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Ozone disrupts adsorption of *Rhododendron tomentosum* volatiles to neighbouring plant surfaces, but does not disturb herbivore repellency

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A B S T R A C T

The perennial evergreen woody shrub, *Rhododendron tomentosum*, confers associational resistance against herbivory and oviposition on neighbouring plants through passive adsorption of some of its constitutively emitted volatile organic compounds (VOCs). The adsorption process is dependent on transport of VOCs in the air. In polluted atmospheres, the VOCs may be degraded and adsorption impeded. We studied the effect of elevated ozone regimes on the adsorption of *R. tomentosum* volatiles to white cabbage, *Brassica oleracea*, and the oviposition of the specialist herbivore *Plutella xylostella* on the exposed plants. We found evidence for adsorption and re-emission of *R. tomentosum* volatiles by *B. oleracea* plants. Ozone changed the blend of *R. tomentosum* volatiles and reduced the amount of *R. tomentosum* volatiles recovered from *B. oleracea* plants. However, plants exposed to *R. tomentosum* volatiles received fewer *P. xylostella* eggs than control plants exposed to filtered air irrespective of whether *R. tomentosum* volatiles mixed with ozone. Ozone disrupts a volatile mediated passive plant-to-plant interaction by degrading some compounds and reducing the quantity available for adsorption by neighbouring plants. The change, however, did not affect the deterrence of oviposition by *P. xylostella*, suggesting that aromatic companion plants of *Brassica* crops may confer pest-deterring properties even in ozone-polluted environments.

1. Introduction

Biogenic volatile organic compounds (BVOCs) are secondary organic metabolites that mediate plant interactions within and across trophic levels (Dicke and Baldwin, 2010). These interactions include plant-to-plant communication, herbivore foraging, oviposition and pollination (Dicke and Baldwin, 2010; Holopainen and Blande, 2013). Some of these interactions are dependent on transport of BVOCs in the air (Karban et al., 2006), where they are subject to atmospheric reactions that may hinder the ecological processes they mediate, especially in polluted atmospheres (Blande et al., 2010). Tropospheric ozone is one of the most important atmospheric pollutants with levels expected to increase in many parts of the world in the future due to global warming and land cover changes (Martin et al., 2015; Prather et al., 2013). Currently, background ozone levels in the northern hemisphere range between 35 and 45 ppb, with common occurrences of peak emissions of above 100 ppb (Cionni et al., 2011; Fowler et al., 2008). Although the global average ozone concentrations are not expected to increase significantly over the coming years, average 8-h daily averages of up to 80 ppb are still experienced in some areas (Cionni et al., 2011; Oksanen et al., 2013).

At higher ozone levels, some volatile compounds are degraded, resulting in the disruption of their ecological roles. Volatile mediated-herbivore foraging (Li et al., 2016), pollinator attraction (Farré-Armengol et al., 2016) and plant-to-plant interactions (Girón-Calva et al., 2016; Li and Blande, 2015) have all been shown to be disrupted under elevated ozone regimes. Volatile-mediated plant-to-plant interactions may be active, whereby volatiles trigger a physiological response in the receiver plant (Frost et al., 2008; Heil and Kost, 2006; Kost and Heil, 2006) or passive, whereby volatiles stick to the surfaces of neighbouring plants (Li and Blande, 2015). Both active and passive processes may confer herbivore resistance on receiving plants in a process known as associational resistance (Kost and Heil, 2006; Karban et al., 2006; Himanen et al., 2010; Himanen et al., 2015). Elevated ozone regimes have been shown to disrupt active plant-to-plant interactions by degrading the volatiles and reducing the effective interaction distance between emitter and receiver plants (Blande

et al., 2010). The effects of elevated ozone on passive plant-to-plant interactions remain largely unstudied.

