from neighbouring plants, but this may prove difficult to assess in scenarios when both the neighbouring and sampled plants synthesize similar compounds.

1.4 PLANT SURFACES

1.4.1 Plant cuticular waxes

Plant surfaces represent the first point of physical contact in volatile-mediated plant-to-plant and plant-insect interactions and as such, the physical and chemical properties of plant surfaces are important for these interactions. Plant cuticles are typically composed of a cutin matrix and a wax layer (Müller and Riederer, 2005). The cutin is composed of hydroxy- and hydroxyepoxy fatty acids derived from cellular fatty acids and C16 saturated and C18 unsaturated fatty acids (Müller and Riederer, 2005). Cuticular waxes on the other hand are esters of long chain fatty acids. Wax layers are typically

lipophilic and serve plants in protection against water loss, insect herbivory and pathogen attack (Schoonhoven et al., 2005). External factors such as season, temperature, light, CO₂ and ozone, and internal factors such as developmental stage and organ-specific regulation may affect the quantitative and qualitative composition of plant waxes (Müller and Riederer, 2005).

The process of volatile-mediated plant-arthropod interactions may be broadly divided into 3 phases: searching, selection and acceptance (Schoonhoven et al., 2005). Searching involves the use of airborne VOCs to determine host location, selection of a host plant involves physical contact between the plant and arthropod, after which the leaf surface characteristics, both physical and chemical, modifies the insect's behaviour and acceptance of a host (Schoonhoven et al., 2005). Waxy surfaces, for example, may prevent adherence of herbivores on leaf surfaces, which may be necessary for their feeding (Eigenbrode, 2004). *P. xylostella* preferred to oviposit on glossy surfaced *Brassica* spp. compared to waxy surfaced cabbage (Badenes-Perez et al., 2004). The presence of epicuticular waxes also increased the slipperiness and reduced the survival rates of herbivorous psyllids on *Eucalyptus globulus* (Brennan and Weinbaum, 2001). The wax surface structure may also determine optical properties of a plant leaf, which in turn may affect herbivore foraging (Schoonhoven et al., 2005).

The chemical properties of plant cuticular waxes are also important as they determine whether the plant is accepted or not by an herbivore. VOCs exiting plant tissues or taken up from the atmosphere accumulate in the cuticular wax layer (Himanen et al., 2010; Joensuu et al., 2016), where they are sensed by visiting arthropods and may either stimulate or deter herbivory and oviposition (Eigenbrode and Espelie 1995; Eigenbrode, 2004). The hydrophobic nature of plant leaf surfaces due to their wax layer makes for the possibility of adsorption of lipophilic VOCs from the atmosphere within the cuticle. The presence of exogenous volatile compounds within a plant's cuticle affects herbivore feeding and oviposition (Himanen et al., 2010; 2015).

1.4.2 Plant trichomes

Plant surfaces may also have unicellular or multicellular appendages emerging from epidermal cells on stems and leaves called trichomes. Trichomes can act as physical and chemical barriers against abiotic and biotic stresses. Plant trichomes show a large diversity and can be broadly divided into non-glandular and glandular trichomes (Schoonhoven et al., 2005;

Werker, 2000). Non-glandular trichomes do not produce or secrete plant chemicals, but serve in plant resistance by restricting herbivore movement, oviposition and feeding on plant surfaces (Schoonhoven et al., 2005; Li et al., 2018). For example, the number of eggs deposited on a natural population of *A. thaliana* plants by *P. xylostella* decreased with increasing leaf trichome density (Handley et al., 2005). Genetically increasing trichome production in *Brassica napus* seedlings decreased feeding by the crucifer leaf beetle, *Phyllotreta cruciferae* (Soroka et al., 2011). However, increasing trichome production may disrupt indirect defence by inhibiting the mobility of herbivore natural enemies (Van Lenteren et al., 1995; Dalin et al., 2008). Plants may also produce trichomes as a response to abiotic and biotic stresses (Dalin et al., 2008; Harada et al., 2010).

