Communications Earth & Environment https://doi.org/10.1038/s43247-025-03175-3

Article in Press

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Received: 4 April 2025

Accepted: 30 December 2025

[redacted]

Cite this article as: Simin, T., Ryalls, J.M., Welling, O.E. *et al.* Between-plant interactions in Scots pine are not impaired by air pollutants. *Commun Earth Environ* (2026). https://doi.org/10.1038/s43247-025-03175-3

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Between-plant interactions in Scots pine are not impaired by air pollutants

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Abstract

Herbivore-induced plant volatiles (HIPVs), consisting of volatile organic compounds (VOC), can induce and prime defence-related responses in neighbouring plants. However, atmospheric pollutants such as tropospheric ozone (O_3) and nitrogen oxides (NO_X) can disrupt these interactions by accelerating VOC oxidation and inducing oxidative stress. Here, we investigated the effects of O_3 and diesel exhaust pollution on interactions between Scots pine (*Pinus sylvestris*) seedlings by examining the responses of undamaged receiver plants to cues from weevil-damaged neighbours. Using a novel Free-Air Diesel and Ozone Enrichment (FADOE) platform, we exposed seedlings to elevated O_3, diesel exhaust (NO_X), both in combination, and ambient air. Receiver seedlings exhibited a 49% reduction in bark damage, a 15% increase in net photosynthesis, and priming of green leaf volatile emissions compared to controls and altered blend of emitted VOCs. Despite air pollution affecting photosynthesis, stomatal conductance and VOC emissions, neighbour-induced defences against herbivory remained effective under polluted conditions.

Keywords

Between-plant interactions, Plant-plant communication, Ozone, O_3, Nitrogen oxides, NO_X, Diesel, *Pinus sylvestris*, *Hylobius abietis*, VOC, Photosynthesis, HIPV, FADOE

1 Introduction

Plants are sessile organisms and collectively synthesise a rich diversity of different organic compounds via their specialised metabolism[1]. Herbivores, particularly insects, are important biotic stressors of plants and have been shown to induce the emission of volatile organic compounds (VOCs)[2,3], which can mediate interactions with other organisms, including other plants[4,5]. Here are two major pathways for traversal of informative chemicals between emitter and receiver plants[6]. Phytochemicals can traverse the distance between plants either aboveground through the air or belowground through the soil matrix[6]. The aboveground passage of VOCs between plants has been implicated as providing important cues in numerous studies[5,7–11]. Belowground, information may pass from plant to plant in the form of VOCs[12] or exudates released from roots[13], while there is some evidence that common mycorhhizal networks may also play a role in mediating interactions[14–16].

VOCs are emitted from various aboveground organs of the emitter plant and taken up together with CO_2 and other gases through stomata on the surface of the leaves of the receiver plant[17]. Exposure to herbivore-damaged emitters has been shown to increase the production of phytohormones[9], extrafloral nectar[18,19], proteinase inhibitors[20] and VOCs[4,7,9,19] and to upregulate expression of defence-related genes[10,21] in receiver plants. However, sometimes, changes in plant physiology are not immediately visible, but only after subsequent feeding by insect herbivores. This is known as priming [22] and can be observed as reduced herbivore damage[4,7,23] or elevated VOC emissions[4,7–9,20] after subsequent herbivore damage in primed plants. The blend of emitted VOCs is often highly dependent on plant species and intraspecific variation between individual plants[24,25].

The efficacy of between-plant interactions may be compromised by air pollutants such as tropospheric ozone (O_3) and nitrogen oxides (NO_x). Ozone, a secondary pollutant formed from reactions between VOCs and NO_x in the presence of sunlight[26], and NO_x, primarily emitted from diesel exhaust[27], are known to oxidise some VOCs. Background O_3 levels in forests vary between 30 and 50 ppb globally[28], whereas NO_X levels are comparatively low, often around 10 ppb, if recorded far away from roads, agricultural sources or forest fires[29], but soil and microbial emissions can contribute locally[30]. Ozone oxidation can alter the composition and concentration of VOCs, potentially disrupting their role as signalling molecules[31,32]. Previous studies have demonstrated that O_3 can degrade floral scents, impairing pollinator attraction[33], and reduce the effectiveness of VOC-mediated plant–insect interactions[34,35]. Field-based studies on insect-induced between plant interactions are scant. A study on within-plant signalling in hybrid aspen in the field[36] showed that herbivore feeding on the upper branches induced higher VOC emission rates in lower, undamaged branches, as well as a significant change in the VOC emission blends. Another study on HIPV-mediated between-plant interactions in cabbage plants in a Free Air Concentration Enrichment (FACE) facility[11] showed a significant priming effect on VOC emissions in ambient O_3 levels (34 ppb), but the priming effect was impaired at higher levels (54 ppb). Therefore, O_3 has the potential to disturb HIPV-mediated interactions in the field[34]. However, the impact of other pollutants such as NO_x alone or in combination with O_3 on insect-induced between-plant interactions remains poorly understood, particularly in field conditions.

Boreal forests cover approximately 27% of global forested area and are dominated by conifers, including Scots pine (*Pinus sylvestris*), a species of significant ecological and economic importance for forestry economies in several countries[37,38]. Its vulnerability to herbivores, such as the large pine weevil (*Hylobius abietis*), underscores the need to investigate how air pollution might impair its natural defence mechanisms[39,40]. The large pine weevil, which feeds on the bark of young seedlings, can girdle and kill them, leading to substantial economic losses[41].

Secondary organic aerosols (SOAs) can be formed as a result of VOC oxidation[42]. Recent laboratory-based studies showed that HIPVs[7] and SOAs formed from those HIPVs[8] can mediate interactions between Scots pine seedlings, which resulted in a significant (66%) reduction in bark damage caused by weevils, increases in net photosynthesis (A_N; up to 99%) and stomatal conductance (G_S; up to 170%) and substantial induction (142%) and priming (426%) of VOC emissions. The authors argued that the increase in G_S may result in higher VOC and CO_2 uptake through stomata. Another recent study showed that herbivory by *H. abietis* induced changes in belowground HIPV emission (a potential mediator of interactions) that increased or decreased, depending on the year and environmental conditions, such as warming and fertiliser addition[43]. Biotic interactions shape the structure and functioning of terrestrial ecosystems[44,45] and both pathways of interaction are naturally open in plants growing outdoors[6], so studies on the effectiveness of this natural protection mechanism of Scots pine in the free-air environment should take both pathways into account, especially if they involve the presence of other environmental factors.

This study investigates whether O_3 and NO_x from diesel exhaust disrupt herbivore-induced interactions between Scots pine seedlings, thereby reducing their defence against herbivores *in situ*. Using the University of Reading’s Free-Air Diesel and Ozone Enrichment (FADOE) field platform, we exposed seedlings to elevated levels of O_3, diesel exhaust (primarily rich in NO_x but due to presence of other compounds, referred to as diesel exhaust in this article), combination of O_3 and diesel exhaust addition, and ambient controls. By examining the responses of undamaged receiver plants to cues from weevil-damaged neighbours, we assessed the impact of air pollution on between–plant interactions and herbivore resistance. Specifically, we measured bark damage, $\underline{A_N}$, G_S, and VOC emissions to determine whether pollution impairs the ability of receiver plants to mount effective defences in response to damage-associated cues from emitter plants.

Through this research, we show that air pollution had a significant effect on A_N, G_S and VOC emission, but did not disrupt the interactions in Scots pine, which is reflected by a 49% reduction in large pine weevil damage. In addition, A_N was significantly increased by exposure to damaged emitters (15%) while G_S was not. VOC emissions were not induced by the interactions, but green leaf volatiles (GLVs) were significantly primed. These field-based observations extend laboratory findings, highlighting resilience in natural settings while revealing pollution-specific nuances.

2 Results

2.1 Pollution levels

NO_X and O_3 concentrations reported from the FADOE rings are overall means over the 10-h daily operational periods, averaged across the study duration. The average concentration of O_3 in the ambient rings between 5th May (121 Day of Year, DOY) and 1st July 2023 (182 DOY) was 31 ppb (Figure 1), which matched with local ambient measurements from the nearest air pollution monitoring station in New Town, Reading, UK[46]. In rings with O_3 enrichment, the average O_3 concentration was 39.5 ppb, which is similar to the O_3 concentration limits for vegetation protection in the 2024/2881 directive (40 ppb[47]). In the diesel exhaust enrichment rings the O_3 concentration was 16 ppb, which was the lowest of all the treatments. In rings with both diesel exhaust and O_3 enrichment, the O_3 concentration was 35.8 ppb (8h mean), which was higher than local ambient concentrations measured in New Town, Reading, but below the 2024/2881 directive limits.

The NO_X concentration in ambient air and O_3 enrichment rings was 25.3 ppb and 20.9 ppb respectively, which were both above the vegetation protection limits in the 2024/2881 directive (20 ppb) and local ambient air measurements from an urban monitoring station in London Road, Reading, UK (19 ppb). Average NO_X concentrations in diesel enrichment rings was 2.7 times higher than ambient at 69.7 ppb, while in combined O_3 and diesel exhaust enrichment rings, it averaged 27 ppb.