Here, we studied the effect of ozone on interactions between *Rhododendron tomentosum* and *Brassica oleracea*, a model system for passive plant-to-plant interactions. *Rhododendron tomentosum* is a small woody perennial evergreen shrub distributed throughout boreal ecosystems (Butkienė et al., 2008). The species has a high volatile terpenoid content stored in glandular trichomes distributed throughout its leaves and stem that gives it a characteristic smell. Some of these terpenoid compounds are myrcene ($C_{10}H_{16}$), which is the main monoterpene compound, as well as species-specific C15 semi-volatile compounds, ledene ($C_{15}H_{24}$), ledol ($C_{15}H_{26}O$), and palustrol ($C_{15}H_{26}O$). (Dampc and Luczkiewicz, 2013; Himanen et al., 2010; Himanen et al., 2015). *R. tomentosum* extracts and essential oils have been shown to have herbivore repellent properties (Egigu et al., 2011; Jaenson et al., 2005).

Passive adsorption of *R. tomentosum* volatiles on neighbouring plant surfaces was first reported by Himanen et al. (2010) when the species-specific volatile sesquiterpenes − palustrol, ledene and ledol were recovered from the surfaces of neighbouring silver birch branches. *Betula pendula* and *Brassica oleracea* plants exposed to volatiles from neighbouring *R. tomentosum* showed increased resistance to herbivore-feeding and *Plutella xylostella* oviposition (Himanen et al., 2010; Himanen et al., 2015). Plant volatiles are used as cues in host finding and selection by *P. xylostella*, once a plant is selected, the leaf surface physical and chemical characteristics are used to determine its suitability for oviposition (Renwick and Chew, 1994; Badenes-Perez et al., 2004).

The volatile constituents of *R. tomentosum* are mostly terpenoids, which are prone to oxidation reactions with ozone in the atmosphere (Atkinson and Arey, 2003). Elevated ozone may change the blend of *R. tomentosum* volatiles in the air by degrading some of its volatile constituents and subsequently reducing the availability for adsorption to neighbouring plants. Degradation reactions may also produce compounds whose ecological significance remains unknown. We tested the effects of an elevated ozone regime on the volatile blend of *R. tomentosum* after emission and the adsorption of these compounds to *B. oleracea* plants. We also tested the effects of adsorption of volatile compounds emitted by *R. tomentosum* on oviposition on *B. oleracea* by *P. xylostella*.

2. Materials and methods

2.1. Plant material

We collected *Rhododendron tomentosum* (henceforth referred to as RT) plants in August 2016 from a ditched pine forest site in Suonenjoki, Finland (62.6456° N, 27.0649° E) and stored them at 4 °C for 2 weeks before the start of experiments. White cabbage, *Brassica oleracea* convar. *capitata* var. *alba* seeds were sown in a mixture of peat:mull:sand (3:1:1) in 1 L pots and grown in a plant growth chamber (Weiss Bio 1300, Germany) [Day 16 h (photosynthetically active radiation 300 $\mu mol^{-2} s^{-1}$), 23 °C, 60% humidity: Night 8 h dark, 18 °C, 80% humidity].

2.2. Exposure system

In the exposure system (Fig. 1), 30 g of RT shoots were arranged in an Erlenmeyer flask filled with water and enclosed in a pre-cleaned (+120 °C for 1 h) polyethylene terephthalate (PET) bag (45 × 55 cm). Activated carbon-filtered air was passed through Teflon tubes into the RT enclosure at 2 L min^{-1} and the outlet air from the RT enclosure was split evenly into two 22.4 L glass desiccators (mixing chambers). One of the mixing chambers was supplemented with ozone-enriched air up to a level of 100 ppb and
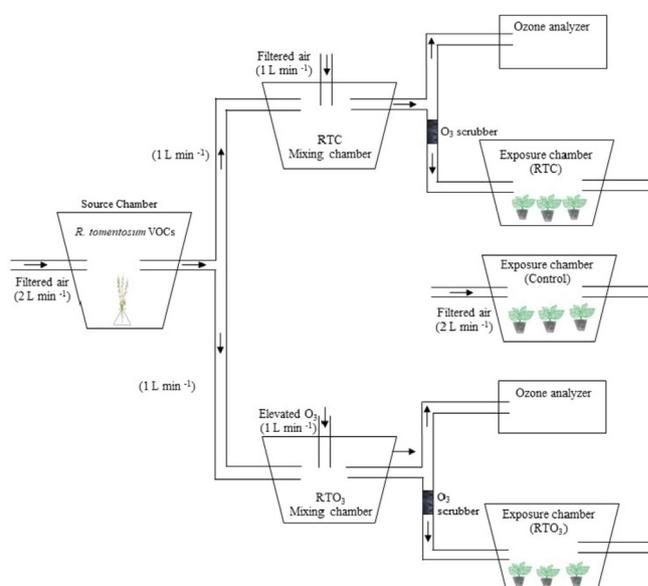

