

Accepted Manuscript

Air pollutants degrade floral scents and increase insect foraging times

Jose D. Fuentes, Marcelo Chamecki, T'ai Roulston, Bicheng Chen, Kenneth R. Pratt



PII: S1352-2310(16)30521-0

DOI: [10.1016/j.atmosenv.2016.07.002](https://doi.org/10.1016/j.atmosenv.2016.07.002)

Reference: AEA 14728

To appear in: *Atmospheric Environment*

Received Date: 21 April 2016

Revised Date: 28 June 2016

Accepted Date: 1 July 2016

Please cite this article as: Fuentes, J.D., Chamecki, M., Roulston, T., Chen, B., Pratt, K.R., Air pollutants degrade floral scents and increase insect foraging times, *Atmospheric Environment* (2016), doi: 10.1016/j.atmosenv.2016.07.002.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Air pollutants degrade floral scents and increase insect foraging times

Jose D Fuentes^{a,*}, Marcelo Chamecki^b, T'ai Roulston^c, Bicheng Chen^a, Kenneth R Pratt^a

^a*Department of Meteorology, The Pennsylvania State University, University Park, PA, USA*

^b*Department of Atmospheric and Oceanic Sciences, University of California at Los Angeles, Los Angeles, CA, USA*

^c*Blandy Experimental Farm, University of Virginia, Boyce, VA, USA*

Abstract

Flowers emit mixtures of scents that mediate plant-insect interactions such as attracting insect pollinators. Because of their volatile nature, however, floral scents readily react with ozone, nitrate radical, and hydroxyl radical. The result of such reactions is the degradation and the chemical modification of scent plumes downwind of floral sources. Large Eddy Simulations (LES) are developed to investigate dispersion and chemical degradation and modification of floral scents due to reactions with ozone, hydroxyl radical, and nitrate radical within the atmospheric surface layer. Impacts on foraging insects are investigated by utilizing a random walk model to simulate insect search behavior. Results indicate that even moderate air pollutant levels (e.g., ozone mixing ratios greater than 60 parts per billion on a per volume basis, ppbv) substantially degrade floral volatiles and alter the chemical composition of released floral scents. As a result, insect success rates of locating plumes of floral scents were reduced and foraging times increased in polluted air masses due to considerable degradation and changes in the composition of floral scents. Results also indicate that plant-pollinator interactions could be sensitive to changes in floral scent composition, especially if insects are unable to adapt to the modified *scentscape*. The increase in foraging time could have severe cascading and pernicious impacts on the fitness of foraging insects by reducing the time devoted to other necessary tasks.

*Corresponding author

Email address: jdfuentes@psu.edu (Jose D Fuentes)

Keywords: Ozone; hydroxyl radical; pollination; pollution; hydrocarbons; fragrances; floral scents

1. Introduction

Plants emit a plethora of volatile organic compounds through organs such as roots, leaves, flowers, and fruits (Fuentes et al., 2000). Flowers typically release complex blends of volatile compounds (Knudsen et al., 2006) that give each plant species unique and characteristic fragrances. Although terpenoids, benzenoids, and fatty acid derivatives dominate the floral volatiles, the particular compounds produced by a given species vary among plant groups. For instance, flowers of the mustard plant family (*Brassicaceae*) typically emit nitrogen-containing compounds (Dobson, 2006) while flowers of the dogbane family (*Apocynaceae*) produce sulfur-containing compounds (Von Helversen et al., 2000). Once biosynthesized, emission rates of floral volatiles depend on biotic and abiotic factors. Biotic influences include flower ontogeny, pollination status, and insect infestation whereas abiotic conditions involve temperature, photosynthetically active radiation, and atmospheric carbon dioxide (CO₂) concentration. Therefore, in downwind areas from sources, ambient concentrations of floral volatiles should exhibit pronounced temporal and spatial variability. Once released into the atmosphere, floral hydrocarbons play key ecological roles such as attraction of pollinators and seed dispersers, defense against herbivores, protection against pathogens, and plant-to-plant signaling (Dötterl and Vereecken, 2010; Wright and Schiestl, 2009). Floral scents provide insect and animal pollinators the necessary cues about location and identity of plant species. Other ecological functions of volatile organic compounds include protection of foliage against abiotic stresses such as high solar radiation loadings and elevated temperature (Sharkey et al., 2001) or oxidative stress (Loreto et al., 2001).

One of the least studied aspects of floral volatile composition is the post-emission modifications caused by the reactions with atmospheric oxidants. As floral volatiles are transported by the wind from their sources, they can undergo rapid reactions with air pollutants such as ozone (O₃), hydroxyl radical (OH), and nitrate radical (NO₃). As they traverse landscapes, reactions reduce the strength and the integrity of the chemical cues that floral scents provide

27 to insects. Their reactions lead to the formation of secondary long-chain hydrocarbon prod-
28 ucts, some of which have common chemical characteristics to the parent floral fragrances
29 (McFrederick et al., 2008). The destruction of primary signals and formation of secondary
30 cues are poorly quantified, but are potentially crucial to understanding ecological and evo-
31 lutionary conditions for organisms that depend on olfactory cues in polluted environments.
32 Perturbations of scent signals hasten the destruction and also change the identity of scent
33 plumes, both of which can affect the probability of detection by insects. Chemical degrada-
34 tion and changes in the composition of floral scents may increase the time that insects need
35 to locate flowers, thereby potentially disrupting processes such as pollination. Flowers could
36 alter the synthesis and the basal emissions of volatiles when exposed to heavy doses of ozone
37 (e.g., > 150 ppbv, Loreto and Schnitzler (2010)) but such influences are not well known.

38 While previous studies examined the influences of habitat fragmentation (Bhattacharya
39 et al., 2003; Montero-Castaño and Vilà, 2012), reductions in native habitat (Goulson et al.,
40 2008), pesticide exposure (Whitehorn et al., 2012; Stanley et al., 2015), and diseases (Cameron
41 et al., 2011) on insect communities, only limited attention (Pinto et al., 2007; McFrederick
42 et al., 2008; Blande et al., 2010; Fuentes et al., 2013; Li and Blande, 2015) has been given to
43 investigate the indirect impacts of air pollutants on the plant-insect interactions mediated
44 via floral scents. Changes in composition and reduced amounts of the scent bouquet can lead
45 to insects spending greater amounts of time foraging for food. With the continued changes
46 in OH concentrations (Prinn et al., 2005) and in some cases increases in ground-level O₃ con-
47 centrations in the rural atmosphere (Jaffe and Ray, 2007; Cooper et al., 2012; Parrish et al.,
48 2013), the modified atmospheric chemistry of floral scents can interfere with their ecological
49 roles. A pressing concern is that the alteration of the natural *scentscape* (McFrederick et al.,
50 2009) by air pollutants may be adding to the stresses already contributing to the decline
51 of pollinator populations (Biesmeijer et al., 2006) likely in response to increased pollinator
52 foraging times and decreased pollination efficiency, and exposure to pesticide residues (Stan-
53 ley et al., 2015). Despite the potential environmental and economic consequences of the
54 disruption of insect pollination, no information exists to quantitatively evaluate direct and

55 indirect influences of airborne pollutants on the ability of pollinators to sense plant chemical
56 signals.

57 Therefore, this study evaluates the hypothesis that *current levels of airborne pollutants*
58 *sufficiently alter the composition and reduce the quantity of floral scents in such a manner*
59 *that they perniciously increase insect foraging times*. Several objectives are achieved to
60 evaluate the hypothesis. Large Eddy Simulations (LES) coupled with chemical reactions
61 allow us to determine degradation rates of individual floral volatiles as air parcels carry
62 scents away from sources, exposed to different levels of air pollutants. Also, changes in
63 the composition of floral volatile mixtures are calculated in response to different levels of
64 air pollutants and distances travelled away from scent sources. Finally, foraging times of
65 insects that have different thresholds of floral volatile detection are estimated in response to
66 chemical degradation and modified composition of scent mixtures. A random walk model is
67 developed to estimate insect foraging times as a function of modified scent plumes.