2.2 Bark damage

When exposed to herbivore-damaged emitter plants, the receiver seedlings incurred an average 49% less large pine weevil damage compared to the control seedlings and this was consistent across all air pollution treatments ($p=0.002$, Table 1; Figure 2a). This demonstrates that the receiver seedlings gained increased resistance to herbivores even in polluted free-air environments.

Air pollution generally did not affect the amount of damage caused by large pine weevils.

2.3 Photosynthesis and stomatal conductance

Photosynthesis (A_N) and stomatal conductance (G_S) can be affected by environmental conditions and diurnal variation. A_N correlated positively with leaf temperature (Pearson, r=0.209, p=0.008, n=160), but the timing of measurements (within a 6-hour window) ensured that diurnal effects were minimised. Exposure to damaged emitters increased the rate of A_N in receiver seedlings by an average 15% compared to controls (p=0.046; Figure 2b, Table 1). The effect of exposure to damaged emitter seedlings on A_N was stronger than the direct effect of herbivory (phase 2 of the experiment; p=0.066, Table 1). The Gs of receivers, unlike A_N did not correlate with leaf temperature (Pearson, r=0.06, p=0.47 n=160). The Gs of receivers was also not significantly affected by exposure to damaged emitters or direct herbivory (phase 2 of the experiment; Figure 2c, Table 1). The acclimation of G_S to time of day-related growth light variations can be an important strategy for maintaining A_N under field conditions[48].

In general, air pollution had a significant effect on the rate of A_N (p=0.031, Table 1) and Gs (p=0.037, Table 1; Figure 2c). However, we found that diesel exhaust treatment alone did not substantially affect A_N (p=0.647, Dunnett's test) or G_S (p=0.99, Dunnett's test). The slight increase of A_N and G_S in O_3-enrichment rings was in contrast to our expectations, but it most likely reflected the air-temperature variations correlating with A_N, as discussed in detail by Simin et al.[25]. Finally, the combination of O_3 and diesel exhaust significantly affected the photosynthetic process of pine. In this air pollution treatment, Gs was, on average, 20.5% lower (p=0.019, Dunnett's test) and the A_N 16% lower (p=0.019, Dunnett's test) compared to controls.

2.4 VOC emissions

We found 123 individual VOCs emitted from Scots pine, which we grouped into non-oxygenated monoterpenes (MTs), oxygenated monoterpenes (oMTs), sesquiterpenes (SQTs), green-leaf volatiles (GLVs), benzenoids (BZs) and other non-isoprenoids (ONIs; Figure 3). On average, MTs were the most abundant VOC group (86%; Figure 3a), followed by oMTs (5%), SQTs (4%), ONIs (3%), BZs (1%) and GLVs (1%; Figure 3b), but the proportions of these groups varied across treatments (Figure 3). Exposure to damaged emitters did not significantly increase the emissions of total VOCs (Figure 3a, Table 1) or different VOC groups (Figure 3b, Table 1) compared to undamaged emitters, meaning that VOC emission rates were not induced by exposure to neighbours damaged by insect herbivores.

However, air pollution had a strong direct effect on the VOC emission rates and blends. The clustering of samples in the PCA showed that the VOC emission blends were affected by the air pollution treatments because they differed clearly from each other across the score plot (Figure S1a and b). Emission rates of oMT, GLVs, BZs, ONIs as well as total VOC emissions were significantly affected by the air pollution, while the emission of MTs was marginally affected (Table 1). For example, in the combined O_3 and diesel exhaust addition rings, and compared to the ambient control rings, the emissions of oMTs increased by an average of 78 % (p=0.046, Table 1, Figure 3b), GLVs increased by an average of 358% (p=0.001, Table 1; Figure 3b), the emissions of BZs increased by 182% (p<0.001, Table 1, Figure 3b), ONIs by 145% (p<0.001, Table 1; Figure 3c) and finally the emission of total VOC emissions increased by 85% (p<0.001, Table 1, Figure 3c). These increases in VOC emissions and blends can be attributed to the damage the air pollutants caused to the plants directly.

Insect herbivory is one of the strongest biotic stressors for plants, known to induce significant increases in VOC emissions[49]. Following insect herbivory, emissions of terpenoid groups and total VOC emissions were significantly elevated in receiver seedlings: 97.4% higher in MTs ($p<0.001$, Table 1, Figure 3a), 68.8% higher in oMTs ($p<0.001$, Table 1, Figure 3b), 12% higher in SQTs ($p=0.046$, Table 1, Figure 3b) and 88% higher for total VOC emissions ($p<0.001$, Table 1, Figure 3a).

Damage area-based increases in VOC emission indicated a priming effect of the exposure to damaged emitters on VOC emissions in receivers (Figure 3 c, d). GLVs showed the most consistent response (26% increase in seedlings exposed to damaged vs Control receivers; $p=0.038$, Table 1, Figure 3 d, Table S1), but exposure to damaged emitters also potentially affected the ONI emission increase (266% increase compared to exposure to control emitters, $p=0.054$, Figure 3d, Table 1, Table S1) and total VOC emission increase (133% higher compared to exposure to control emitters; $p=0.074$, Figure 3c, Table 1, Table S1). Our results demonstrated that exposure to damaged emitters primes the receiver seedlings for GLV emission, and possibly for other non-terpenoids and total VOC emissions with subsequent herbivory by the large pine weevil.

2.5 Pine bark palatability

Herbivorous insects make decisions on which plants to feed upon based on VOC emissions[50,51], which indicate the palatability of the plant tissue. To identify which Scots pine VOCs are most effective in protecting against large pine weevil herbivory, we conducted a partial least squares (PLS) regression[52] analysis on the bark damage area (DA) of receiver seedlings. We focussed on VOCs with a Variable Importance in the Projection (VIP) score >1, isolating the most important compounds for protection. The sesquiterpene, β-elemene, was the only compound negatively correlated with bark damage (Figure 4a).

In contrast, bark damage was positively correlated with the emissions of an oxygenated monoterpene, two benzenoids, and three other non-isoprenoids, which may be reliable host plant indicators.

Score plots of the PLS analysis revealed that between-plant interactions alter the VOC blends (Figure 4b). Receiver seedlings exposed to damaged emitters exhibited VOC blends that differed significantly from seedlings exposed to control emitters along the diagonal of the score plot ($p = 0.007$, MANOVA). In the loadings plot, the score averages of receiver seedlings exposed to damaged emitters clustered around SQTs (Figure 4c).

Emission rates of VOCs that correlated significantly with bark damage are presented in Figure 4d. The emission of the sesquiterpene β-elemene was not influenced by emitter exposure, air pollution treatment or herbivory phase. The emission of 7-methyl pentadecane, a non-terpenoid compound, was affected by air pollution treatment ($p=0.03$, LMM), showing an increase in the presence of O_3. The same trend is true for another non-isoprenoid VOC, 6,9-dimethyl tetradecane ($p<0.001$, LMM). Alcohol 1 (labelled this because of the lack of a high match factor in the NIST 20 library) was influenced by air pollution (higher in O_3 addition and combined ozone and diesel exhaust addition rings; $p<0.001$, LMM), experimental phase (higher after herbivory, in general; $p=0.011$; LMM) and the combination of the treatments (higher before herbivory in O_3 addition rings only; $p<0.001$, LMM). The emission of linalool, an oMT, was similarly affected by air pollution (increased by both treatments, $p=0.047$, LMM), experimental phase (higher after herbivory in general, $p<0.001$, LMM) and the combination of pollution and experimental phase (in O_3 rings, emission is higher before herbivory; $p<0.001$, LMM). The emission of ethylbenzene, a BZ, was significantly higher before rather than after herbivory ($p<0.001$, LMM) and similar is true for the other BZ, benzaldehyde, but it was not statistically significant.

3 Discussion

3.1 Between-plant interactions in the field

In this study, we demonstrated that between-plant interactions in the field rendered Scots pine seedlings more resistant to damage by bark-feeding herbivores, increased photosynthesis and primed GLV emissions. The main result of our study shows that enhanced defence resulting from exposure to damaged emitters, first observed in laboratory conditions[7,8], is preserved in the free-air environment and is not compromised by O_3 and NO_X pollution. Activation of defence against herbivory is indicative of a broad and physiologically relevant change in several important metabolic processes.