Glandular trichomes serve as storage structures for a number of plant secondary metabolites including volatile and non-volatile terpenoids (Gershenzon and Dudareva, 2007) and phenylpropanoids (Xie et al., 2008). They may also contain and exude non-volatile natural products including phenolics, flavonoids, acyl sugars and glycerides (Levin, 1973; Werker, 2000; Liu et al., 2019). These compounds may be exuded directly onto the plant surface or into the atmosphere upon mechanical or insect damage and may deter or repel insects or attract their natural enemies (Levin, 1973; Romero et al., 2008; Luo et al., 2010). The secreted compounds may also be sticky, gluing smaller arthropod species to plant surfaces (Krimmel and Pearse, 2013). Secretions from glandular trichomes may also play a role in plant defence against oxidative stress. Jud et al (2016) reported that cis-abienol, and other foliar surface semivolatiles of *N. tabacum* plants react with ozone, reducing stomatal uptake and oxidative stress. Release of volatile and non-volatile glandular trichome exudates is also dependent on temperature. Increasing temperature may lead to the release of volatile exudates into the atmosphere via diffusion, from where they may be oxidized or condensate on foliage of the emitting plant and surrounding plants as temperatures decrease (Holopainen and Blande, 2013; Niinemets et al., 2014).

1.5 TROPOSPHERIC OZONE

1.5.1 Formation and distribution

Ozone (O₃) is a reactive gas that exists in two layers of the atmosphere – stratospheric and tropospheric ozone. In the stratosphere, ozone is a naturally occurring constituent formed by the photolysis of molecular

oxygen by UV-radiation, this layer of ozone serves in the protection of the Earth's surface against lethal UV-radiation from the sun (Fowler et al., 2008). In the troposphere, however, ozone is a secondary pollutant formed from complex photochemical reactions involving oxides of nitrogen (NO_x), methane (CH_4), and VOCs (Liu et al., 1980; Fowler et al., 2008). The process of tropospheric ozone formation involves the oxidation of VOCs by hydroxyl (OH) radicals to form alkyl peroxy (RO_2) and hydroperoxy (HO_2) radicals. Nitric oxide (NO) is oxidized to nitrogen dioxide (NO_2) by these radicals and sunlight separates NO_2 into NO and oxygen atoms (O), which bind to naturally occurring oxygen (O_2) to form tropospheric ozone (O_3) (Pinto et al., 2010; Holopainen and Blande 2013). A range of anthropogenic and natural sources release ozone precursors. VOCs are largely from biogenic sources like vegetation, while oxides of nitrogen (NO_x) and methane (CH_4) are mostly anthropogenic in their origin (Amann, 2008; Fenger, 2009). Tropospheric ozone shows strong seasonal and diurnal variations in urban areas; concentrations are usually highest in the summer and during afternoons. Availability of ozone precursors coupled with high temperatures and intense solar radiation results in peak ozone concentrations (Amann, 2008; Stocker et al., 2013). Global ozone distribution is dependent on local concentrations of precursors and long-range transport of ozone; the long atmospheric lifetimes of many ozone precursors allow them to be transported over long distances (Amann, 2008).

Global tropospheric ozone levels have increased since pre-industrial times due to increase in human population and expansion of anthropogenic activities that result in ozone precursor emissions. In rural Europe, tropospheric ozone concentrations increased from about 10-15ppb at the end of the 19th century to 20-30ppb in the 1980s (Volz and Kley, 1988). Background ozone levels currently range between 35 – 45 ppb in the northern hemisphere, there are however occurrences of peak emissions of up to 100ppb (Mills et al., 2018). In general, due to the reduction in anthropogenic emissions of ozone precursors, ozone levels in the United states and Europe have decreased (Simpson et al., 2014; Lin et al., 2017). Precursor emissions have largely shifted from Europe and North America to Asia since the beginning of the 1990s (Zhang et al., 2016; Mills et al., 2018). Global average ozone concentrations are expected to decrease, largely remain the same or slightly increase in the coming years according to various models (Cionni et al., 2011; Kim et al., 2015), however, it is still expected that daily averages of up to 80 ppb will be experienced in some areas (Xu et al., 2016; Chang et al., 2017) .