68 2. Methods

69 The understanding of how air pollutants deteriorate interactions between plants and in-
70 sects requires knowledge of atmospheric chemistry and animal ecology and physiology. On
71 the atmospheric side, knowledge of air turbulence is required to determine the transport of
72 scents as they traverse the local landscape. Kinetics of floral volatiles released into the at-
73 mosphere are necessary to determine how individual compounds are altered by amounts and
74 types of pollutants in the air mass. On the insect side, knowledge is required of the particular
75 floral volatiles or mixtures of compounds that can be distinguished, concentration thresholds
76 required to elicit a response, and the relative importance of scent over other sensory modal-
77 ities (e.g., vision) in mitigating the interactions. Currently, no natural system is sufficiently
78 well known to bring together all of the necessary information for reliable predictions in a
79 realistic ecological framework. There is, however, existing theoretical and laboratory work
80 indicating that current air pollutant levels may already be impacting important ecological
81 interactions in natural environments (Fuentes et al., 2013; Farré-Armengol et al., 2016). We,

82 therefore, seek to quantify the impacts of air-pollutant modified scents on plant-insect in-
 83 teractions by overlaying a spatially explicit numerical model of volatile degradation under
 84 specified environmental conditions (realistic wind velocities and air pollution regimes) with
 85 a foraging model that challenges insects to locate pollutant-modified scent plumes on the
 86 landscape.

87 Large eddy simulations, combined with air chemistry, allow us to determine the turbulent
 88 transport and chemical reactions of floral volatiles. The model predicts the time evolution
 89 of scent plumes under the influences of varying levels of turbulence mixing and chemical
 90 reactions at small spatial scales, thereby providing detailed information of floral scent plume
 91 composition with high temporal and spatial resolution (Figure 1). Therefore, in the absence
 92 of detailed information from field observations, LES outputs are the most reliable source of
 93 information for studying transport and chemical degradation of scent plumes. A random
 94 walk model is developed and applied to compute foraging times based on insect detection
 95 threshold of floral scents and modified *scentscape*.

96 2.1. Description of the LES

97 The LES model used in this study to determine dispersion of floral volatiles by the
 98 wind is described in detail elsewhere (Chamecki et al., 2009) and only a brief description is
 99 included here. In the LES, the filtered three-dimensional wind field ($\tilde{\mathbf{u}}$) is determined from
 100 the solution of the filtered momentum and mass conservation equations which in vectorial
 101 form are expressed as (∇ is the vector differential operator)

$$\nabla \cdot \tilde{\mathbf{u}} = 0 \quad (1)$$

$$\frac{\partial \tilde{\mathbf{u}}}{\partial t} + (\tilde{\mathbf{u}} \cdot \nabla) \tilde{\mathbf{u}} = -\frac{1}{\rho} \nabla \tilde{p} - \nabla \cdot \boldsymbol{\tau}_{\text{sgs}}. \quad (2)$$

102 In equation (2), the term $-(1/\rho)\nabla \tilde{p}$ is the filtered pressure gradient force and $\boldsymbol{\tau}_{\text{sgs}}$ is the
 103 subgrid-scale (SGS) stress tensor representing the effect of the scales smaller than the LES
 104 grid size on the resolved wind field. Viscous effects are neglected on the basis of the
 105 large Reynolds number of the flows considered in this study. Additional filtered advection-

106 diffusion-reaction equations were included in the LES model to represent the temporal vari-
 107 ations of floral volatile concentrations ($\partial[\widetilde{\chi}_i]/\partial t$)

$$\frac{\partial[\widetilde{\chi}_i]}{\partial t} + \nabla \cdot (\widetilde{\mathbf{u}}[\widetilde{\chi}_i]) = -\nabla \cdot \boldsymbol{\pi}_{\chi_i} + Q_{\text{src},i} - k_{\text{O}_3}[\widetilde{\chi}_i][\text{O}_3] - k_{\text{HO}}[\widetilde{\chi}_i][\text{HO}] - k_{\text{NO}_3}[\widetilde{\chi}_i][\text{NO}_3]. \quad (3)$$

108 In equation (3), $[\widetilde{\chi}_i]$ is the concentration of the i^{th} floral volatile, $\boldsymbol{\pi}_{\chi_i}$ is the SGS floral
 109 volatile flux representing the mixing caused by turbulence scales not explicitly included in
 110 the simulation, $Q_{\text{src},i}$ represents the emission of scent from flower patches, and the three last
 111 terms on the right-hand side of equation (3) represent the loss of $[\widetilde{\chi}_i]$ due to reaction with
 112 O_3 , OH , and NO_3 with reaction rate coefficients k_{O_3} , k_{HO} , and k_{NO_3} . To close the set of
 113 equations, the SGS momentum flux is parameterized using the Lagrangian scale-dependent
 114 dynamic Smagorinsky model (Bou-Zeid et al., 2005). The SGS floral volatile fluxes are then
 115 parameterized using the resulting SGS eddy viscosity and the SGS Schmidt number (Sc_τ)
 116 which in this study is assumed to be 0.8.

117 The momentum equations are discretized using a fully de-aliased, pseudo-spectral ap-
 118 proach in the horizontal directions and a second-order centered finite-difference scheme in
 119 the vertical direction. Model lateral boundary conditions are periodic. A no-stress boundary
 120 condition is imposed at the top boundary and an equilibrium wall-model (Bou-Zeid et al.,
 121 2005) is used to parameterize the bottom boundary conditions. The advection-diffusion-
 122 reaction equation (3) is discretized following a finite-volume method, with the bounded
 123 third-order upwind advection scheme SMART (Gaskell and Lau, 1988). The coupling be-
 124 tween the pseudo-spectral discretization for momentum and the finite volume discretization
 125 for reactive scalars uses a conservative interpolation scheme (Chamecki et al., 2008). The
 126 lateral boundary conditions for the floral volatiles are specified as zero values for inflow and
 127 zero gradients for outflow boundary conditions and zero-flux conditions are specified at the
 128 top and bottom boundaries. The time integrations of wind velocity and floral volatile con-
 129 centrations are carried out using the second-order Adams–Bashforth scheme (Peyret and
 130 Taylor, 1983). The flow is driven by an imposed mean pressure gradient, which is adjusted
 131 to generate different wind conditions (corresponding to friction velocity $u_* = 0.1 \text{ m s}^{-1}$ and

132 $u_* = 0.2 \text{ m s}^{-1}$). Neutral thermal stratification is assumed in all simulations. The resulting
 133 vertical variations of averaged zonal wind speed (\bar{u}) and standard deviation of the vertical
 134 velocity (σ_w) are included in Figure 2 for the assumed u_* values.

135 The simulation domain consists of a volume of $1000 \text{ m} \times 350 \text{ m} \times 50 \text{ m}$ ($L_x \times L_y \times L_z$),
 136 covered by a sparse vegetation of height $h = 1 \text{ m}$ (represented by a constant surface roughness
 137 $z_0 = 0.05 \text{ m}$). This domain is discretized using $400 \times 140 \times 100$ grid points, resulting in a
 138 grid resolution of $2.5 \text{ m} \times 2.5 \text{ m} \times 0.5 \text{ m}$. Flower patches are randomly distributed within an
 139 area of $180 \text{ m} \times 250 \text{ m}$ near the upwind edge of the domain (Figure 1). Five hundred flower
 140 patches (with $2.5 \text{ m} \times 2.5 \text{ m}$ each) are included in the simulations. Flowers are assumed to
 141 emit blends of volatiles comprised of β -caryophyllene, β -ocimene, β -myrcene, linalool, and
 142 α -pinene (i.e., $i = 1, \dots, 5$ in Equation 3 and Table 1). The chosen volatiles (Table 1) are
 143 common components of floral fragrances and play numerous ecological functions, including
 144 attracting pollinators (Byers et al., 2014), herbivores (Mayer et al., 2008), and parasitoids
 145 of herbivores (Ozawa et al., 2008). Herbivore feeding on plants enhances production of β -
 146 myrcene as a way of attracting parasitoids to control the herbivores (Van Poecke et al.,
 147 2001). Basal emission rates ($E_{s,i}$) for a nominal temperature $T_s = 303 \text{ K}$ (Table 1) for each
 148 floral volatile are determined from experimental data (Wright et al., 2005), assuming a leaf
 149 area index equal to 2. Effective emission rates (E_i) corresponding to a flower temperature
 150 of $T = 298 \text{ K}$ are used in the simulation, and are determined employing equation (4)

$$E_i(T) = E_{s,i} \exp[\beta(T - T_s)], \quad (4)$$

151 where β is a constant taken as 0.06 K^{-1} . The floral volatile emission per unit volume required
 152 in equation (3) is then calculated as $Q_{\text{src},i} = E_i(T)/dz$, where dz is the vertical grid spacing
 153 used in the simulation. Each simulation is executed for 2 hours with a time step $dt = 0.1 \text{ s}$.
 154 Data analyses are performed for the final hour of the simulations, when gas concentration
 155 fields are statistically stationary.