A recent meta-analysis on regulation of photosynthesis (A_N) in plants proposed three levels of regulation: stomatal conductance (G_S), mesophyll conductance and biochemical capacity[53]. Due to fieldwork-related time restrictions, we did not measure mesophyll conductance, a complex plant trait that refers to the transfer of CO_2 between intercellular air space and mesophyll cells inside the leaves (or pine needles). However, we have observed an increase in A_N as a response to exposure to damaged emitters, which was lower than observed in previous laboratory-based studies[7,8] (15% vs 99%), but still significant ($p=0.045$). This suggests that between-plant interactions prepare receivers for potential herbivore attack, by compensating for these losses in advance and increasing resources available for activating defense responses through elevated carbon assimilationrates. However, contrary to findings of Yu et al.[7,8] we did not observe a significant increase in *Gs* after exposure to damaged emitters. This suggests that biochemical and not stomatal processes, such as Ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) activity (*Vcmax*) or RuBP regeneration (*Jmax*) in the chloroplasts may be involved in elevating the A_N [53,54]. It is possible that between-plant interactions increase the efficiency of RuBiSCO directly, but this would need to be confirmed in separate laboratory-based studies. Since the belowground pathway of interaction was also available for Scots pine in our experiment, it is possible that rhizosphere-mediated interactions induced the A_N increase Indeed, underground fungal connections can mediate interactions between two species of grass which result in a significant increase in A_N[55] for both plants. Another aspect that could suggest that underground rather than stomatal processes were involved in the interactions was that unlike laboratory-based studies[7,8] there was no significant induction of VOC emissions after exposure to damaged emitters, even after standardising them to temperature and light. The idea that underground interactions increase A_N without increasing G_S requires further investigation using laboratory studies.

The priming of GLVs after exposure to damaged emitters that we observed in the field, has also been reported in recent laboratory-based studies[7,8,19]. These increased VOC emissions are a part of a broader plant defence mechanism induced by interactions with damaged neighbours[4,56]. GLVs were among the first identified mediators of between-plant interactions[50,56,57] and have a significant effect on local atmospheric conditions, through formation of secondary organic aerosols in areas with high GLV emission such as local insect outbreak events[58].

There is a need for more studies investigating field-based VOC emissions under herbivory stress[59]. Our study contributes to this goal, but it also further complicates the interpretation by demonstrating significant increases in abiotic stress-related VOC emissions after exposure to herbivore-damaged neighbours. Similarly, there is a need for field-based measurements of photosynthesis[60] and, in addition to this, our study contributes to the growing body of scientific publications in the field of chemical ecology indicating that carbon assimilation is elevated after exposure to damaged emitters [7,8,19], which requires further experimental scrutiny, discussion and potential inclusion into Earth system models. Moreover, since the phenomenon of interactions between damaged and undamaged neighbouring plants resulting in photosynthesis increase has only been observed in a couple of species[7,8,61] , there is a need for broader replication in other plant and insect systems to determine if it is a generalised plant response to damage-induced between-plant interactions. Our field-based study shows considerable alterations in gas exchange traits induced by between-plant interactions, and as such, has implications for terrestrial carbon sink and biosphere-atmosphere interactions.

3.2 The effect of air pollution

Air pollutants enter the leaf intercellular space together with CO_2 through the stomata where they can cause oxidative stress[17]; plants can regulate their exposure to air pollution by controlling the G_S[62]. The significant decrease in A_N and G_S we observed in the combined O_3 and diesel exhaust treatment is likely due to NO_x-induced stomatal closure (NO_X gases are a major product of diesel combustion), which protects the leaves against oxidative stress[62] and toxic pollutant (e.g. peroxynitrite) formation[62]. Reduced Gs can also affect the perception of HIPVs, because the VOCs enter the plant through stomata together with CO_2 and other gases[63,64]. Our study suggests that stomatal closure might have interfered with take-up of HIPVs[17] and possibly prompted the plants to utilise the belowground route to mediate the interactions, although this needs to be further tested and confirmed in future experimental studies.

Exposure to O_3 and NO_X is well-known to cause physical damage to leaves (as discussed by Oksanen and Kontunen-Soppela[65]), so the increase in emissions of VOCs in pollution rings could be due to mechanical damage to surface or internal structures of the pine seedlings; the needles and the bark[32]. NO_X from the diesel exhaust treatment did not negatively affect these emissions, but O_3 is known to oxidize a variety of plant VOCs[31], and could have interfered with the priming process of receiver plants. Moreover, a laboratory-based study with O_3 levels double those in the FADOE O_3 rings found that O_3 compromises priming of certain VOCs and VOC groups in Scots pine after exposure to damaged emitters[7], but that the overall induced herbivore protection remained intact.

The lack of significant air pollution effects on the result of between-plant interactions suggests that plants utilize a variety of VOC blends resilient to oxidation and other signalling strategies to induce herbivore protection in the field. One of those strategies, in addition to belowground interactions, could be the potential effect of HIPV-derived SOAs. VOCs readily oxidise in normal atmospheric environments forming SOAs[66] and especially so in O_3-polluted environments[31], but are typically offset in NO_X-rich air[67]. A recent laboratory-based study demonstrated SOA-mediated interactions in Scots pine. In addition to activating defences against large pine weevil herbivory and elevating A_N, SOA exposure primed the emissions of MTs and total VOC emissions, but did not induce the VOC emissions in receiver plants immediately after exposure. These findings resemble our field-based results, which suggests that SOAs might indeed be active and currently under-studied mediators of between-plant interactions in forest ecosystems, especially in polluted environments which affect the rates of VOC emission and SOA formation. Therefore, more studies on SOA-mediated between-plant interactions are needed, primarily in the free-air environment.

3.3 Pine bark palatability

Terpenoids are found in the resin of pines and attract pine-feeding bark beetles but are also toxic at high vapour pressures and thus are considered an important component of the defence response of pines[68].

β-elemene, a SQT we found to be negatively correlated with large pine weevil damage, forms a part of many essential oils and was previously reported to be highly toxic to weevils[69]. Linalool is an oMT that was positively correlated with large pine weevil damage in our study and has also been found to be strongly induced in Scots pine by large pine weevil damage[70]. oMTs have been shown to increase large pine weevil feeding rates[71], likely because the large pine weevil feeds exclusively on coniferous trees and has developed tolerance to oMTs produced by Scots pine. Another important role of oxygenated monoterpenes that has been observed is their involvement in pheromone biosynthesis of bark-feeding beetles following bark consumption[68].

Clustering of score averages of damaged emitter-treated samples around SQTs in the PCA that accompanied our PLS regression analysis (Figure 4c) suggests that SQTs may reduce bark palatability, thereby protecting the seedlings from large pine weevil attacks. This finding is supported by evidence that SQTs are highly toxic to other species of weevils from lower latitudes[72].

Finally, the possibility that insect feeding manipulated the plant VOC emissions to benefit them rather than the plant needs to be considered. For example, benzenoid compounds are known to be emitted from roots and bark of woody plants[73] and it has been shown in bioassays that benzyl alcohol has a strong antifeedant property for the large pine weevil, while weevils react more neutrally to benzaldehyde[74]. In our experiment, ethylbenzene (very similar to benzyl alcohol) and benzaldehyde correlated positively with large pine weevil bark damage, but their emission was actually stronger before and reduced following herbivory (especially for ethylbenzene; Figure 4d). It is possible that large pine weevils, through a yet unknown mechanism, have caused a shift in the physiology of pine resulting in reduced synthesis of compounds that deter herbivory.

4 Conclusions

Exposure to damaged emitters reduced bark damage by 49%, increased A_N by 15% and primed GLV emissions, enhancing Scots pine seedling resistance against large pine weevils. Emission of β-elemene correlated negatively with bark damage, which suggests its protective role and highlights VOC specificity in defence. While these findings indicate that between-plant interactions could strengthen the natural defences of Scots pine seedlings against large pine weevil attacks, the herbivory in this study was applied under controlled conditions. Therefore, further research is required to validate these effects in natural, uncontrolled settings, where factors like infestation levels and environmental conditions can vary widely. In addition, there is a need to further understand how plants differentially receive and process HIPVs and underground cues from damaged conspecific neighbours. Separate testing of the belowground and aboveground mediated plant-plant interactions in Scots pine seedlings would lead to a better understanding of the mechanisms underpinning the induction of photosynthesis in undamaged plants with damaged neighbours.

Finally, while O_3 and diesel exhaust directly affected plant physiology in our study, they did not compromise the induced defence outcomes; neither O_3 nor diesel exhaust, individually or interactively, impaired the defences induced by interactions between Scots pine seedlings in the field. These findings highlight the ability of plants to emit and receive informative chemical signals either above or belowground, even in air-polluted environments.

Acknowledgments

Funding for this work was provided by the Research Council of Finland (Suomen Akatemia) under the decision number 339575. Tihomir Simin was supported by the Ella and Georg Ehrnrooth Foundation and the Finnish Cultural Foundation. James Ryalls was supported by a Leverhulme Trust Early Career Fellowship (ECF-2020-017) and the University of Reading's NIRD Trust. The construction of FADOE was supported by a NERC Capital Call grant (NE/T009012/1). We are grateful to the Entomology Department of Forest Research, UK for providing the large pine weevils used for herbivory. We would also like to thank Alex Guenther for advice on VOC modelling, Alex Jackson for accommodation in Reading and Richard Casebow, Nephele Swann, Caroline Hadley, and Menow the dog for assistance with fieldwork.