Fig. 1. Schematic illustration of exposure to RT volatiles, RT volatiles +100 ppb ozone and filtered air (control). Exposure lasted for 24 h in each experiment and was repeated five times.

ozone-free air was added to the other mixing chamber at a rate of 1 L min^{-1}. Ozone (O_3) was produced from filtered air with an ozone generator (Dasibi 1008-RS; Dasibi Environmental Corp., Glendale, CA, USA) and ozone analysers (Environnement S.A O342M, Environnement S.A, Poissy, France) were used to monitor ozone levels. Outgoing air from each mixing chamber was split into two; one stream passed into an ozone analyser and the other was passed through O_3 scrubbers [potassium iodide (KI) coated copper tube] to remove ozone before passing into 22.4 L chambers (exposure chambers) each containing three 4-week-old cabbage plants. The setup also included a control exposure chamber through which activated carbon-filtered air was passed at a rate of 2 L min^{-1}. Thus, there were three treatments: control plants exposed to filtered air, plants exposed to RT emissions (RTC) and plants exposed to RT emissions after they had been mixed with ozone (RTO$_3$). Outgoing air from the exposure chambers was released into a fume hood. Each exposure treatment period lasted 24 h (16 h light, 8 h dark) and was repeated five times.

2.3. Volatile analysis

All volatiles were collected in stainless steel tubes filled with 200 mg Tenax TA 35/60 adsorbent (Markes International, UK). Volatiles were collected from the air space of mixing chambers 2 h after setup for 10 min at ~0.2 L min^{-1} with a suction pump (KNF, Neuberger D-79112, Germany) in order to measure the concentrations of *R. tomentosum* volatiles in the mixing chamber. The mixing chamber concentrations were expressed in ng L^{-1}. The exposure system was established five times with two *B. oleracea* plants from each exposure chamber selected for plant volatile analysis and leaves detached from the 3rd plant and used for oviposition tests. In a 5th exposure cycle, one plant was used for volatile analysis and two for oviposition tests. In total, we collected volatiles from nine plants and used thirty-six detached leaves for oviposition tests per treatment. Dynamic headspace analysis was used for plant volatile collection; plant shoots were enclosed in a pre-cleaned PET bag (25 × 55 cm) and filtered air was passed through one end of the bag at ~ 0.3 L min^{-1}. A Tenax TA adsorbent-filled tube was attached to the other end of the bag with a suction

tube pulling air through the adsorbent-filled tube at ~0.2 L min^{-1}. The collected volatiles were thermally desorbed and analysed using gas chromatography–mass spectrometry (GC-MS). Blande et al. (2010), describes the volatile collection and analysis in detail. After volatile collection, individual *B. oleracea* shoots and leaves were cut and dried at 60 °C for 72 h, subsequently the leaf dry weights (DW) were measured. Volatile emission rates from *B. oleracea* were expressed in ng g^{-1} (DW) h^{-1}.

2.4. Oviposition test

Petioles of detached leaves from the three treatments were inserted into water-filled glass tubes and placed in square-based $33 \times 33 \times 60$ cm Perspex cages with meshed fabric sides. Each leaf was placed equidistant from the centre of the cage where a 30% honey solution (food source) was placed. Thirty *Plutella xylostella* adults from a stock population reared on broccoli plants were introduced into each cage, and after 24 h, the leaves were inspected under a stereo microscope and the number of eggs counted.