156 2.2. Model of insect foraging flight

157 Random walk models are frequently used to represent the foraging behavior of animals
 158 (Codling et al., 2008). Typically, resources are represented as points distributed throughout

Table 1: Floral volatiles, emission rates, and reaction rate coefficients used in the model simulations. ‡: Values of reaction rate coefficients were obtained from Atkinson et al. (1999).

Index	Species	Emission rate (E_s) (nmoles m^{-2} min^{-1})	K_{O_3} (cm^3 molec^{-1} s^{-1})‡	K_{OH} (cm^3 molec^{-1} s^{-1})‡	K_{NO_3} (cm^3 molec^{-1} s^{-1})‡
1	β -Caryophyllene	15	1.10×10^{-14}	2.00×10^{-10}	1.90×10^{-11}
2	β -Ocimene	82	5.40×10^{-16}	2.52×10^{-10}	2.20×10^{-11}
3	β -Myrcene	25	4.70×10^{-16}	2.13×10^{-10}	1.27×10^{-11}
4	Linalool	6.5	4.30×10^{-16}	1.59×10^{-10}	1.12×10^{-11}
5	α -Pinene	10	8.09×10^{-17}	5.33×10^{-11}	6.16×10^{-12}

159 the landscape and random walks are then used to represent the movement of animals as they
 160 survey the surroundings in search of resources. A radius of detection is typically assigned to
 161 the forager and once a resource is within this radius then the search is considered success-
 162 ful. In this typical approach, the existence of chemical cues such as scent plumes is either
 163 neglected or is included in the detection radius of the insect. Therefore, external factors
 164 (such as turbulence and air pollutant levels) that influence composition and spatial extent
 165 of the floral scent plumes cannot be studied. In the present work, we address this issue by
 166 explicitly representing the spatial extent of floral scent plumes that are generated from the
 167 LES model outputs.

168 From all the possible random walk models, Lévy walks have received significant attention
 169 (Viswanathan et al., 1999; Reynolds and Rhodes, 2009; Reynolds, 2010). Under some specific
 170 circumstances, Lévy walks represent optimal search strategies (Viswanathan et al., 1999;
 171 Raposo et al., 2009). More recently, the idea of composite searches (Plank and James, 2008)
 172 in which insects invest foraging times in resource rich areas has gained attention. Basically,
 173 insects move back and forth between two strategies: an intensive search is adopted in regions
 174 rich in resources and an extensive foraging strategy is adopted elsewhere. Thus, insects
 175 first use extensive searches to locate resources, and then they alternate to intensive searches
 176 within areas with resources. If searches are not successful then insects move back to extensive

177 foraging to cover larger areas in search of other resource rich areas. Even in composite search
 178 strategies, Lévy walks seem to be the most profitable approach (Reynolds and Bartumeus,
 179 2009). Despite recent criticism regarding the optimality of Lévy walks as a foraging strategy
 180 (Pyke, 2015), the approach is still useful as an idealized model to investigate the effects of
 181 environmental characteristics on insect foraging.

182 We adopt the Lévy walk to represent insects searching for floral scent plumes. In the
 183 context of composite searches, this can be viewed as the extensive strategy of locating the
 184 first resource location within an unknown landscape (Reynolds and Bartumeus, 2009; Nolting
 185 et al., 2015). In the model, insect flights are determined by a step length (l) and a horizontal
 186 angle (θ). Step lengths are drawn from a power-law distribution given by

$$P(l) = \left(\frac{l}{l_0}\right)^{-\mu}. \quad (5)$$

187 In equation (5), l_0 is the minimum step length and μ is a parameter whose value ranges from
 188 1 to 3. Note that $\mu = 3$ corresponds to Brownian motion and $\mu = 2$ is a super-diffusive Lévy
 189 walk. The model with $\mu = 2$ represents optimal search strategies (Viswanathan et al., 1999)
 190 and it is used in the current study. Horizontal angles are drawn from a uniform distribution.

191 Two source distributions representing landscapes with different amounts of resources are
 192 investigated. In the first case, only one simulated plume is included, representing a landscape
 193 with scarce resources. Insects are released from the downwind corner of the simulation
 194 domain ($x = 1000$ m and $y = -175$ m), corresponding to a distance of nearly 1 km from
 195 the center of the flower patch (Figure 1, top panel). A landscape rich in resources is also
 196 considered. For that purpose, eight copies of the scent plumes produced by the LES are
 197 placed in a circular pattern around the insect release location (Figure 1, bottom panel). In
 198 both cases, the initial height (z) of the insects is set to 1 m, and this value is kept constant
 199 during the insect flights. Each insect flight step is broken into substeps of size l_0 ($l_0 = 1$ m
 200 is used here) and, after each substep, the local floral scent concentration is compared to the
 201 insect detection threshold for a given compound to decide whether the insect is capable of
 202 recognizing the scent plume at that location. If the gas concentration is greater than the
 203 detection threshold, the flight ends and the insect is considered successful in locating the

204 scent plume. In the model, it is assumed that insects fly at a constant speed of 2 m s^{-1} and
205 terminate their flights if the scent plume is not found within 3 hours. For each scenario (see
206 description in Section 2.3), 18 instantaneous LES-generated scent plumes are considered. For
207 each plume, a total of 5,000 insect flights are considered, and statistics are computed over the
208 accumulated 90,000 flights. Simulations are performed for detection thresholds varying from
209 0.1 pptv to 25 pptv. These detection thresholds are within the lowest-observed responses of
210 insects (Dusenbery, 1992).

211 2.3. Pollution scenarios

212 Six scenarios (Table 2) are considered to determine changes in scents in response to
213 varying levels of air pollutants as air parcels travel away from flowers. The first scenario
214 (Sc0) considers no air pollutants to determine the spatial variation of floral volatiles away
215 from sources in response to turbulent transport and to serve as the basis for comparison
216 with the rest of scenarios. The second scenario (Sc1) includes 20 ppbv of O_3 , 0.02 part per
217 trillion on a volume basis (pptv) ($5.0 \times 10^5 \text{ radicals cm}^{-3}$) of OH, and 0 pptv of NO_3 . This
218 scenario may be viewed as the prevailing O_3 levels during pre-industrial times (Marenco
219 et al., 1994), with limited photochemical activity (and hence low OH levels) and no nitrogen
220 oxides to generate NO_3 . The third scenario (Sc2) involves the levels of 0.2 pptv (5.0×10^6
221 radicals cm^{-3}), 40 ppbv, and 0 pptv of OH, O_3 , and NO_3 , respectively. The fourth scenario
222 (Sc3) uses the levels of 0.3 pptv ($1.0 \times 10^7 \text{ radicals cm}^{-3}$), 60 ppbv, and 1 pptv for HO, O_3 ,
223 and NO_3 , respectively. The fifth scenario (Sc4) involves the levels of 0.40 pptv (2.0×10^7
224 radicals cm^{-3}), 80 ppbv, and 2 pptv for OH, O_3 , and NO_3 , respectively. The last scenario
225 (Sc5) involves the levels of 0.80 pptv ($2.0 \times 10^7 \text{ radicals cm}^{-3}$), 120 ppbv, and 5 pptv for
226 OH, O_3 , and NO_3 , respectively. We choose these last two scenarios to reflect the broad
227 ranges in air pollutant deviations from pre-industrial times (Marenco et al., 1994; Prinn
228 et al., 2005) to current summertime conditions in regions such as the eastern United States
229 where maximum O_3 levels can sometimes exceed 120 ppbv (Fiore et al., 2002). Pollutants
230 are assumed to logarithmically vary with altitude, and the values listed here are specified
231 at a height $z = 1.5 \text{ m}$ (the value at the top of the domain is twice the value at 1.5 m). For

232 simplicity and convenience, for a given scenario, the ambient mixing ratios of OH, O₃, and
 233 NO₃ remain constant in time and space throughout the course of model simulations.