Author contributions

Tihomir Simin conceptualised the study, conducted fieldwork, analysed and visualised the data, wrote the original draft, reviewed and edited the manuscript. James W. Ryalls maintained the FADOE field site, helped with preparation and conceptualisation of the study and fieldwork, and reviewed and edited the manuscript and figures. Oliver E. Welling conducted fieldwork, analysed data and provided feedback on the original draft. Robbie D. Girling acquired funding for construction of the FADOE site, assisted in conceptualization of and preparation for the study and provided valuable feedback and editing of the manuscript. Neil J. Mullinger built the FADOE facility and provided technical support and editing of the manuscript. James D. Blande conceptualised and supervised the study, acquired funding for the work and provided guidance in data interpretation and editing of the manuscript.

Competing interests

Authors declare no competing interests.

5 Methods

5.1 The experimental site and setup

The experiment was conducted at the University of Reading's Free-Air Diesel and Ozone Enrichment (FADOE) facility in Sonning, UK (51°28'54.1"N 0°53'43.4"W; Figure 1a). The facility, covering an area of 13,124 m^2, includes a central control unit and 12 rings (arranged in 3 sets of 4) that deliver specific air pollution treatments: elevated ozone (O_3), elevated diesel (D) exhaust gases (including $NO_x = NO + NO_2$), combined elevated O_3 and diesel exhaust gases (O_3 + D), and ambient air control (Figure 1b). The air is pumped to each ring using regenerative blowers (R4110-2, Gast, Benton Harbor, MI, USA), the O_3 treatment is provided by three O_3 generators (CD2000P, ClearWater Tech, San Luis Obispo, CA, USA) and the diesel treatment is provided by a diesel generator (SSDK12W Kubota 12.6 kVA, SGS Engineering Ltd, Cramlington, UK). Each ring has a diameter of 8 m and is surrounded by pipes that deliver the air, controlled by a system of relays. The O_3 and diesel exhaust pollution levels in the FADOE rings are relevant for studying field-based biotic interactions in the context of achieving national and international clean environment goals[46,47,75]. For a detailed description of the FADOE facility, refer to Mofikoya et al.[46].

Within each ring, four containers were established (Figure 1c), each measuring 53 cm in height, 67 cm in diameter and 155 L in volume (Nuova Pasquini & Bini, Altopascio, Italy; Figure 1d). The containers were filled with a soil mixture consisting of two parts coarse sand and one part natural ericaceous soil with a low pH (4.5 – 5.5; Premium Topsoil Supplies, Broadbridge Heath, UK). The experiment utilised two-year-old Scots pine seedlings from the Meggernie provenance in Scotland (56°35'25.8"N 4°18'14.4"W; grown from seed by and purchased from Alba Trees Ltd, Gladsmuir, UK; Figure 1e). Four seedlings were planted in each container on 4 May 2023 (124 DOY), one in the centre and three around the edges, approximately 120° apart (Figure 1c). In general, between-plant interactions experiments involve damage to emitter plants by insect herbivores, which in turn send airborne and/or below-ground cues to neighbouring receiver plants, resulting in them being better prepared for potential herbivore attack[6]. In our experimental setup, the central seedling in the container served as the emitter seedling, and two of the three edge seedlings were designated as receiver trees. The average distance between emitter and receiver seedlings was 26.7 cm. There was a 2m distance between the containers.

The trees were watered as needed to maintain soil moisture, with a volumetric water content between 10 % and 17 %. This soil condition is appropriate for pine and has been used in previous similar experiments[7,76]. After potting, the trees were left to acclimate and develop new growth for 26 days. Measurements were conducted in sets of four rings at a time: the first set was measured from 30th May to 2nd June 2023 (150 – 153 DOY); the second from 18th June to 21st June 2023 (169 – 172 DOY); and the last from 28th June to 1st July 2023 (179 – 182 DOY). The first set included only the ambient air and combined O_3 and diesel exhaust treatments.

The herbivory treatment (to emitter or receiver seedlings) consisted of placing three adults of the large pine weevil, *H. abietis* (Figure 1f), onto the bark of selected trees and enclosing the insects and the bark in a white mesh bag (Eurokangas, Orimattila, Finland). The weevils were starved for 24 hours before placement. They were collected from tree trunks in Scotland the previous year, kept in captivity at low temperature (16 °C at night and 9 °C during the day) and fed pine and spruce branches regularly.

The experiment had two phases: the first involved placing the weevils onto the emitter tree for 5 days and then measuring the receiver trees' responses. The second phase involved placing weevils onto the receiver trees for 38 hours and measuring bark damage, in addition to repeating the measurements from the first phase.

5.2 Environmental data

Solar radiation data was used for modelling the VOC emissions and was obtained from the satellite radiation dataset SOLCAST (Bright, 2019; https://solcast.com/) for the location of FADOE, between 30th May and 1st July 2023 (150-182 DOY). Following the method established by Akitsu et al. (2022), the photosynthetic photon flux density (PPFD) was calculated according to Eq. 1:

$$PPFD = (DNI + GHI + DHI + GTI) \times 0.46 \qquad (1)$$

where *DNI* = Direct Normal Irradiance, *GHI* = Global Horizontal Irradiance, *DHI* = Diffuse Horizontal Irradiance and *GTI* = Global Tilted Irradiance.

The calculated PPFD and the air temperature derived from SOLCAST radiation dataset are shown in Figure 1g and Figure 1h respectively.

Soil moisture was measured in the middle of each pot using a Theta Probe ML3 (Delta T-Devices, Cambridge, UK) after the gas exchange measurements.

5.3 Gas exchange measurements

Photosynthesis (A_N) and stomatal conductance (G_S) were measured using a LI-6400 XT portable photosynthesis system (LI-COR Inc, Lincoln, NE, USA) equipped with an opaque conifer chamber (6400-22) and 6400-18/A RGB light source. The chamber was positioned on a tripod and carefully enclosed around one of the side branches of each tree, so that it would not damage the needles. The branch inside was left to acclimate to the conditions set by the instrument until the rate of net photosynthesis reached a steady state (approximately 10 minutes). The flowrate was set to 500 mol s^{-1}; PPFD in the chamber was set to 1500 µmol m^{-2} s^{-1} to achieve the light saturation of photosynthesis and to simulate the peak sunlight conditions of summer days in the UK; the reference CO_2 concentration in the conifer chamber was set to 400 µmol mol^{-1} through the Mixer system of the instrument; the temperature inside the chamber varied with the outside temperature and was 28 ± 0.3 °C; relative humidity in the chamber was 48 %. Results were scaled to needle area, as described in section 5.5.

The aboveground VOC collection was performed by positioning a polyethylene terephthalate (PET) bag (25 cm x 38 cm; Cooke & Miller, Gem Imports Ltd, Hoyland, UK) around the whole aboveground part of the tree and tying it securely around the main stem of the seedling. Next, a temperature logger (Thermochron, OnSolution Pty Ltd, Castle Hill, Australia) was inserted into the bag. Air, free from particles and background hydrocarbons, filtered by a charcoal filter (Supelco Inc., Bellefonte, Penssylvania, USA), was pumped into the bag at a rate of 750 ml min^{-1} for 30 minutes before and during sampling, and VOCs were collected on a stainless-steel adsorbent cartridge (200 mg Tenax TA, Markes International Ltd, Llantrisant, UK) for 10 min at 200 ml min^{-1}. Blank measurements taken from empty PET bags were performed in situ once per sampling day at the FADOE facility, to account for VOCs derived from the sampling materials and the analysis instrument. After sampling, cartridges were sealed and stored at 5 °C until analysis.

5.4 Herbivore damage analysis

Herbivore damage was assessed as described by Yu et al.[7] In short, after the weevils were removed from the bark of the seedlings, the area damaged by the weevils was traced onto paper, scanned, and calculated using ImageJ software (v. 1.53k; Wayne Rasband, National Institute of Health, Bethesda, USA).

5.5 Needle area determination

Needle area was calculated to scale results from the LI-6400 XT and aboveground VOC emission using Eq. 2 [7,79]:

$$At = ((k_1 \times L - k_2) \times N)/100 \qquad (2)$$

where *At* = needle area (cm^2), k_1 = needle semi-fusiform factor constant = 4.2235, *L* = average needle length (mm), k_2 = needle breadth and thickness constant = 15.6835 and *N* = total needle number. For the detailed analysis of the formula see Flower-Ellis and Olsson (1993)[77].

N for the LI-6400 XT measurements was the number of needles in the opaque conifer chamber, while for the VOC measurements, it was the number of needles in the PET bag, i.e. the total number of needles on the tree.

5.6 VOC analysis

Adsorbent cartridges were transported to Kuopio, Finland and analysed using gas chromatography-mass spectrometry (GC-2010 Plus + GCMS-QP2020; Shimadzu Corporation, Kyoto, Japan) after thermal desorption (TD-30R; Shimadzu corporation, Kyoto, Japan). The carrier gas was helium and the temperature in the oven was kept at 40 °C for 1 min, rising to 125 °C by 5 °C min^{-1}, and then to 260 °C at 10 °C min^{-1}. A ZB-5MS plus capillary column (60.0 m length, 0.25 mm diameter, 0.25 µm film thickness) was used for compound separation.