2.5. Statistical analyses

Data from mixing chambers were log transformed (Log 10 (x+1)) to fulfil criteria for normality and compared with a paired sample *t*-test. Non-parametric Kruskal-Wallis tests with multiple pairwise comparisons (Mann-Whitney U with Bonferroni corrections) were used to test differences in volatile emission rates between cabbage plants exposed to filtered air (control), RTC emissions and RTO$_3$ emissions. Linear Mixed Models ANOVA with Bonferroni adjustments were used to test for differences in *Plutella xylostella* oviposition (egg number) with exposure treatment as the fixed factor and exposure number as a random factor.

3. Results and discussion

In total, we found 36 compounds in the RTC and RTO$_3$ mixing chambers, including monoterpenes, alkenes, aromatics, aldehydes, alkenes, sesquiterpenes and other compounds (Table 1). Ozone reduced the concentration of the RT-sesquiterpenes, α-gurjunene, β-caryophyllene, isoledene, aromadendrene and ledene as well as the monoterpenes, myrcene, neo-alloocimene and limonene (P < 0.05, in all cases) within the RTO$_3$ mixing chamber (Table 1). However, the concentration of the dominating RT volatile, the sesquiterpene alcohol palustrol, was not affected by the 100 ppb concentration of ozone. On the other hand, there was an increase in the concentrations of hexanal, 4-methylene-5-hexenal, 6-methyl-5-hepten-2-one and decanal (P < 0.05, in all cases) in the RTO$_3$ mixing chamber (Table 1). This suggests that these compounds may be reaction products of volatile oxidation reactions (Fruekilde et al., 1998).

Monoterpenes and sesquiterpenes are prone to ozonolysis in the atmosphere due to the presence of C=C double bonds (Atkinson and Arey, 2003), which are lacking in oxygenated sesquiterpenes like palustrol (Tran and Cramer, 2014). The rate of ozonolysis of volatile compounds in the air is dependent on ozone air levels as well as the chemical composition of the air mass containing the BVOCs (Atkinson and Arey, 2003; Kim et al., 2010). Increase in ozone levels is likely to degrade volatiles and reduce their atmospheric lifetimes (Kim et al., 2010). Elevated ozone levels of 50 and 100 ppb disrupted the ability of *P. xylostella* to find its host plant by degrading the plant's volatile constituents used in herbivore foraging (Li et al., 2016). Furthermore, 80−120 ppb ozone levels degraded volatiles and reduced the effective distance of plant-to-plant interactions in lima bean (Blande et al., 2010) and pollinator attraction to *Brassica nigra* (Farré-Armengol et al., 2016).

Table 1
Volatile organic compound concentration (ng L^{-1}) in RT + filtered air (RTC) and RT + elevated ozone (RTO$_3$) mixing chambers 2 h after the start of the experiment. Significant difference in concentration of compounds between mixing chambers are emboldened (P < 0.05), paired samples *t*-test, (n = 8).