1.5.2 Impact of ozone on plants

Ozone is a phytotoxic air pollutant and the severity of its damage on plants depends on the concentration and duration of exposure (Runeckles and Krupa 1994; Sandermann, 1996). Chronic exposure to background levels of ozone over a long period may lead to symptoms similar to premature senescence due to inhibition of photosynthesis, alteration of sugar metabolism and production of reactive oxygen species (ROS) (Schraudner et al., 1997; Kangasjärvi et al., 2005). Exposure to high concentrations over a short period (acute exposure) leads to the formation of chlorotic flecks, foliage bronzing and cell death (Saitanis and Karandinos, 2002). In exposed plants, ozone may directly interact with surface tissues or be taken up by the plant into the mesophyll layer through the stomata where they cause oxidative stress and eventually cell death (Kerstiens and Lendzian, 1989; Baier et al., 2005). In agricultural plants, the physiological effects of elevated ozone exposure may lead to a decrease in yield and quality in ozone-sensitive crops (Aunan et al., 2000; Soja et al., 2004; Piikki et al., 2007).

Ozone uptake through the plant cuticle is thought to be negligible; however, a number of reactions involving ozone may occur on the leaf surface. Recently, plant surface semivolatiles have been shown to react with ozone and may play a role in ozone quenching at the surface thereby reducing uptake by plants (Jud et al., 2016). In addition, monoterpenes (Loreto et al., 2004) and sesquiterpenes (Palmer-Young et al., 2015) present within the leaf or leaf boundary layer may also serve as ozone quenchers. Chronic ozone exposure may also lead to increased production of leaf wax compounds as an acclimation response (Kontunen-Soppela et al., 2007).

Once taken in through the stomata into the mesophyll cells, ozone is degraded into reactive oxygen species (ROS) which at high levels may trigger signalling pathways (Jaspers and Kangasjärvi, 2010) and activation of defence mechanisms (Baier et al., 2005), including the emission of VOCs. Plants may emit VOCs as a response to ozone stress. Vuorinen et al. (2004) reported that acute exposure to ozone induced the emission of a GLV and DMNT, compounds that are also induced by herbivory in Lima bean plants. Chronic exposure to non-damaging levels of ozone also increased monoterpene and GLV emissions in Scots pine (Kivimäenpää et al., 2016). Exposure to ozone may also reduce terpene emission rates because of reduced photosynthesis, which may coincide with the emission of GLVs and

other compounds related to ozone-induced membrane damage (Loreto and Schnitzler, 2010).

1.5.3 Effects of ozone on volatile mediated interactions

Ozone affects plant volatile-mediated interactions in a number of ways. Firstly, on the emitter plant; ozone exposure may alter the volatile signal of the emitter plant by inducing, increasing or decreasing their VOC emissions (Vuorinen et al., 2004; Loreto and Schnitzler, 2010).

Secondly, within the air transport medium, the presence of high ozone levels in the atmosphere may degrade VOCs and subsequently disrupt their ecological functions. Once VOCs are released into the air, they are subject to dilution and degradation especially in ozone-polluted air (Pinto et al., 2010). Plant VOCs have varying atmospheric lifetimes ranging from less than two minutes to many years, and atmospheric lifetimes of some reactive VOCs are dependent on the concentration of oxidants in the atmosphere (Atkinson and Arey, 2003a; Kim et al., 2010). Terpenes with one or more C = C bonds are especially susceptible to degradation by ozone while saturated or oxygenated compounds are less prone (Calogirou et al., 1996; Pinto et al., 2010). Ozone degradation of plant volatiles in the air changes the composition of the VOC blend, which may in turn alter their signalling efficacy (Mc Frederick et al., 2009; Pinto et al., 2010). Elevated ozone regimes degraded some constituents of *B. oleracea* VOCs, thus changing the blend and disrupting the fidelity of the signal and ability of *P. xylostella* to use the plant VOCs as cues for host location (Li et al., 2016). Pollinator attraction by black mustard, *Brassica nigra*, VOCs was also reduced over a distance gradient when their volatiles were passed through air with elevated ozone levels (Farré-Armengol et al., 2016). Elevated ozone may also reduce effective distances in plant-to-plant interactions. The effective distance for volatile-mediated plant-to-plant interactions between herbivore-damaged Lima bean plants and their intact neighbours was reduced from 70cm to 20cm under elevated ozone regimes (Blande et al., 2010). The effect of ozone on volatile degradation in passive plant-to-plant interactions is still largely understudied, although there is evidence that ozone may degrade sesquiterpenes adsorbed to neighbouring plant surfaces (Li and Blande, 2016).