Chromatograms were analysed using PARADISe[80] (v.6.0.0.18; https://ucphchemometrics.com/paradise/). The identification of VOCs was based on 34 authentic standards (Table S2) and NIST 20 library mass spectra (National Institute of Standards and Technology, Gaithersburg, MD, USA) for compounds without standards. Compounds for which the NIST 20 Match Factor was < 800 were identified to the level of a broad compound group. Sample concentrations were quantified based on the standards. The VOCs were classified into non-oxygenated monoterpenes (MTs), oxygenated monoterpenes (oMTs), sesquiterpenes (SQTs), green leaf volatiles (GLVs; oxygenated hydrocarbons containing 6 C atoms), benzenoids (BZs) and other non-isoprenoids (ONIs). Compounds for which no standard was available were quantified using the most appropriate standard, based on compound structure and mass, as in Simin et al. [81].

VOC concentrations in blanks were subtracted from the Scots pine VOC sample concentrations, and high-concentration compounds in blanks were considered as measurement system contaminants and omitted.

The rate of VOC emission (ng m^{-2} h^{-1}) was calculated using Eq. 3:

$$Emission\ rate = \frac{(C_{out} - C_{in}) \times F}{Leaf\ area} \tag{3}$$

where C_{out} and C_{in} are the outlet and inlet VOC concentrations and F is the flowrate through the PET bag. Since the incoming air was going through a hydrocarbon trap, the concentration in C_{in} was presupposed to be zero[82].

5.7 Modelling of VOC emissions

Since the VOCs were collected in varying environmental conditions throughout the season, we standardized the emissions to a specific temperature (30 °C) and light intensity (1000 µmol m^{-2} s^{-1}). The equation for calculating this standardised emission rate (emission factor, EF; µg m^{-2} h^{-1}) was adopted from Guenther et al.[83] and simplified for the purpose of standardizing to temperature and light in Eq. 4:

$$Emission\ factor = \frac{Emission\ rate}{\gamma_T \times \gamma_P} \tag{4}$$

where γ_T = the temperature activity factor and γ_P = the light activity factor.

The γ_P was determined according to Eq. 5 [83]

$$\gamma_P = (1 - LDF) + LDF \times \gamma_{P,LDF} \tag{5}$$

where *LDF* = the light dependent fraction of each compound, as defined by Guenther et al. 2012[83]

However, the light-dependent activity factor, $\gamma_{P,LDF}$, was defined as C_L by Guenther et al. in 1993[84] (Eq. 6):

$$\gamma_{P,LDF} = C_L = \frac{0.0027 \times 1.066 \times L}{\sqrt{1 + 0.00000729 \times L^2}} \tag{6}$$

where L = PPFD at the time of VOC collection (µmol m^{-2} s^{-1}).

Due to the lack of precise long-term air-temperature data at the level of the seedlings, the γ_T was also calculated by combining the formulas from 2012 and 1993 (Eq. 7).

$$\gamma_T = (1 - LDF) \times \left(exp\left(\beta(T - 303.15\ K)\right)\right) + LDF \times \gamma_{T,LDF} \tag{7}$$

where β= an empirical constant defined for each VOC and compound group[83] (Eq. 8).

$$\gamma_{T,LDF} = C_T = \frac{\exp \frac{95000\ Jmol^{-1} \times (T - 303.15\ K)}{8.314\ JK^{-1}mol^{-1} \times 303.15\ K \times T}}{1 + \exp \frac{230000\ Jmol^{-1} \times (T - 314\ K)}{8.314\ JK^{-1}mol^{-1} \times 303.15\ K \times T}} \tag{8}$$

To quantify the increase in VOC emissions associated with herbivore damage, we calculated the difference in emission factors before (phase 1) and after herbivory (phase 2) and normalised this by the bark damage area (DA)[7,8] (Eq. 9).

$$VOC\ emission\ increase = \frac{VOC\ EF\ after\ infestation - VOC\ EF\ before\ infestation}{bark\ damage\ area} \quad (9)$$

5.8 Statistical analysis

Linear Mixed Models (LMM) were used to analyse all receiver-tree-response data using IBM SPSS Statistics software (v.29.0.2.0 (20); The International Business Machines Corporation, Armonk, NY, USA). The variables tested included net photosynthesis rate, stomatal conductance rate, bark damage area, VOC emission rate, and damage-based VOC emissions increase. Fixed factors were pollution exposure (Ambient, O_3, diesel and diesel + O_3), emitter exposure (whether the receiver seedling was subjected to damaged or control emitters) and herbivory phase (before and after herbivory on receiver trees). Random factors included the pot number nested within the FADOE ring number and seasonality (30th May- 2nd June (150 – 153 DOY); 18th June- 21st June (169 – 172 DOY) ; 28th June- 1st July (179 – 182 DOY)). The significance of main effects and their interactions was assessed at various levels: $p<0.001$ (***), $p<0.01$ (**), $p<0.05$ (*) and $p<0.1$ (†). Data were log-transformed if the assumption of normality of residuals was not met; log (x + 1) was used for most variables, while log (x) was used for damage-based VOC increases. A similar LMM test was performed on emission rates ofindividual VOCs that correlated significantly with bark damage.

Partial Least Squares (PLS) regression analysis was used to assess the covariance between the receiver-tree bark damage area (DA; dependent variable, Y) and the emission factors of individual VOCs (independent variables, X) using SIMCA 17.0.2 (Sartorius Stedim Data Analytics AB, Goettingen, Germany). VOCs with a VIP (Variable Importance for the Projection) < 1 were excluded from the models to identify the compounds most highly correlated with bark damage. The independent variables included the emission rates of the following VOCs: cis-caryophyllene; norbourbonone; bornyl acetate; d-germacren-4-ol; β-elemene; β-cyclogermacrene; α-humulene; terpinen-4-ol; 1,3,8-p-menthatriene; m-cymene; β-bourbonene; α-copaene; p-mentha-1,5-dien-8-ol; β-thujene; eucarvone; p-cymenol; α-phellandrene; trans-caryophyllene; β-cadinene; limonene diepoxide; α-muurolene; car-3-en-5-one; terpinolene; β-sabinene; piperitenone; isoterpinolene; 1,5,8-p-menthatriene; γ-terpinene; γ-cadinene; berbenone; 7-methyl-pentadecane; 6,9-dimethyl-tetradecane; 2,4-Thujadiene; 2-hexyl-1-Decanol,; 2,6-Diphenylphenol; trans-β-farnesene; α-longipinene; linalool; ethylbenzene; benzaldehyde; camphor; 1-octen-3-ol; eucalyptol. The extracted PLS model had three components and was tested using the analysis of variance of the cross-validated residuals[85].

To determine if between-plant interactions were significantly affected by the VOC blends, multivariate analysis of variance (MANOVA) was used in SPSS to test the significance of the scores on both PC1 and PC2 of the PLS model simultaneously, using the exposure to damaged (HIPV) vs undamaged (Control) neighbours as the fixed effect. Only the VOCs identified in the PLS regression analysis (those with VIP < 1) were used as X variables. Unit-variance scaling of individual compound emission factors (in addition to DA) was used to extract the PCA components. The pattern of relative abundance of the individual VOCs (and DA) was used to cluster the samples and illustrate the difference between the exposure treatments.

Principal component analysis (PCA) was performed on the VOC emission rates using SIMCA to assess how the air pollution treatments affected the VOC emission blends. Clustering of samples shows similarities and difference between the samples based on the patterns in relative abundances of all individual VOCs.

Data availability statement

Data obtained during fieldwork and used for statistical analysis and generating figures for this article is available openly in form of a dataset at the following address:

https://doi.org/10.5281/zenodo.17911209

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Figure 1: Research facility and methods. a) Map of the study area indicating the Free-air diesel and ozone enrichment (FADOE) research facility. The base image is from © Google Earth Pro 7.3.0 (2017); Image details- Sonning, United Kingdom, 51.48, -0.89; 95 m.a.s.l. b) Mean concentrations (± SE; 8 hour mean) of ozone (O_3) and nitrogen oxides ($NO_X = NO + NO_2$) within treatment rings. Treatments are indicated on the X-axis (D – diesel). Stacked concentrations of nitric oxide (NO) and nitrogen dioxide (NO_2) are included in the bars with the dark outline (NO_X). Local concentrations of O_3 and NO_X from the nearest monitoring station in Reading, UK (New Town for O_3 and London Road for NO_X) and vegetation protection standards set by the 2024/2281 EU Air Quality Directive are indicated as horizontal lines. c) The layout of pine seedlings in the pots: a single emitter seedling (E) was surrounded by three receiver seedlings (R). d) The layout of pots in a single FADOE ring; weevils were administered to emitter seedlings in two of the four pots (HIPV) and the other two were assigned as controls. Study plant species was e) *Pinus sylvestris*, Scots pine, and the herbivore used was f) *Hylobius abietis*, the large pine weevil. g) Photosynthetic photon flux density (PPFD) and h) air temperature in the FADOE area derived between 5th May and 1st July 2023 (121 – 183 Day of Year). Map lines delineate study areas and do not necessarily depict accepted national boundaries.