Table 2: Ambient mixing ratios of the ozone, hydroxyl radical, and nitrate radical included in the scenarios of the numerical simulations.

Scenario	O ₃ (ppbv)	HO (pptv)	NO ₃ (pptv)
Sc0	0	0.00	0
Sc1	20	0.02	0
Sc2	40	0.20	0
Sc3	60	0.30	1
Sc4	80	0.40	2
Sc5	120	0.80	5

234 2.4. Data analysis techniques

235 In total, twelve LES runs are done to include the six air pollutant scenarios under the
 236 influences of two turbulence levels. Average floral volatile concentrations are calculated
 237 to determine the chemical degradation of scent plumes in response to varying levels of air
 238 pollutants. For each floral scent ($i = 1, \dots, 5$, Table 1) and scenario (Sc_j , $j = 0, \dots, 5$),
 239 temporal averages are performed (for periods defined from initial time (T_0) to some later
 240 time (T_f)) and crosswind direction to yield mean gas concentration as a function of x and z

$$\overline{[\chi_i]_{Sc_j}}(x, z) = \frac{1}{L_y(T_f - T_0)} \int_{T_0}^{T_f} \int_{-L_y/2}^{L_y/2} \widetilde{[\chi_i]_{Sc_j}}(x, y, z, t) dy dt. \quad (6)$$

241 Resulting average scent concentrations are reported in two ways. First, to illustrate the
 242 effects of air pollutants on scent concentrations downwind from sources, gas concentrations
 243 are normalized to concentrations for the scenario without air pollutants ($\overline{[\chi_i]_{N_j}}(x, z)$) and
 244 are determined using Equation (7) for scent species $i = 1, \dots, 5$.

$$\overline{[\chi_i]_{N_j}}(x, z) = \frac{\overline{[\chi_i]_{Sc_j}}(x, z)}{\overline{[\chi_i]_{Sc_0}}(x, z)} \quad (7)$$

245 Second, to emphasize the effects of air pollutants on the changes in the composition of scent
 246 plumes, fractional composition ($\overline{[\chi_i]_{F_j}}(x, z)$) of scent plumes are computed using Equation
 247 (8) for each scenario.

$$\overline{[\chi_i]_{F_j}}(x, z) = \frac{\overline{[\chi_i]_{Sc_j}}(x, z)}{\sum_{k=1}^5 \overline{[\chi_k]_{Sc_j}}(x, z)} \quad (8)$$

248 Only values for the height of insect flight ($z = 1.0$ m) are reported below (i.e., $\overline{[\chi_i]_{N_j}}(x, 1.0$ m),
 249 $\overline{[\chi_i]_{F_j}}(x, 1.0$ m)). For the fractional composition, values are reported at the discrete down-
 250 wind distances (x) of 200, 300, 400, and 800 m.

251 For insect foraging times, statistics are calculated for each flower volatile and for each air
 252 pollution scenario individually. Calculations are done separately for landscapes scarce and
 253 rich in scent resources. Summary statistics are presented for the discovery of floral plumes
 254 based on three detection thresholds. The cumulative distributions of insect discovery times
 255 of floral plumes and the proportion of insects discovering floral plumes within 3 hours are
 256 presented.

257 3. Results

258 3.1. Chemical degradation of floral volatiles

259 The chemical degradation of floral scents depends on the reactivity of volatiles and am-
 260 bient levels of air pollutants. For the chosen air pollutant levels, floral chemical species
 261 exhibit a broad range of lifetimes (for the reaction with O_3 , the individual floral scent (χ_i)
 262 lifetime is defined as $\tau_{\chi_i, O_3} = (K_{\chi_i, O_3} [O_3])^{-1}$; similar expressions can be defined for $\tau_{\chi_i, OH}$
 263 and τ_{χ_i, NO_3}). Concerning the O_3 reactivity, β -caryophyllene is the most reactive scent and
 264 its lifetime decreases from 12 to 2 minutes for O_3 levels between 5 and 120 ppbv (Figure
 265 3). Linalool, β -ocimene, and β -myrcene have an intermediate reactivity with respect to O_3
 266 and their lifetimes vary from 200 to 10 minutes when O_3 changes from 5 to 120 ppbv. In
 267 these simulations, α -pinene is the least reactive with O_3 and its lifetime changes from 30 to 1
 268 hours for O_3 levels between 5 and 120 ppbv (Figure 3). With regard to the OH reactivity, β -
 269 ocimene, β -myrcene, and β -caryophyllene are the most short lived scents and their lifetimes
 270 range from 50 hours to 5 minutes when OH changes from 0.001 to 0.8 pptv. Concerning

271 the NO_3 reactivity, β -ocimene and β -caryophyllene are the most reactive species and their
272 lifetimes range from 18 hours to 5 minutes as NO_3 varies from 0.01 to 5 pptv. In polluted air
273 masses (i.e., $[\text{OH}] > 0.3$ pptv), all floral scents have lifetimes of few (< 30) minutes (Figure
274 3).

275 Source strength of floral volatiles, levels of air turbulence, and rates of chemical reac-
276 tions dictate the three-dimensional characteristics of the scents downwind from sources. For
277 example, Figure 4 displays iso-surfaces of time averaged scent mixing ratios in the three-
278 dimensional space (i.e., a surface formed by all the points with a chosen constant gas mixing
279 ratio value) downwind from the chosen floral patches. Blue iso-surfaces represent mixing
280 ratios of 0.6 pptv for myrcene and β -caryophyllene (under the influences of scenarios Sc0,
281 Sc3, and Sc5), indicating that all the points inside the blue surface have scent levels above
282 0.6 pptv and all the points outside the surface have scent mixing ratios below 0.6 pptv.
283 The volume inside the blue iso-surface represents the portion of the plume that an insect
284 with a threshold detection of 0.6 pptv can detect. Similarly, the volume inside the purple
285 iso-surfaces represents the portion of the scent plume that insects with a detection threshold
286 of 4.8 pptv can detect.

287 Ambient scent distribution downwind from sources is inversely related to turbulence
288 levels (Figure 4). For the same floral volatile emission rates, scent levels are higher under
289 the influence of low air turbulence (this feature is clearly noticeable on the purple plumes).
290 This effect is due to the reduced dilution rates of scents caused by lower mean wind speeds
291 associated with the low turbulence (Figure 2). Also, under the influences of the two adopted
292 levels of turbulence and no chemistry, relatively elevated gas mixing ratios prevailed across
293 the landscape, with scent levels above 3.2 pptv extending as far as 300 m away from flowers
294 (note that the source ends at $x = 200$ m, so the location at $x = 500$ m is 300 m downwind
295 from the flower patch). Sufficient levels (>0.4 pptv) of β -myrcene (Figure 4A) and β -
296 caryophyllene (Figure 4B) reached about 800 m downwind from floral volatile sources. Such
297 scent spatial distribution patterns and abundances were deemed adequate for most insects to
298 locate the floral scent plumes (Dusenbery, 1992). In effect, the resulting spatial distribution

299 of floral scents provided information on the effective plume “footprint” of a particular floral
300 patch. For polluted conditions (scenarios Sc3 and Sc5), the plumes of floral volatiles such as
301 β -myrcene, with medium reactivity, could only reach 400 m downwind from sources (Figure
302 4). For the highly reactive compounds such as β -caryophyllene, sufficient levels were only
303 found near flowers. Therefore, in polluted air masses, the “volume” of scent plumes is
304 drastically reduced due to the chemical reactions, thereby making it harder for insects to
305 locate food.