Finally, ozone exposure may affect plant-to-plant interactions by altering the ability of the receiver organism to access the signal. In receiver plants, ozone may trigger stomatal closure by increasing cytosolic calcium in guard cells (Vainonen and Kangsjärvi, 2015); ozone may also induce stomatal sluggishness in different plant species (Paoletti and Grulke, 2010). Stomatal

uptake is an important medium of VOC-mediated plant-to-plant interaction (Sugimoto et al., 2016), and ozone induced-stomatal responses may affect this process. Elevated ozone may also react with passively adsorbed SVOC compounds present on leaf surfaces (Li and Blande 2015) and disrupt the susceptibility or resistance they confer. Increasing ozone may also affect an insect's ability to perceive volatiles: western honeybees (*Apis mellifera*) exposed to ozone showed a reduced antennal response to (*Z*)-3-hexenyl acetate, a widespread GLV usually perceived by bees (Dötterl et al., 2016).

1.5.4 Atmospheric transformation of plant volatile organic compounds

Once released into the atmosphere, many plant VOCs react with atmospheric oxidants such as ozone (O₃), hydroxyl (OH) and nitrate radicals (NO₃) (Atkinson and Arey, 2003b); these reactions as well as the deposition of their reaction products on vegetation remove VOCs from the atmosphere (Karl et al., 2005, 2010). For example, canopy scale air measurements of tree plantations typically contain methyl vinyl ketone (MVK) and methacrolein (MAC), which amount to about 80% of the carbon from the first stage of isoprene oxidation (Calogirou et al., 1999; Karl et al., 2005). These compounds show a bidirectional flux and may be deposited on vegetation or be transformed into other compounds in the atmosphere (Karl et al., 2005; Brilli et al., 2016).

Unsaturated terpenes and GLVs are particularly prone to ozonolysis and NO₃-induced oxidation in the atmosphere because of the number of C = C bonds (Calogirou et al 1999; Atkinson and Arey, 2003a). These reactions are usually by addition to a C = C bond to produce a primary ozonide and organic peroxy radical that may react further to form a variety of stabilised oxygenated compounds including carbonyls, alcohols and carboxylic acids (Calogirou et al., 1999; Atkinson and Arey 2003a; Palm et al., 2017). NO₃ radicals photolyse rapidly in the daytime and are more important for night time reactions (Atkinson and Arey 2003b). OH radicals in the atmosphere, as well as those produced from VOC ozonolysis (Atkinson and Arey, 2003b), also react with VOCs via H abstraction as well as addition to a C = C bond to form reaction products and SOA (Atkinson and Arey, 2003b; Palm et al., 2017).

Oxidation products of VOCs in the atmosphere are typically less volatile than their precursors and upon further oxidation may partition into the particle phase or be adsorbed by pre-existing aerosol particles (Hallquist et al., 2009; Seinfeld and Pandis, 2012). A significant amount of plant emitted

VOCs end up in SOA particles, which act as cloud condensation nuclei (CCN) that scatter radiation and influence the radiation balance of the earth and climate (Virtanen et al., 2010; Riipinen et al., 2011; Scott et al., 2014). The chemical structure of plant VOCs along with other factors such as the concentration of atmospheric oxidants determine their atmospheric fate (Atkinson and Arey, 2003a; Kim et al., 2010). Volatile compounds with multiple C = C bonds, such as limonene, can potentially form more particles compared to open chain hydrocarbons such as ocimene and linalool compounds (Hoffmann et al., 1997). The oxidation of limonene by ozone has been shown to produce more than 1000 different organic compounds (Kundu et al., 2012). Semivolatile sesquiterpenes are very reactive with oxidants in the atmosphere and their reaction products can be efficiently transformed into SOA. For example, β -nocaryophyllone aldehyde, a reaction product of β -caryophyllene has been identified and quantified in ambient SOA samples (Parshintsev et al., 2008). The presence of products originating from induced emissions in aerosol samples suggests that herbivory as well as abiotic stressors may enhance SOA formation (Joutsensaari et al., 2015; Zhao et al., 2017).