Compounds	RTC	RTO$_3$	P-Value
Monoterpenes			
α-Pinene	40.4 ± 7.5	25.3 ± 3.6	0.312
β-Pinene	8.0 ± 2.9	3.4 ± 1.3	0.163
Myrcene	1246.2 ± 168.1	667.4 ± 127.7	**<0.001**
Limonene	399.1 ± 145.0	208.4 ± 76.9	**<0.001**
Δ-3-Carene	37.3 ± 9.3	29.1 ± 6.2	0.672
(Z)-β-Ocimene	39.4 ± 11.8	32.0 ± 10.0	0.266
(E)-β-Ocimene	18.6 ± 4.4	14.2 ± 4.8	0.544
Neo-alloocimene	346.9 ± 159	224.8 ± 102.8	**0.021**
GLVs			
3-Hexen-1-ol	24.3 ± 5.5	16.6 ± 5.6	0.434
1-Hexanol	274.9 ± 55.5	285.1 ± 65.4	0.892
Alkenes			
1-Hexadecene	13.8 ± 8.0	33.9 ± 23.5	0.991
6-Dodecene	11.0 ± 5.4	13.1 ± 5.1	0.417
Aromatics			
Ethylbenzene	110.4 ± 29.9	76.3 ± 18.7	0.531
1,3-dimethyl-benzene	90.9 ± 25.7	70.9 ± 24.2	0.699
Benzyl alcohol	76.6 ± 51.5	25.5 ± 6.5	0.950
Benzene	12.1 ± 4.3	6.1 ± 2.4	0.237
1-propenyl-benzene	18.8 ± 6.0	12.0 ± 5.0	0.448
Aldehydes			
Benzaldehyde	151.0 ± 37.8	180.2 ± 46.9	0.470
Hexanal	148.7 ± 30.9	241.4 ± 36.5	**0.034**
Octanal	119.3 ± 31.0	88.6 ± 15.0	0.808
Heptanal	48.0 ± 7.5	60.4 ± 10.4	0.276
Nonanal	270.2 ± 34.4	341.7 ± 60.4	0.281
Decanal	272.1 ± 28.7	392.8 ± 57.7	**0.048**
Alkanes			
Tridecane	9.6 ± 5.3	15.5 ± 4.6	0.182
Naphthalene	31.5 ± 9.6	19.7 ± 10.9	0.187
1-Tetradecane	32.8 ± 4.8	27.8 ± 2.8	0.327
2-Methyltetradecane	40.0 ± 6.5	69.4 ± 28.2	0.436
Sesquiterpenes			
α-Gurjunene	86.7 ± 36.4	24.5 ± 3.6	**0.008**
β-Caryophyllene	43.5 ± 9.9	7.3 ± 3.1	**0.007**
Isoledene	86.8 ± 33.8	41.4 ± 23.0	**0.009**
Ledene	104.3 ± 25.4	17.5 ± 3.9	**<0.001**
Aromadendrene	70.9 ± 31.2	4.4 ± 2.1	**0.031**
Palustrol	1052.2 ± 548.8	1460.1 ± 449.2	0.379
Other Compounds			
6-Methyl-5-hepten-2-one	37.8 ± 4.6	122.9 ± 37.3	**0.036**
4-Methylene-5-hexenal	48.5 ± 23.7	149.1 ± 33.7	**0.021**
1,2-Benzisothiazole	34.7 ± 5.8	25.0 ± 4.4	0.482

Degradation of plant volatiles may also occur on plant surfaces where volatiles are exuded by plant surface trichomes (Jud et al., 2016; Fruekilde et al., 1998), but the reactions of ozone on *B. oleracea* surfaces are negligible in our experiments due to the air from the ozone-mixing chamber passing through ozone scrubbers.

The reaction products from ozonolysis of volatiles may be short-lived early stage products or less volatile and more stable products (Holopainen et al., 2017). Known reaction products of sesquiterpenes, 6-methyl-5-hepten-2-one (Fruekilde et al., 1998) and of myrcene, 4-methylene-5-hexenal (Zhao et al., 2012) had concentration levels that were higher in the RTO$_3$ mixing chamber than the RTC chambers. These products have been reported as part of the RT volatile bouquet especially from aged shoots (Butkienė et al., 2008). Aldehydes like decanal have also been measured in higher quantities when volatiles react with ozone (Li and Blande, 2015). The effects of volatile reaction products on plant interactions is still largely unknown although there are some observations that some volatile reaction products may affect plant-species interactions (Wenhao et al., 2009).

There was evidence of adherence of RT monoterpenoids and

Table 2
Median values and inter quartile range (IQR) (n = 9) for volatile emission rates (ng g^{-1} h^{-1}) from white cabbage exposed to RT volatiles (RT) and RT + 100 ppb ozone (RTO$_3$) and control. P-values from Kruskal-Wallis tests are shown, statistically significant values emboldened. Different letters [ab] represent significant (p < 0.05) differences between groups (multiple pairwise comparison). In the cases of adhered RT compounds (nd = not detected in control), the Mann-Whitney U test was used to compare RT and RTO$_3$ emissions.