306 Air pollutant levels and reactivity of floral scents exert control on the spatial extent of
307 floral volatile transported away from sources. Horizontal cross sections (Figure 5) provide the
308 spatial distribution of floral scents downwind from sources under the influences of different
309 levels of air pollutants. To some extent, they represent the *scentscape* that insects can
310 detect while foraging for food resources. The unpolluted case (Sc0) serves as a basis for
311 comparison and shows similar spatial distributions of β -myrcene and β -caryophyllene (see
312 color scales, Figure 5), confirming that the difference in source strength between the two
313 compounds (about 60 %, see Table 1) is not the dominant factor in determining their spatial
314 distributions. Under moderate levels of air pollutant (Sc3), significant levels of β -myrcene
315 (~ 1 pptv) can reach about 800 m downwind from floral sources whereas similar levels of
316 β -caryophyllene reach at most 100 m downwind from sources. The most dramatic effect
317 occurs in polluted air masses (Sc6) when plumes of β -myrcene remain within 400 m of scent
318 sources; in contrast, plumes of β -caryophyllene can only be found directly above the floral
319 patches.

320 While foraging for resources most insects use non-directional sensory cues and instantane-
321 neous plumes of scents to identify areas that warrant searches (Nolting et al., 2015; Bell,
322 1990). Instantaneous scent plumes provide information to allow foraging insects to directly
323 orient themselves to habitat resources and determine the appropriate search strategy (i.e.,
324 intensive or extensive search modes). Time-averaged plumes (Figure 5) differ substantially
325 compared to instantaneous ones (Figure 6). Whereas time-averaged scent plumes provide
326 relatively smooth scent concentration gradients along horizontal transects, instantaneous flo-

327 ral fragrance plumes reveal greater heterogeneity in the spatial distribution of gases. Some
328 areas can be almost devoid of floral scents while the contiguous surroundings exhibit high
329 loading of scents (e.g., scenarios Sc3 and Sc5 for β -caryophyllene, Figure 6). The character-
330 istic features in the spatially heterogeneous gas distribution in instantaneous plumes result
331 in response to erratic turbulent fluctuations that allow for the rapid transport of gases. In
332 the instantaneous plumes, the intensity of the spatiotemporal scent fluctuations increases
333 with air turbulence (data not shown). Consequently, at any given location and time, scent
334 concentrations within plumes can erratically and substantially vary compared to the time-
335 averaged plumes (compare Figure 5 with Figure 6). These results (Figure 6) suggest that
336 foraging insects likely use olfactory information provided by instantaneous plumes to influ-
337 ence search behavior at the habitat level that can impact search strategies at the patch, and
338 search at the patch can affect foraging for individual resources (Bell, 1990).

339 Ambient scent levels downwind from sources depend on rates of chemical destruction
340 and turbulence intensity. Under the influences of the assumed air turbulence conditions (u_*
341 = 0.1 m s^{-1} and $u_* = 0.2 \text{ m s}^{-1}$), the normalized time-averaged concentrations of floral
342 volatiles (i.e., $[\overline{\chi}_i]_{N_j}$ for floral scents $i = 1, \dots, 5$ and air pollution scenarios $j = 1, \dots, 5$, see
343 Methods Section) provide a qualitative measure of the influences of chemical reactions on
344 the distances traveled by scent plumes away from sources. Compounds such as β -myrcene
345 and β -caryophyllene can exhibit different abundances along transects from downwind of
346 sources in response to the reactivities of floral volatiles (Figure 7). For example, under
347 the influences of low air pollutant concentrations (Sc1), only 75 to 80% of the emitted β -
348 myrcene reaches 800 m away from floral sources, when $u_* = 0.1 \text{ m s}^{-1}$ and $u_* = 0.2 \text{ m s}^{-1}$,
349 respectively. In contrast, only 5% of the emitted β -caryophyllene reaches 800 m when $u_* =$
350 0.1 m s^{-1} and 400 m away from sources when $u_* = 0.2 \text{ m s}^{-1}$. For highly polluted conditions
351 (Sc6), only approximately 25% of the original β -myrcene remains within distances of 100 m
352 downwind from floral sources (Figure 7). As air pollutant concentrations increase, amounts
353 of scents exponentially decrease with distance away from floral sources. Based on these
354 results (Figure 7), it is concluded that reductions in the amounts of floral scents transported

355 away from sources can impair the ability of insects locating floral scents due to the reductions
356 of olfactory cues below the insect detection thresholds.

357 3.2. *Modification of floral volatile mixtures*

358 Generalist insects such as honeybees respond to floral bouquets instead of a specific scent
359 (Wright et al., 2005; Raguso, 2008). Also, generalist insects respond to compound blends but
360 detect ratios as indicators to judge potential success of locating resources (Raguso, 2008).
361 Because of the different reaction rates for each floral volatiles, however, the composition of
362 the floral scents can change as they react with air pollutants, thereby altering the floral bou-
363 quet. To show the potential changes in the ratios of these components, LES results were used
364 to track the composition of scent plumes as they traveled away from from sources. Figure
365 8 depicts the differences between the floral composition at the source and the composition
366 of scent plumes at several downwind distances from sources. While the initial composition
367 of the scent was comprised of 60 % β -ocimene, 20 % β -myrcene, 8 % β -caryophyllene, 7 %
368 β -pinene, and 5 % linalool at the source, it is evident (Figure 8) the fragrance composition
369 changed substantially as air parcels traveled downwind in polluted conditions. For instance,
370 at 800 m away from sources, β -pinene, rather than β -ocimene, became the predominant
371 compound in the floral mixture, due to the slower reaction rates. Even by the short traveled
372 distance of 250 m, the floral bouquet did not include β -caryophyllene due to its destruction
373 via chemical reactions. Therefore, the results indicate that the insects associated with origi-
374 nal floral volatile blends would become increasingly 'confused' and unable to distinguish the
375 appropriate composition of the volatile mixture away from the source under polluted con-
376 ditions. The addition of pollutants, however, makes this task of identifying floral mixtures
377 more laborious as the scent composition changes much more rapidly with increasing levels
378 of oxidants.

379 For those insects that have evolved to rely upon the unique signature of a specific flower,
380 a change in the composition of these scents could be troubling, depending upon how sensitive
381 their antennae are to detecting particular compounds Skiri et al. (2005) and their tolerance
382 for shifts in relative concentration among plume components. Many insect species hone

383 in on specific scents because it increases their likelihood of being consistently rewarded.
384 If particular flowers are proven to be reliable sources of nectar for foraging insects then
385 they can train themselves to that specific scent, what is known as flower constancy (Gegear
386 and Laverty, 2005). In polluted conditions, however, the plume of floral volatiles may no
387 longer be recognized as such because its composition no longer corresponds to the scent
388 that insects associate with a particular flower. Moreover, because plant odors mediate both
389 mutualistic and antagonistic relationships between plants and insects, a disruption in the
390 communication system could either help or hurt plants depending on which insects are most
391 affected. In cases where antagonists and mutualists respond to different volatiles from the
392 same plant (e.g., Andrews et al. (2007)), the outcome will depend partly on the reactivity
393 of the different compounds. More generally, however, mutualistic relationships may be more
394 sensitive to disruption because they typically rely on repeated tracking of scent to source
395 (e.g., pollinators and natural enemies searching for new resources) whereas antagonists such
396 as herbivores may find sufficient resources at a single resource once discovered and rely less
397 on long-distance plant signals from that point forward.