VOC oxidation products as well as SOA particles may be present and emitted from leaf surfaces either by atmospheric deposition or by leaf surface reactions (Karl et al., 2005; Holopainen et al., 2017; Acton et al., 2018). The ecological implications of the presence of these compounds on plant surfaces have not been adequately elucidated.

1.6 STUDY SYSTEMS

1.6.1 *Rhododendron tomentosum*

Marsh Labrador tea, *Rhododendron tomentosum* Harmaja is a perennial woody evergreen shrub distributed widely through boreal ecosystems of northern America, Asia and northern and central Europe (Dampc and Luczkiewicz, 2013). They can grow up to 150 cm tall and have a characteristic fragrance owing to the high terpenoid and secondary compound content present in their essential oils. The terpenoid content in the plant may vary with habitat, age, vegetation phase and plant part (Zhao et al., 2016). Historically, *R. tomentosum* extracts have been used in ethno-medicine due to their anti-inflammatory, antimicrobial, analgesic and antioxidant properties (Dampc and Luczkiewicz, 2013). The plant extract also has insect repellent properties, which have been effective against bedbugs, cloth moths, as well as pests of

forest trees and agricultural crops (Sõukand et al., 2010; Egigu et al., 2011; Himanen et al., 2010; 2015). In 2010, Himanen et al. reported the adsorption and re-emission of *R. tomentosum* VOCs by neighbouring silver birch seedlings in a boreal forest and that this passive adsorption subsequently increased the resistance of the exposed plants to herbivores. *R. tomentosum* is a model plant for the study of passive plant-to-plant interactions due to it being a constitutive emitter of large quantities and varieties of sesquiterpenes that are typically adsorbed on neighbouring plant surfaces and have been shown to mediate passive plant-to-plant interactions. In addition, *R. tomentosum* plants emit species-specific sesquiterpenoid compounds such as palustrol, ledene and ledol that are not common to many other plant species. Consequently, adsorption and re-emission of these compounds by neighbouring plants in nature can be measured.

1.6.2 Mountain birch

Mountain birch, *Betula pubescens ssp. czerepanovii*, is a clonal tree species with a wide distribution in central and northern Europe as well as Asia: in north-western Europe, mountain birch trees form the latitudinal and altitudinal tree line (Macdonald et al., 1984; Sveinbjörnsson et al., 1996; Haukioja, 2003). In nature, birch trees commonly co-exist with *R. tomentosum* shrubs (Urcelay et al., 2003). In northern Finland, mountain birch trees are short and slow growing and have *R. tomentosum* and other shrubs growing in the understorey. In this thesis, the process of volatile-mediated passive plant-to-plant interactions between *Rhododendron tomentosum* and *B. pubescens* in a natural subarctic forest is explored.

1.6.3 *Brassica* spp, *Plutella xylostella* and *Carausius morosus*

Brassica plants as well as their lepidopteran pest, the diamondback moth, *Plutella xylostella* L. have proved a successful model system for studying plant volatile-mediated interactions (Giron-Calva et al., 2016, 2017). Brassicaceous plants including vegetables and oilseeds are of great global economic significance. According to the FAO, global production of brassica plants was over 71 million tons in 2016. However, the production of these crops is hampered by the presence of a variety of insect pests leading to economic losses. In this thesis, white cabbage, *Brassica oleracea* var. *capitata* L. was used

as a receiver plant for the adsorption of *R. tomentosum* volatiles and deposition of α -pinene reaction products. The effects of these adsorption and deposition processes on herbivores were tested with the specialist brassica pest, *P. xylostella* and the generalist Indian stick insect, *Carausius morosus*.

P. xylostella is an important pest of brassicaceous species, estimated to contribute to global economic losses of between 4 – 5 billion dollars annually (Zalucki et al., 2012). *P. xylostella* owe their widespread distribution to their ability to migrate over long distances of over 3000 km (Talekar and Shelton, 1993). They use a combination of visual and olfactory cues in foraging and host selection (Badenes-Perez et al., 2004). Upon plant landing, the chemical composition of plant surfaces determines oviposition (Badenes-perez et al., 2004; Schoonhoven et al., 2005). In this thesis, the system of *Brassica* spp. and *P. xylostella* was used to study the effect of ozone on passive plant-to-plant interactions and the effects of deposition of SOA particles and VOC oxidation products on plant VOC emissions and interactions with herbivores.