Figure 2. Individual and combined effects of *in situ* air pollution exposure on the herbivore-damage and gas exchange responses of Scots pine seedlings exposed to damaged and control emitters. Filled markers denote herbivory phase: unfilled = phase 1 (pre-herbivory), filled = phase 2 (post-herbivory). **a**) Bark damage area. **b)** Net photosynthesis rate (A_N). **c)** Stomatal conductance rate (G_S). Cross symbols (×) indicate air temperature inside the conifer chamber during measurement. n=8 for ozone (O_3) and diesel exhaust (D) treatments, n=12 for Ambient and O_3+D treatments. Error bars show standard error of the mean.

Figure 3. **Individual and combined effects of in situ air pollution exposure on the VOC emissions of Scots pine seedlings exposed to damaged and control emitters.** Filled bars denote herbivory phase: unfilled = phase 1 (pre-herbivory), filled = phase 2 (post-herbivory). a) Emission rates (mg m^{-2} needle area h^{-1}) of MTs, other VOC groups and the total VOC emission. MT, non-oxygenated monoterpenes; oMT, oxygenated monoterpenes; SQT, sesquiterpenes; GLV, green-leaf volatiles; BZ, benzenoids; ONI, other non-isoprenoids. b) Emission rates (mg m^{-2} needle area h^{-1}) of other VOC groups, oMTs, SQTs, GLVs, BZs and ONIs. c) Bark damage area (DA)-based increase in emissions for MTs together with other VOC groups and total VOCs (mg m^{-2} h^{-1} cm^{-2} DA), based on emission factors = emission rates standardized to a temperature of 30°C and a photosynthetic photon flux density (PPFD) of 1000 μmol m^{-2} s^{-1}. d) Bark damage area-based increase (mg m^{-2} h^{-1} cm^{-2} DA) for other VOC groups. n=8 for ozone (O3) and diesel exhaust (D) treatments, n=12 for Ambient and O3+D treatments. Error bars show standard error of the mean of total emissions.

Figure 4. The blend of VOCs emitted by receiver Scots pine seedlings correlating with protection against herbivory. a) Average regression coefficients from the partial least squares (PLS) regression model on bark damage area (DA). Only the individual VOCs with the Variable Importance for the Projection (VIP) values of over 1 were included. Significant VOCs are shown in black. Error bars show 1.96 x standard deviation of the regression coefficients. [1] and [2] signs indicate VOCs identified with standards or tentatively via the NIST 20 library, respectively. The model was tested using CV-ANOVA and is highly significant ($p < 0.001$). **b)** PLS score plot showing VOC blend separation (n=39; p=0.007, MANOVA) between seedlings exposed to damaged and control emitters. The variance explained by each principal component (PC) is shown in parentheses. **c)** PLS loading variables consist of DA and individual VOCs and are presented according to the compound group: MT, non-oxygenated monoterpenes; oMT, oxygenated monoterpenes; SQT, sesquiterpenes; GLV, green-leaf volatiles; BZ, benzenoids; ONI, other non-isoprenoids. **d)** Emission rate ($\mu g\ m^{-2}\ h^{-1}$) of VOCs that correlated significantly with DA across different treatments. Filled bars denote herbivory phase: unfilled = phase 1 (pre-herbivory), filled = phase 2 (post-herbivory). n=8 for ozone (O_3) and diesel exhaust (D) treatments, n=12 for Ambient and O_3+D treatments.

Table 1. Results of the linear mixed models (LMM). The tests were performed on bark damage area, net photosynthesis rate (A_N), stomatal conductance rate (G_S), VOC emission rates and damage area-based increases in VOC emissions. Fixed factors were air pollution (O_3 enrichment, diesel exhaust enrichment, combination of O_3 and diesel exhaust enrichment as well as ambient air), emitter exposure (damaged and control), herbivory phase (phase 1 = pre-herbivory, phase 2 = post-herbivory) and their two-way interactions. $p < 0.001$ ***, $p < 0.01$ **, $p < 0.05$ *, $p < 0.1$ †. MT, non-oxygenated monoterpenes; oMT, oxygenated monoterpenes; SQT, sesquiterpenes; GLV, green-leaf volatiles; BZ, benzenoids; ONI, other non-isoprenoids. Herbivory phase did not apply to damage area and damage-based VOC emission increase. NA, data not available. NS, models not significant

	Variable	Air pollution	Emitter exposure	Herbivory phase	Air pollution x Emitter exposure	Air Pollution x Herbivory phase	Emitter exposure x Herbivory phase
	Bark damage area	NS	F=11.62 p=0.002 **	NA	NS	NA	
Photosynthetic traits	A_N	F=3.387 p=0.031 *	F=4.326 p=0.046 *	F=3.343 p=0.066 †	NS	F=2.180 p=0.094 †	NS
	G_S	F=3.202 p=0.037 *	NS	NS	NS	F=2.317 p=0.079 †	NS
VOC emission rate	MT	F=2.653 p=0.066 †	NS	F=17.932 p<0.001 ***	NS	NS	NS
	oMT	F=3.007 p=0.046 *	NS	F=27.565 p<0.001 ***	NS	F=5.846 p<0.001 ***	NS
	SQT	NS	NS	F=4.066 p=0.046 *	NS	F=3.864 p=0.011 *	NS
	GLV	F=5.541 p=0.001 **	NS	NS	NS	NS	NS
	BZ	F=8.969 p<0.001 ***	NS	NS	NS	F=2.675 p=0.051 †	NS
	ONI	F=14.971 p<0.001 ***	NS	NS	NS	NS	NS
	TOTAL	F=3.864 p=0.019 *	NS	F=16.928 p<0.001 ***	NS	NS	NS
Damage-based VOC emission increase	MT	NS	NS	NA	NS	NA	
	oMT	NS	NS		NS		
	SQT	NS	NS		NS		
	GLV	NS	F=4.926 p=0.038 *		NS		
	BZ	NS	NS		NS		
	ONI	NS	F=4.563 p=0.054 †		NS		