398 *3.3. Potential impact on insect success and foraging times*

399 Air pollutants, type of hydrocarbons, detection thresholds of insects, and number of floral
400 patches on the landscape impact insect discovery times of floral sources. These effects are
401 illustrated in Figure 9, where the cumulative number of insects that locate the scent plume is
402 displayed as a function of foraging time (up to the limit of 3 hours). Each panel corresponds
403 to a combination of hydrocarbon used by insects and corresponding insect detection threshold
404 limit, and results under different pollution scenarios are compared for landscapes scarce and
405 rich in resources (solid and dashed lines, respectively). By itself, detection threshold sets
406 severe constraints on how far away scent plumes can be detected when transported downwind
407 from sources. When there is only a single floral patch on the landscape (Figure 9 – solid
408 lines), the proportion of foragers that locate the scent within 180 minutes in the unpolluted
409 environment decreases from about 80 % with a detection threshold of 0.1 pptv (Figure 9A-C)
410 to approximately 20 % in an unpolluted environment with a detection threshold of 3.9 pptv

411 (Figures 9G-I). These results are due to the fact that insects with low olfactory detection
412 threshold can detect greater foraging areas in response to greater scent loadings (Figure 6).
413 Therefore, olfactory detection threshold values explain the broad computed foraging times
414 for the investigated scents (Figure 9).

415 The reactivity of the hydrocarbon being modeled strongly influences the effect of air
416 pollutants on scent plume detectability. For the most reactive floral volatile, β -caryophyllene,
417 even modest levels of air pollutants (e.g., $[O_3] = 20$ ppbv, $[OH] = 0.02$ pptv) can have
418 dramatic effects on both discovery times and probability of discovery within 180 minutes,
419 thereby reducing the likelihood of discovery by 65 % and increasing the discovery time from
420 about 10 minutes to approximately 180 minutes for the first 20 % of foragers to locate
421 the scent plume (Figures 9C and F). As air pollutant levels increase, the size of the scent
422 plume diminishes (Figure 6) which increases the insect foraging times. For a hydrocarbon
423 of intermediate reactivity such as β -myrcene, the plume discovery can broadly differ across
424 all pollutant levels (Figures 9B and E), while for α -pinene, the least reactive hydrocarbon
425 included in the foraging model, a notable effect of air pollutants is only observed at an
426 intermediate level of detectability (i.e., 0.6 pptv, Figure 9D). Again, size of scent plumes and
427 characteristic features of spatial gas distribution (Figure 6) impact the insect discovery times
428 of flower patches. Number of floral patches present throughout the landscape also influences
429 the outcome of foraging trials. As floral patches become prevalingly common (Figure 9 –
430 dashed lines), most foragers encounter scent plumes within 180 minutes. At the extreme,
431 over 50 % of foragers encounter scent plumes within 15 minutes while searching for the
432 most reactive compound in unpolluted environments, but similar numbers of foragers take
433 about 60 minutes for discovery of scent plumes under modest pollution levels (Figure 9F).
434 Therefore, these results indicate that floral scent reactivity, pollutant levels, and detection
435 thresholds all strongly mediate the ability of insects to locate scent plumes.

436 In our foraging model, insects searched for a particular scent in the landscape, following
437 it when it was encountered above a threshold concentration. Because insects are capable
438 of associative learning (Hollis and Guillette, 2015), they could potentially learn to follow

439 the altered plume to the original plume and reach the reward. Second order conditioning
440 (associating one stimulus with another stimulus) has been demonstrated in the laboratory
441 with honeybees exposed consecutively to two distinct odors (Hussaini et al., 2007). It would
442 be challenging, however, for an insect to learn distinct stimuli under polluted conditions as
443 the odor would be continuously changing with distance and with diurnal patterns of pollutant
444 concentrations. While we cannot currently evaluate the likelihood of an insect learning to
445 track the altered plume, we recognize this effect is an interesting study area with broad
446 implications for insect response to environmental change.

447 **4. Summary and Conclusions**

448 This study concludes that even moderate air pollutant levels (e.g., $[O_3] > 60$ ppbv) sub-
449 stantially degrade the chemical constituents of released floral scents. The chemical degrada-
450 tion of floral volatiles contributes to substantial reductions in the concentrations of scents as
451 they are transported away from sources. Decreases in scent abundances away from sources
452 show steeper decreases with increasing levels of air pollutants. In the most polluted air
453 masses ($[O_3] = 120$ ppbv), compounds such as β -ocimene decrease to 25 % of the original
454 abundance within a downwind distance of 100 m from sources whereas β -caryophyllene re-
455 tains only 10 % of the original amount within 50 m of sources. In all scenarios examined,
456 concentrations of the studied floral volatiles substantially decrease in response to increasing
457 levels of air pollutants and rates of scent destruction depend on gas reactivity with respect
458 to O_3 , OH, and NO_3 . Because individual components of floral scents degrade at different
459 rates, the scent itself changes as a function of reactant concentrations and time evolution
460 of the scent plumes. At downwind distances of 800 m, the least reactive compounds (e.g.,
461 α -pinene) dominate the composition of scents whereas the more reactive compounds (e.g.,
462 β -caryophyllene) are chemically destroyed.

463 The likelihood of foraging insects discovering a particular flower patch depends on air
464 pollutant levels, antennal sensitivity, and the component(s) of the floral scent that the insects
465 recognize and follow. Taken together, these variables determine the perceptual footprint of
466 scent plumes, and the size of that footprint determines both the speed and the likelihood of

467 patch discovery. Our simulations indicate that air pollution will have the greatest impact
468 on patch discovery time when highly reactive volatiles elicit foraging responses at low scent
469 concentrations.

470 Increased discovery time of flower patches may have pernicious effects on insects. Many
471 insect species rely on flowers for food, mating and oviposition sites, and follow odor trails
472 to locate them (Byers et al., 2014; Chen et al., 2009; Cunningham et al., 2004; Maia et al.,
473 2014; Urru et al., 2011). The longer insects must forage for resources, the less efficient they
474 become and the greater risk they face from predators and parasites (e.g., Goodell (2003)).
475 Thus, pollution may reduce insect fitness through changes in food detectability. Such effects
476 however, are likely to be species specific and context specific in severity. Insects following
477 relatively rare scent plumes in their foraging environment may be more detrimentally affected
478 than insects relying on locally common odor plumes. Similarly, insects needing to locate a
479 scent plume only once to complete a life stage, such as ovipositing in a flower just prior to
480 death (Dunn et al., 2014), might be less affected than those that must repeatedly locate
481 flowers, given that the inherent advantage of insects finding a bigger plume target would
482 be compounded by repetition. Additionally, insects that wander throughout the landscape
483 searching for odor plumes each time a resource is needed may be more affected than central-
484 place foragers that locate resource patches and return to them repeatedly using spatial
485 memory (Menzel et al., 2005). The severity of the effects may also be mitigated by whether
486 an insect navigates using single compounds or complex plumes as stimuli. Insects tracking
487 single scents will be able to follow a scent trail as long as it occurs above the detection
488 threshold. For insects following a floral plume, however, detectability depends on both the
489 reactivity of the individual components of that plume and the ability of insects to recognize
490 and track the plume despite variation in plume composition.

491 Modifications of floral scent quality and quantity can have broad impacts on plant-
492 insect interactions, not just insect fitness. The most reactive compounds in our study,
493 β -caryophyllene and β -myrcene, are common components of floral volatiles and play diverse
494 ecological roles, such as attracting pollinators, herbivores, and parasitoids of herbivores. If

495 mutualist insects such as pollinators are less efficient at finding hosts then visitation to host
496 plants may be less frequent and pollination services may be reduced. Similarly, if predators
497 and parasites are less able to follow the scent trail released by plants that are attacked by
498 herbivores then the ecological services they provide to plants will also be diminished.