The Indian stick insect, *Carausius morosus*, order Phasmida, is a nocturnal, stick-like, slender, wingless, generalist herbivore species (Carlberg, 1987). Originally local to southern India, the insects became the subject of scientific inquiry in the early 20th century, when their life history and habits were described by Meissner (1909) and their colour variability by Macbride and Jackson (1915). Populations mostly consist of parthenogenetic females, with a few males sometimes found (Clark, 1976). They have been used to test the palatability of herbicide treated crops (Holopainen et al., 1991) and can be representative generalist feeders in insect feeding studies due to their polyphagous nature. The stick insects used in this thesis were reared on *Brassica* spp. and were selected as generalist feeders in tests to determine the effects of the deposition of SOA and VOC oxidation products on plant surfaces on generalist insect feeding.

1.7 OBJECTIVES AND HYPOTHESES

This thesis explores the phenomenon of volatile mediated passive plant-to-plant interactions and the protective functions of plant VOCs and their degradation products on plant surfaces. It involved field and laboratory measurements of VOCs and exposure of plants to VOCs from neighbouring plants as well as VOC oxidation products. The role of glandular trichomes in VOC emissions and plant-to-plant interactions was also explored. The effects of elevated ozone on passive plant-to-plant interactions was tested and discussed and the effects of the deposition of SOA and reaction products of

VOC oxidation on plant VOC emission and herbivore responses were also explored. A summary of the objectives, hypotheses and main questions of this thesis is presented in Table 1.

The phenomenon of passive adsorption of *R. tomentosum* volatiles to the surface of neighbouring plants was tested in a natural setting (Chapter 2). Earlier observations of the phenomenon had been studied in nature with potted seedlings and in the laboratory (Himanen et al., 2010, 2015). Here, I studied the phenomenon with naturally occurring *R. tomentosum* growing in the understorey of mountain birch trees in the Finnish subarctic. I also explored the effects of *R. tomentosum* density, glandular trichomes and growing season on the passive adsorption and re-emission process.

Secondly, the effects of ozone on volatile mediated plant-to-plant interactions was tested (Chapter 3); earlier studies have tested the effects of ozone on active plant-to-plant interactions. Studies of ozone effects on passive plant-to-plant interactions have focused on reactions occurring on the receiver surfaces (Li and Blande, 2015). The effects of the degradation of volatiles under elevated ozone regimes in the air on the quality and quantity of VOCs adsorbed by the receiver plant and the corresponding effect on herbivore resistance conferred by adsorption was tested.

Thirdly, the effects of VOC oxidation products on Brassica plant VOC emissions and herbivore responses was tested (Chapter 4). α -Pinene, a ubiquitous monoterpene which accounts for more than 30% of global monoterpene emissions (Sindelarova et al., 2014) was oxidized by ozone and hydroxyl OH radicals to produce SOA and other oxidation products. The products of these oxidation reactions were passed into a chamber containing Brassica plants. The effects of exposure to SOA and oxidation products on Brassica VOC emissions and herbivore responses were tested.

Table 1. Summary of the hypotheses and research questions addressed in the original articles presented in this thesis.