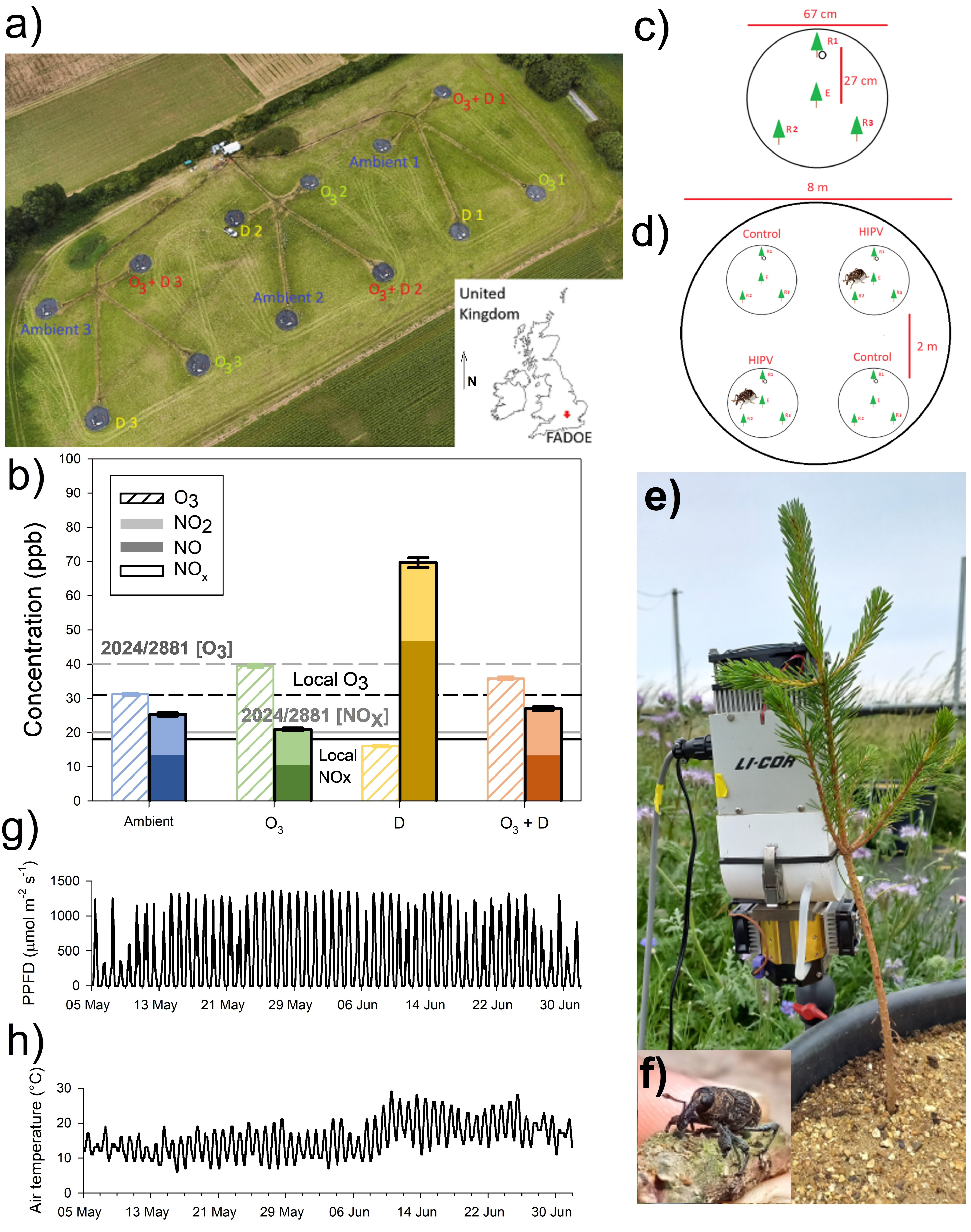
TOTAL	NS	F=3.315 p=0.074 †		NS

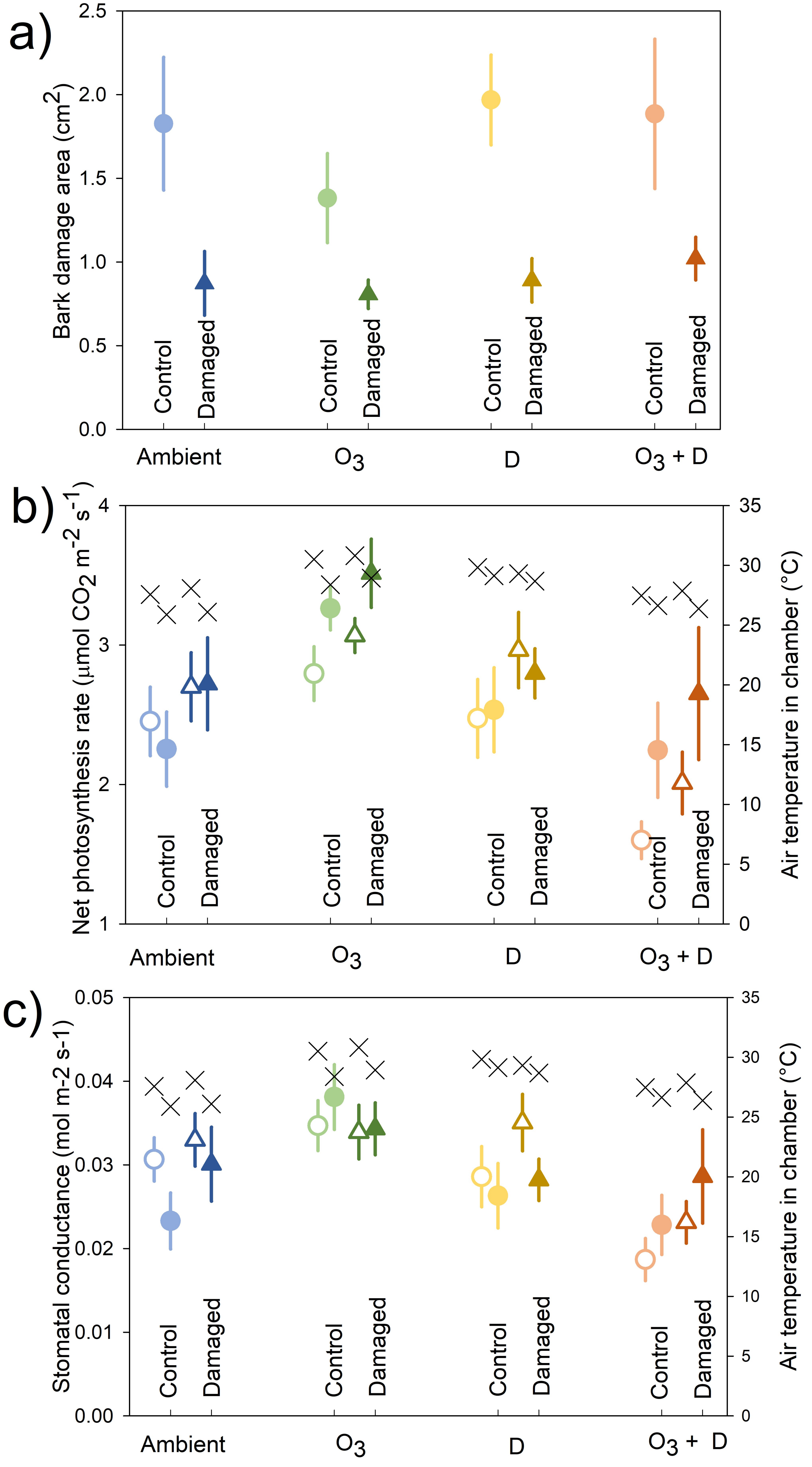
Editorial summary:

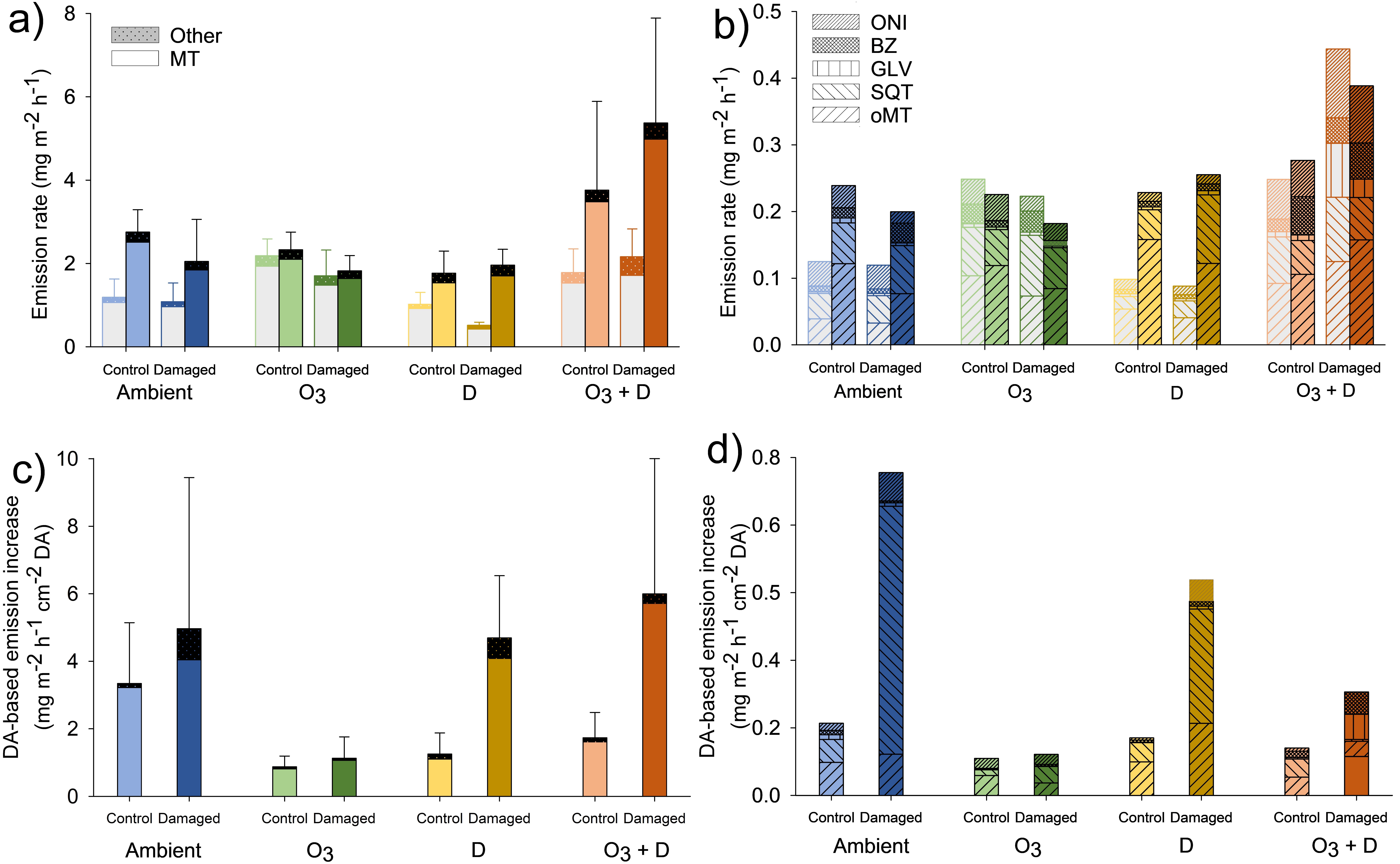
Air pollution does not impair neighbour-induced defence against herbivory in Scots pine seedlings, but it affects photosynthesis, stomatal conductance, and volatile organic compound emission, shown at the Free-Air Diesel and Ozone Enrichment platform.