499 Overall, we predict that existing air pollution levels in urban and industrial corridors
500 can have deleterious impacts on insect foraging efficiency and on plant-insect interactions.
501 Levels of ambient pollutants, types of volatiles comprising the scent plume, sensitivity of
502 insect antennae to plume constituents, the abundance of host plants in the environment and
503 the air conditions (windy versus calm) of the location may all differentially impact the extent
504 of the negative ecological impacts.

505 ***Acknowledgments***

506 The Pennsylvania State University Institutes of Energy and the Environment (PSIEE)
507 provided funding to complete this research. JDF Fuentes also acknowledges support from
508 the National Science Foundation (grant numbers *GEO 0914597* and *AGS 1417914*). Au-
509 thors thank the Editor and two anonymous reviewers for the comments that improved the
510 manuscript. Data used to create the figures in this work are available from the authors'
511 upon request (e-mail: jdfuentes@psu.edu).

512 **References**

- 513 Andrews, E. S., Theis, N., Adler, L. S., 2007. Pollinator and herbivore attraction to cucurbita
514 floral volatiles. *Journal of chemical ecology* 33 (9), 1682–1691.
- 515 Atkinson, R., Baulch, D., Cox, R., Hampson Jr, R., Kerr, J., Rossi, M., Troe, J., 1999.
516 Evaluated kinetic and photochemical data for atmospheric chemistry, organic species:
517 Supplement vii. *Journal of Physical and chemical reference Data* 28 (2), 191–393.
- 518 Bell, W. J., 1990. Searching behavior patterns in insects. *Annual review of entomology* 35 (1),
519 447–467.
- 520 Bhattacharya, M., Primack, R. B., Gerwein, J., 2003. Are roads and railroads barriers to
521 bumblebee movement in a temperate suburban conservation area? *Biological Conservation*
522 109 (1), 37–45.
- 523 Biesmeijer, J. C., Roberts, S., Reemer, M., Ohlemüller, R., Edwards, M., Peeters, T., Schaf-
524 fers, A., Potts, S., Kleukers, R., Thomas, C., et al., 2006. Parallel declines in pollinators
525 and insect-pollinated plants in britain and the netherlands. *Science* 313 (5785), 351–354.
- 526 Blande, J. D., Holopainen, J. K., Li, T., 2010. Air pollution impedes plant-to-plant commu-
527 nication by volatiles. *Ecology Letters* 13 (9), 1172–1181.
- 528 Bou-Zeid, E., Meneveau, C., Parlange, M. B., 2005. A scale-dependent Lagrangian dynamic
529 model for large eddy simulation of complex turbulent flows. *Phys. Fluids* 17, 025105,
530 doi:10.1063/1.1839152.
- 531 Byers, K. J., Bradshaw, H., Riffell, J. A., 2014. Three floral volatiles contribute to differential
532 pollinator attraction in monkeyflowers (*mimulus*). *The Journal of experimental biology*
533 217 (4), 614–623.
- 534 Cameron, S. A., Lozier, J. D., Strange, J. P., Koch, J. B., Cordes, N., Solter, L. F., Griswold,
535 T. L., 2011. Patterns of widespread decline in north american bumble bees. *Proceedings*
536 *of the National Academy of Sciences* 108 (2), 662–667.

- 537 Chamecki, M., Meneveau, C., Parlange, M. B., 2008. A hybrid spectral/finite-volume algo-
538 rithm for large-eddy simulation of scalars in the atmospheric boundary layer. *Boundary-*
539 *Layer Meteorol.* 128, 473–484.
- 540 Chamecki, M., Meneveau, C., Parlange, M. B., 2009. Large eddy simulation of pollen trans-
541 port in the atmospheric boundary layer. *J. Aerosol Sci.* 40, 241–255.
- 542 Chen, C., Song, Q., Proffit, M., Bessière, J.-M., Li, Z., Hossaert-McKey, M., 2009. Pri-
543 vate channel: a single unusual compound assures specific pollinator attraction in ficus
544 semicordata. *Functional Ecology* 23 (5), 941–950.
- 545 Codling, E. A., Plank, M. J., Benhamou, S., 2008. Random walk models in biology. *Journal*
546 *of the Royal Society Interface* 5 (25), 813–834.
- 547 Cooper, O. R., Gao, R.-S., Tarasick, D., Leblanc, T., Sweeney, C., 2012. Long-term ozone
548 trends at rural ozone monitoring sites across the united states, 1990–2010. *Journal of*
549 *Geophysical Research: Atmospheres* (1984–2012) 117 (D22).
- 550 Cunningham, J. P., Moore, C. J., Zalucki, M. P., West, S. A., 2004. Learning, odour prefer-
551 ence and flower foraging in moths. *Journal of Experimental Biology* 207 (1), 87–94.
- 552 Dobson, H. E., 2006. Relationship between floral fragrance composition and type of pollina-
553 tor. *Biology of floral scent*, 147–198.
- 554 Dötterl, S., Vereecken, N., 2010. The chemical ecology and evolution of bee-flower interac-
555 tions: a review and perspectives. the present review is one in the special series of reviews
556 on animal-plant interactions. *Canadian Journal of Zoology* 88 (7), 668–697.
- 557 Dunn, D. W., Jandér, K. C., Lamas, A. G., Pereira, R. A., 2014. Mortal combat and
558 competition for oviposition sites in female pollinating fig wasps. *Behavioral Ecology*, 1–7.
559 doi:10.1093/beheco/aru191.
- 560 Dusenbery, D. B., 1992. *Sensory ecology*.

- 561 Farré-Armengol, G., Peñuelas, J., Li, T., Yli-Pirilä, P., Filella, I., Llusia, J., Blande, J. D.,
562 2016. Ozone degrades floral scent and reduces pollinator attraction to flowers. *New Phy-*
563 *tologist* 209 (1), 152–160.
- 564 Fiore, A. M., Jacob, D. J., Bey, I., Yantosca, R. M., Field, B. D., Fusco, A. C., Wilkinson,
565 J. G., 2002. Background ozone over the united states in summer: Origin, trend, and
566 contribution to pollution episodes. *Journal of Geophysical Research: Atmospheres* (1984–
567 2012) 107 (D15), ACH–11.
- 568 Fuentes, J. D., Gu, L., Lerdau, M., Atkinson, R., Baldocchi, D., Bottenheim, J., Ciccioli, P.,
569 Lamb, B., Geron, C., Guenther, A., et al., 2000. Biogenic hydrocarbons in the atmospheric
570 boundary layer: a review. *Bulletin of the American Meteorological Society* 81 (7), 1537–
571 1575.
- 572 Fuentes, J. D., Roulston, T. H., Zenker, J., 2013. Ozone impedes the ability of a herbivore
573 to find its host. *Environmental Research Letters* 8 (1), 014048.
- 574 Gaskell, P. H., Lau, A. K. C., 1988. Curvature-compensated convective transport: SMART,
575 a new boundedness-preserving transport algorithm. *Int. J. Numer. Methods Fluids* 8, 617–
576 641.
- 577 Gegear, R. J., Laverty, T. M., 2005. Flower constancy in bumblebees: a test of the trait
578 variability hypothesis. *Animal Behaviour* 69 (4), 939–949.
- 579 Goodell, K., 2003. Food availability affects *osmia pumila* (hymenoptera: Megachilidae) for-
580 aging, reproduction, and brood parasitism. *Oecologia* 134 (4), 518–527.
- 581 Goulson, D., Lye, G. C., Darvill, B., 2008. Decline and conservation of bumble bees. *Annu.*
582 *Rev. Entomol.* 53, 191–208.
- 583 Hollis, K., Guillette, L., 2015. What associative learning in insects tells us about the evolution
584 of learning and fixed behavior. *International Journal of Comparative Psychology*. Volume
585 28.