Chapter	Basic information	Hypothesis tested	Research questions
2	<p>Species: <i>Rhododendron tomentosum</i> (RT), <i>Betula pubescens</i> (MB).</p> <p>Treatment: <i>B. pubescens</i> (MB) were grouped based on <i>R. tomentosum</i> understory density. VOC emission and glandular trichome (GT) density and condition was measured from both plant species during the early and late growing season.</p>	<ul style="list-style-type: none"> • RT understory presence and density affects MB VOC emissions. • These emissions are linked to RT and MB glandular trichome density 	<p>Do RT shrubs growing in the understory of MB trees release volatiles that are adsorbed and re-emitted by MB foliage?</p> <p>Is the adsorption dependent on understory RT density?</p> <p>Is GT density linked with VOC emissions in both species? How does this affect passive adsorption of RT volatiles by MB?</p>
3	<p>Species: RT, <i>Brassica oleracea</i>, <i>Plutella xylostella</i></p> <p>Treatment: <i>B. oleracea</i> were exposed to (a) RT volatiles, (b) RT volatiles mixed with 100 ppb ozone and (c) filtered air for 24 hours.</p> <p>VOCs were collected and analysed from the exposed plants and <i>P. xylostella</i> adults were given an oviposition choice test between the three treatments. Number of eggs were counted after 24 hours.</p>	<ul style="list-style-type: none"> • Ozone degrades RT volatiles and changes the quantity and blend available for adsorption by neighbouring plants. • Ozone reduces herbivore resistance conferred by RT volatiles on <i>Brassica</i> plants 	<p>Does ozone disrupt passive adsorption of RT volatiles on neighbouring plants and the herbivore resistance they confer?</p>
4	<p>Species: <i>Brassica oleracea</i>, <i>Plutella xylostella</i>, <i>Carausius morosus</i></p> <p>Treatment: <i>B. oleracea</i> was exposed to SOA and reaction products formed through the oxidation of α-pinene by ozone (O_3) and hydroxyl (OH) radicals in an exposure chamber. We analysed the VOC emission from the exposed plants and tested exposure effects on herbivore feeding and oviposition.</p>	<ul style="list-style-type: none"> • α-pinene oxidation forms lower volatility volatile reaction products and SOA that are deposited on surrounding vegetation. • These deposited compounds affect plant VOC emission and herbivore response 	<p>Does the exposure to SOA and reaction products of α-pinene oxidation affect <i>B. oleracea</i> VOC emission and herbivore response?</p>

6 CONCLUSION AND FUTURE DIRECTIONS

This thesis demonstrates passive adsorption of *R. tomentosum* VOCs and SVOCs to the surface of neighbouring plants and the herbivore resistance that passive volatile adsorption may confer on the receiver plants. In this thesis, evidence for monoterpene and sesquiterpene adsorption from ambient air in nature is provided, which may have far-reaching implications in a number of scenarios. Firstly, in field measurements of VOCs, it raises the possibility that VOCs collected from a plant species may originate from neighbouring plants especially in dense vegetation. Furthermore, the ecological effects of adsorption or uptake of neighbouring plant VOCs could be significant. As has been shown, adsorption of *R. tomentosum* VOCs increases the receiver plant's resistance to herbivory. Monoterpene uptake and sesquiterpenes on foliar surfaces could also have important roles in the receiver plant's response to abiotic stresses such as increased temperature and oxidative stress, which is exemplified by exogenously applied monoterpenes and plant surface sesquiterpenes having been shown to help plants cope with heat and oxidative stress respectively. Finally, the adsorption of neighbouring plant volatiles may potentially be useful in agriculture by providing an extra layer to volatile-based intercropping systems. So far, volatile-based intercropping systems have relied on repulsive "push" crops and attractive "pull" crops based on the volatiles emitted by the plants. *R. tomentosum* VOCs may provide repellence against pests in the air as well as on the surfaces of the focal plants.

The deposition and re-emission of VOC oxidation products reiterates the importance of atmospheric conditions and reactions in plant chemical ecology. In this thesis, the phenomenon was tested with agricultural plants, however forests are important emitters of VOCs for SOA formation, hence the effects of SOA deposition on forest species and the corresponding effects on pests of forest species should be the subject of future enquiry. Using constitutive or induced emissions from forest species, for example conifers, will also be more representative of natural scenarios.

In conclusion, the presence of VOCs, SVOCs and their reaction products on plant surfaces may be endogenous from within the plant or exogenous from the atmosphere, and these compounds may have important implications for plant chemistry and plant interactions with herbivores.

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Semi-volatile organic compounds (SVOCs) are synthesized and emitted by many plant species and are produced by atmospheric oxidation of volatile organic compounds (VOCs). Due to their low volatility, SVOCs tend to adhere to plant surfaces at low temperatures and may affect a plant's ecological interactions. This thesis explores the effects of foliar deposition of SVOCs and their oxidation products on plant volatile emissions and plant defence against herbivores. The results contribute to our knowledge of the sources, foliar behaviour and ecological effects of SVOCs.



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