Compounds	Control	RTC	RTO$_3$	P-Value
Monoterpenes				
α-Thujene	0.0 (0.0—1.9)	0.0 (0.0—0.0)	1.4 (0.0—2.1)	0.424
α-Pinene	21.5 (4.3—47.2)	(4.9—20.9)	9.4 (4.0—29.1)	0.623
Camphene	0 (0.0—0.0)	0.0 (0.0—1.3)	0.0 (0.0—0.0)	0.477
Sabinene	3.3 (0.0—5.7)	4.3 (2.9—5.5)	6.2 (0.0—10.2)	0.670
β-Pinene	0 (0.0—0.0)	0.00 (0.00—2.5)	2.3 (0.0—3.4)	0.698
Myrcene	0 (0.0—2.6)[a]	16.2 (11.5—25.7)[b]	4.3 (3.6—5.1)[c]	**<0.001**
Δ-3-Carene	3.3 (0.7—4.4)	1.7 (1.2—3.5)	0.0 (0.0—4.6)	0.564
Limonene	8.8 (6.0—13.5)	7.2 (4.6—10.7)	10.8 (4.6—17.3)	0.870
1,8-Cineole	6.8 (1.7—8.0)	3.9 (3.0—7.2)	4.4 (0.0—6.6)	0.452
Neoallo-ocimene	nd	95.3 (74.1—107.4)	75.3 (66.6—121.1)	0.965
Sesquiterpenoids				
Isoledene	nd	79.6 (47.0—101.0)	44.5 (34.8—96.1)	0.489
Aromadendrene	nd	7.8 (6.5—10.5)	5.1 (4.8—8.3)	0.297
Ledene	nd	62.7 (45.5—85.4)[a]	11.8 (9.4—21.1)[b]	**0.011**
α-Gurjunene	nd	15.3 (7.9—19.2)	6.1 (4.6—13.9)	0.077
Palustrol	nd	404.7 (288.4—486.0)	616.2 (455.2—712.6)	0.077
GLVs				
(Z)-3-Hexenyl-acetate	10.7 (0.0—16.6)	4.9 (0.0—5.6)	0.0 (0.0—3.2)	0.210
Nonanal	20.4 (9.1—30.6)	9.8 (6.0—15.1)	16.0 (9.5—33.6)	0.385
Other Compounds				
6-Methyl-5-hepten-2-one	1.7 (0.0—0.0)	0.0 (0.0—3.5)	4.9 (0.0—7.2)	0.403