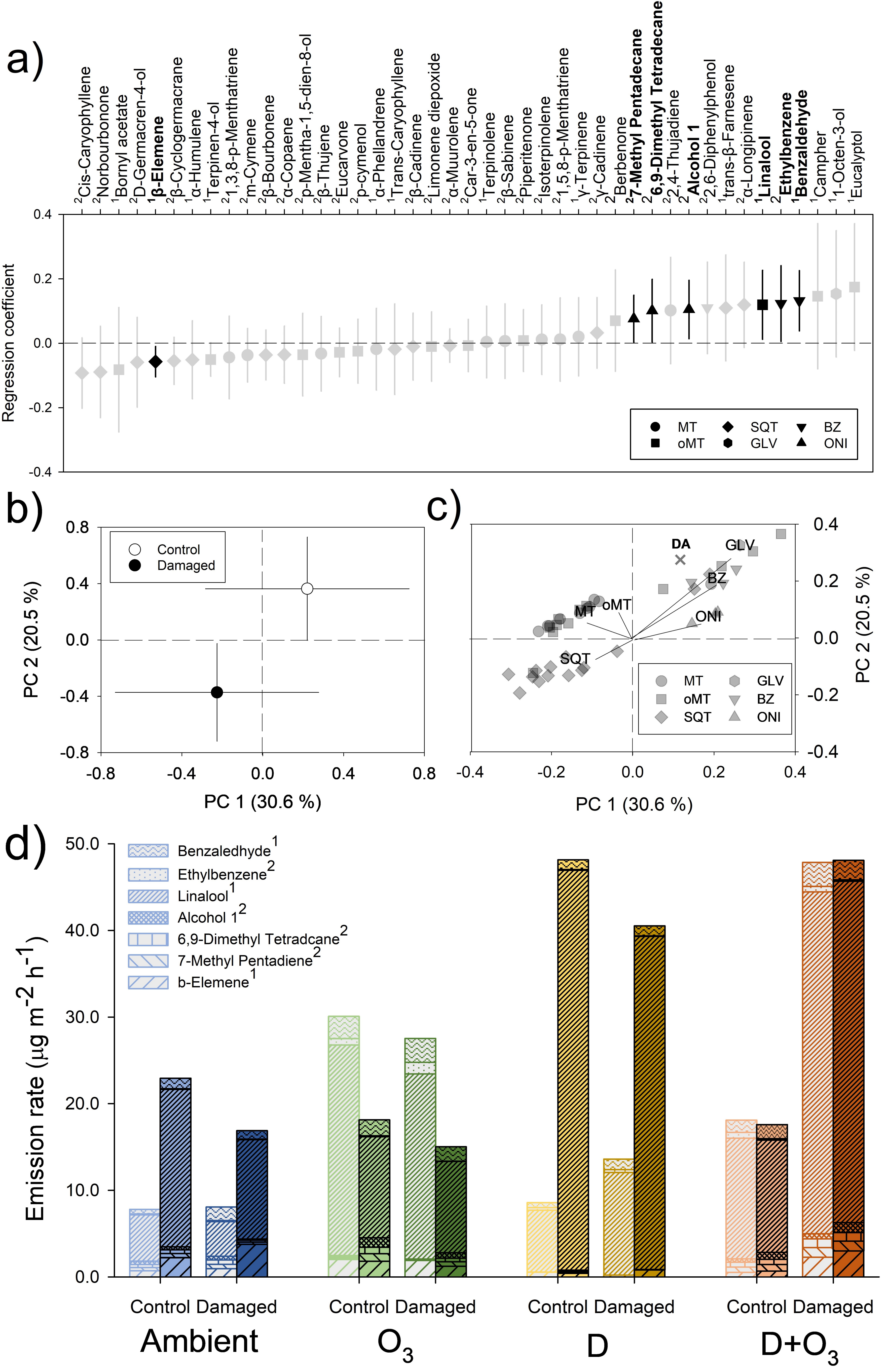
Peer review information:

Communications Earth and Environment thanks Po-An Lin and Anne Charlott Fitzky for their contribution to the peer review of this work. Primary Handling Editors: Nora Zannoni and Mengjie Wang. [A peer review file is available.]


a)
O3 + D 1
Ambient 1
O3 2
O3 1
D 2
D 1
O3 + D 3
Ambient 2
O3 + D 2
Ambient 3
O3 3
D 3
United Kingdom
N
FADOE
b)
Concentration (ppb)
100
90
80
70
60
50
40
30
20
10
0
O3
NO2
NO
NOx
2024/2881 [O3]
Local O3
2024/2881 [NOx]
Local NOx
Ambient
O3
D
O3 + D
c)
67 cm
R1
27 cm
E
R2
R3
8 m
d)
Control
HIPV
2 m
HIPV
Control
e)
LI-COR
f)
g)
PPFD (μmol m-2 s-1)
1500
1000
500
0
05 May
13 May
21 May
29 May
06 Jun
14 Jun
22 Jun
30 Jun
h)
Air temperature (°C)
30
20
10
0
05 May
13 May
21 May
29 May
06 Jun
14 Jun
22 Jun
30 Jun


a)
Bark damage area (cm^2)
2.5
2.0
1.5
1.0
0.5
0.0
Control
Damaged
Control
Damaged
Control
Damaged
Control
Damaged
Ambient
O$_3$
D
O$_3$ + D
b)
Net photosynthesis rate (μmol CO$_2$ m^{-2} s^{-1})
4
3
2
1
Air temperature in chamber (°C)
35
30
25
20
15
10
5
0
Control
Damaged
Control
Damaged
Control
Damaged
Control
Damaged
Ambient
O$_3$
D
O$_3$ + D
c)
Stomatal conductance (mol m-2 s-1)
0.05
0.04
0.03
0.02
0.01
0.00
Air temperature in chamber (°C)
35
30
25
20
15
10
5
0
Control
Damaged
Control
Damaged
Control
Damaged
Control
Damaged
Ambient
O$_3$
D
O$_3$ + D


a)
Other
MT
Emission rate (mg m^{-2} h^{-1})
0
2
4
6
8
Control Damaged
Ambient
O$_3$
D
O$_3$ + D
b)
ONI
BZ
GLV
SQT
oMT
Emission rate (mg m^{-2} h^{-1})
0.0
0.1
0.2
0.3
0.4
0.5
c)
DA-based emission increase
(mg m^{-2} h^{-1} cm^{-2} DA)
0
2
4
6
8
10
d)
0.0
0.2
0.4
0.5
0.6
0.8


a)
2 Cis-Caryophyllene
2 Norbourbonone
1 Bornyl acetate
2 D-Germacren-4-ol
1 β-Elemene
2 β-Cyclogermacrane
1 α-Humulene
1 Terpinen-4-ol
2 1,3,8-p-Menthatriene
2 m-Cymene
2 β-Bourbonene
2 α-Copaene
2 p-Mentha-1,5-dien-8-ol
2 β-Thujene
2 Eucarvone
2 p-cymenol
1 α-Phellandrene
1 Trans-Caryophyllene
2 β-Cadinene
2 Limonene diepoxide
2 α-Muurolene
2 Car-3-en-5-one
1 Terpinolene
2 β-Sabinene
2 Piperitenone
2 Isoterpinolene
2 1,5,8-p-Menthatriene
1 γ-Terpinene
2 γ-Cadinene
2 Berbenone
2 7-Methyl Pentadecane
2 6,9-Dimethyl Tetradecane
2 2,4-Thujadiene
2 Alcohol 1
2 2,6-Diphenylphenol
1 trans-β-Farnesene
2 α-Longipinene
1 Linalool
2 Ethylbenzene
1 Benzaldehyde
1 Campher
1 1-Octen-3-ol
1 Eucalyptol
Regression coefficient
0.4
0.2
0.0
-0.2
-0.4
● MT
■ oMT
◆ SQT
⬢ GLV
▼ BZ
▲ ONI
b)
○ Control
● Damaged
PC 2 (20.5 %)
PC 1 (30.6 %)
0.8
0.4
0.0
-0.4
-0.8
-0.8
-0.4
0.0
0.4
0.8
c)
DA
GLV
BZ
MT
oMT
ONI
SQT
● MT
■ oMT
◆ SQT
⬢ GLV
▼ BZ
▲ ONI
PC 1 (30.6 %)
PC 2 (20.5 %)
-0.4
-0.2
0.0
0.2
0.4
d)
Benzaledhyde 1
Ethylbenzene 2
Linalool 1
Alcohol 1 2
6,9-Dimethyl Tetradcane 2
7-Methyl Pentadiene 2
b-Elemene 1
Emission rate (μg m-2 h-1)
50.0
40.0
30.0
20.0
10.0
0.0
Control Damaged
Ambient
Control Damaged
O3
Control Damaged
D
Control Damaged
D+O3