sesquiterpenoids to cabbage plants (Table 2). The re-emission of the RT-specific sesquiterpenoids, palustrol and ledene from cabbage plants exposed to volatiles from RTC and RTO$_3$ chambers is in line with earlier work done where these compounds were recovered from *B. oleracea* neighbouring RT (Himanen et al., 2015). The sesquiterpenes, aromadendrene, α-gurjunene and isoledene were also recovered from *B. oleracea* exposed to RTC and RTO$_3$ volatiles. Sesquiterpenes are typically mediators of passive plant-to-plant interactions because of their low volatility and condensation properties on various surfaces (Holopainen and Blande, 2013; Schaub et al., 2010). Sesquiterpene compounds from conspecific and heterospecific plants have been shown to adsorb to neighbouring leaves and artificial leaf surfaces, from where they can be re-emitted at higher temperatures (Li and Blande, 2015; Himanen et al., 2015; Himanen et al., 2010). *B. oleracea* plants exposed to RTC and RTO$_3$ volatiles also had higher emission rates of myrcene and re-emitted neo-alloocimene (Table 2), which are quantitatively the most abundant monoterpenes in the RT volatile bouquet (Himanen et al., 2010). This suggests the possibility for monoterpene adsorption and re-emission by non-emitting or neighbouring plant surfaces. The lipophilic properties of plant cuticular waxes mean that uncharged organic volatiles may be adsorbed within the cuticle layer (Müller and Riederer, 2005). Plant volatiles may also be taken up by plants through the stomata, when
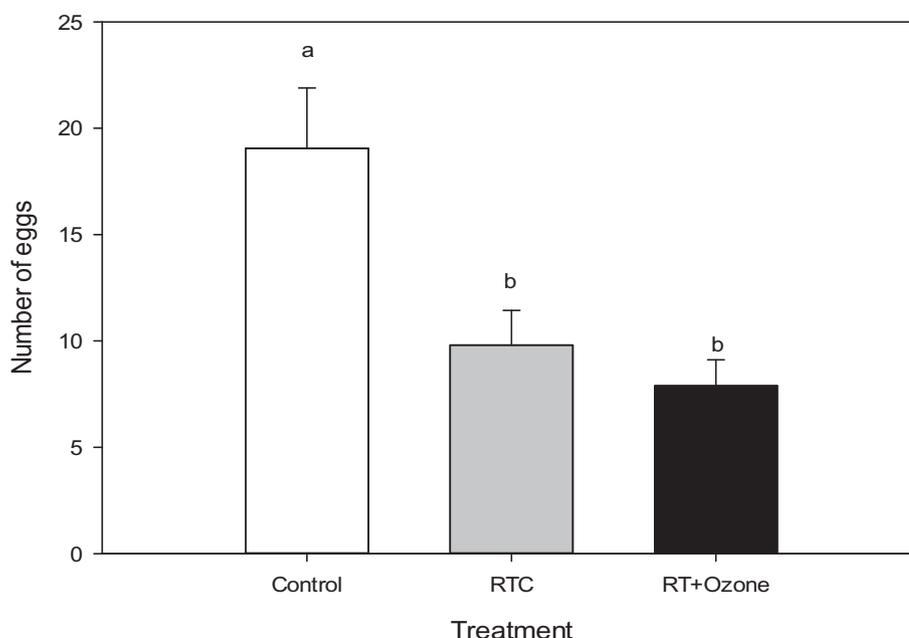
Fig. 2. Oviposition (Mean ± SEM) by *P. xylostella* on white cabbage leaves exposed to RT and RTO$_3$ treatments and control. [ab] represent significant differences between treatments (pairwise comparisons from linear mixed models ANOVA).

air concentrations are higher than within leaf concentration especially in cases of hydrophilic compounds (Niinemets et al., 2014). Laboratory experiments have shown that monoterpene emitting and non-emitting species can adsorb and re-release monoterpenes and the adsorption potential scales positively with the leaf lipid content (Noe et al., 2008). Mixing RT volatiles with ozone reduced the re-release of adsorbed myrcene and ledene from exposed cabbage plants, but there was no difference in the re-release rate of neoallocimene, and other RT sesquiterpenoids irrespective of whether volatiles were mixed with filtered air or elevated ozone.

Detached leaves from cabbage plants exposed to RTC and RTO$_3$ volatiles received a lower number of *P. xylostella* eggs (P = 0.004, Mixed model ANOVA) than those from unexposed control cabbage plants (Fig. 2). However, there was no significant difference in the number of eggs on RTC and RTO$_3$. These results are in support of earlier work where RT exposed cabbage volatiles were less susceptible to *P. xylostella* oviposition (Himanen et al., 2015). The adsorption of neighbouring plant volatiles to the surface of focal plants may alter their leaf surface chemistry and confer associational resistance or susceptibility (Himanen et al., 2015; Li and Blande, 2015). Although sesquiterpenes have been mostly reported as mediators of this process (Li and Blande, 2015; Himanen et al., 2010; Himanen et al., 2015), our results suggest that monoterpene adsorption may also be implicated.

4. Conclusions

Taken together, our results show that ozone changes the blend of RT volatiles in the air by degrading some of the reactive compounds in the bouquet. These degradation reactions affect the recovery of RT compounds myrcene and ledene from exposed neighbours. Ozone, however, did not change the deterrent properties of RT volatiles against *P. xylostella* oviposition on *B. oleracea* plants. Some quantities of ozone degradable RT compounds, as well as stable compounds like palustrol were recovered from RTO$_3$ exposed *B. oleracea* plants, which possibly resulted in the *B. oleracea* plants retaining their deterrent properties. The results suggest that aromatic companion plants may retain the properties that confer associational resistance based on volatiles adhering to crop plants even in ozone-polluted environments.

Acknowledgements

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