- 586 Hussaini, S. A., Komischke, B., Menzel, R., Lachnit, H., 2007. Forward and backward second-
587 order pavlovian conditioning in honeybees. *Learning & Memory* 14 (10), 678–683.
- 588 Jaffe, D., Ray, J., 2007. Increase in surface ozone at rural sites in the western us. *Atmospheric*
589 *Environment* 41 (26), 5452–5463.
- 590 Knudsen, J. T., Eriksson, R., Gershenson, J., Ståhl, B., 2006. Diversity and distribution of
591 floral scent. *The Botanical Review* 72 (1), 1–120.
- 592 Li, T., Blande, J. D., 2015. Associational susceptibility in broccoli: mediated by plant
593 volatiles, impeded by ozone. *Global change biology* 21 (5), 1993–2004.
- 594 Loreto, F., Mannozi, M., Maris, C., Nascetti, P., Ferranti, F., Pasqualini, S., 2001. Ozone
595 quenching properties of isoprene and its antioxidant role in leaves. *Plant Physiology*
596 126 (3), 993–1000.
- 597 Loreto, F., Schnitzler, J.-P., 2010. Abiotic stresses and induced bvocs. *Trends in plant science*
598 15 (3), 154–166.
- 599 Maia, A. C. D., de Lima, C. T., Navarro, D. M. d. A. F., Chartier, M., Giulietti, A. M.,
600 Machado, I. C., 2014. The floral scents of *nymphaea* subg. *hydrocallis* (nymphaeaceae),
601 the new world night-blooming water lilies, and their relation with putative pollinators.
602 *Phytochemistry* 103, 67–75.
- 603 Marengo, A., Gouget, H., Nédélec, P., Karcher, F., et al., 1994. Evidence of a long-term in-
604 crease in tropospheric ozone from pic du midi data series: Consequences: Positive radiative
605 forcing. *Journal of Geophysical Research: Atmospheres* (1984–2012) 99 (D8), 16617–16632.
- 606 Mayer, C. J., Vilcinskas, A., Gross, J., 2008. Pathogen-induced release of plant allomone
607 manipulates vector insect behavior. *Journal of chemical ecology* 34 (12), 1518–1522.
- 608 McFrederick, Q. S., Fuentes, J. D., Roulston, T., Kathilankal, J. C., Lerdau, M., 2009.
609 Effects of air pollution on biogenic volatiles and ecological interactions. *Oecologia* 160 (3),
610 411–420.

- 611 McFrederick, Q. S., Kathilankal, J. C., Fuentes, J. D., 2008. Air pollution modifies floral
612 scent trails. *Atmospheric Environment* 42 (10), 2336–2348.
- 613 Menzel, R., Greggers, U., Smith, A., Berger, S., Brandt, R., Brunke, S., Bundrock, G., Hülse,
614 S., Plümpe, T., Schaupp, F., Schüttler, E., Stach, S., Stindt, J., Stollhoff, N., Watzl, S.,
615 2005. Honey bees navigate according to a map-like spatial memory. *Proceedings of the*
616 *National Academy of Sciences of the United States of America* 102 (8), 3040–3045.
- 617 Montero-Castaño, A., Vilà, M., 2012. Impact of landscape alteration and invasions on polli-
618 nators: a meta-analysis. *Journal of ecology* 100 (4), 884–893.
- 619 Nolting, B. C., Hinkelman, T. M., Brassil, C. E., Tenhumberg, B., 2015. Composite random
620 search strategies based on non-directional sensory cues. *Ecological Complexity* 22, 126 –
621 138.
622 URL <http://www.sciencedirect.com/science/article/pii/S1476945X15000355>
- 623 Ozawa, R., Shiojiri, K., Sabelis, M. W., Takabayashi, J., 2008. Maize plants sprayed with
624 either jasmonic acid or its precursor, methyl linolenate, attract armyworm parasitoids, but
625 the composition of attractants differs. *Entomologia Experimentalis et Applicata* 129 (2),
626 189–199.
- 627 Parrish, D., Law, K. S., Staehelin, J., Derwent, R., Cooper, O., Tanimoto, H., Volz-Thomas,
628 A., Gilge, S., Scheel, H.-E., Steinbacher, M., et al., 2013. Lower tropospheric ozone at
629 northern midlatitudes: Changing seasonal cycle. *Geophysical Research Letters* 40 (8),
630 1631–1636.
- 631 Peyret, R., Taylor, T. D., 1983. *Computational methods for fluid flow*. Springer Berlin
632 Heidelberg.
- 633 Pinto, D. M., Blande, J. D., Nykänen, R., Dong, W.-X., Nerg, A.-M., Holopainen, J. K.,
634 2007. Ozone degrades common herbivore-induced plant volatiles: does this affect herbivore
635 prey location by predators and parasitoids? *Journal of Chemical Ecology* 33 (4), 683–694.

- 636 Plank, M., James, A., 2008. Optimal foraging: Levy pattern or process? *Journal of The*
637 *Royal Society Interface* 5 (26), 1077–1086.
- 638 Prinn, R., Huang, J., Weiss, R., Cunnold, D., Fraser, P., Simmonds, P., McCulloch, A.,
639 Harth, C., Reimann, S., Salameh, P., et al., 2005. Evidence for variability of atmospheric
640 hydroxyl radicals over the past quarter century. *Geophysical Research Letters* 32 (7).
- 641 Pyke, G. H., 2015. Understanding movements of organisms: it's time to abandon the lévy
642 foraging hypothesis. *Methods in Ecology and Evolution* 6 (1), 1–16.
- 643 Raguso, R. A., 2008. Wake up and smell the roses: the ecology and evolution of floral scent.
644 *Annual Review of Ecology, Evolution, and Systematics*, 549–569.
- 645 Raposo, E., Buldyrev, S., Da Luz, M., Viswanathan, G., Stanley, H., 2009. Lévy flights and
646 random searches. *Journal of Physics A: mathematical and theoretical* 42 (43), 434003.
- 647 Reynolds, A., Bartumeus, F., 2009. Optimising the success of random destructive searches:
648 Lévy walks can outperform ballistic motions. *Journal of theoretical biology* 260 (1), 98–
649 103.
- 650 Reynolds, A. M., 2010. Bridging the gulf between correlated random walks and lévy walks:
651 autocorrelation as a source of lévy walk movement patterns. *Journal of the Royal Society*
652 *Interface*, rsif20100292.
- 653 Reynolds, A. M., Rhodes, C. J., 2009. The lévy flight paradigm: random search patterns
654 and mechanisms. *Ecology* 90 (4), 877–887.
- 655 Sharkey, T. D., Chen, X., Yeh, S., 2001. Isoprene increases thermotolerance of fosmidomycin-
656 fed leaves. *Plant Physiology* 125 (4).
- 657 Skiri, H., Strandén, M., Sandoz, J.-C., Menzel, R., Mustaparta, H., 2005. Associative learn-
658 ing of plant odorants activating the same or different receptor neurones in the moth he-
659 *liothis virescens*. *Journal of Experimental Biology* 208 (4), 787–796.

- 660 Stanley, D. A., Smith, K. E., Raine, N. E., 2015. Bumblebee learning and memory is impaired
661 by chronic exposure to a neonicotinoid pesticide. *Scientific reports* 5.
- 662 Urru, I., Stensmyr, M. C., Hansson, B. S., 2011. Pollination by brood-site deception. *Phy-*
663 *tochemistry* 72 (13), 1655–1666.
- 664 Van Poecke, R. M., Posthumus, M. A., Dicke, M., 2001. Herbivore-induced volatile pro-
665 duction by *arabidopsis thaliana* leads to attraction of the parasitoid *cotesia rubecula*:
666 chemical, behavioral, and gene-expression analysis. *Journal of Chemical Ecology* 27 (10),
667 1911–1928.
- 668 Viswanathan, G., Buldyrev, S. V., Havlin, S., Da Luz, M., Raposo, E., Stanley, H. E., 1999.
669 Optimizing the success of random searches. *Nature* 401 (6756), 911–914.
- 670 Von Helversen, O., Winkler, L., Bestmann, H., 2000. Sulphur-containing perfumes attract
671 flower-visiting bats. *Journal of Comparative Physiology A* 186 (2), 143–153.
- 672 Whitehorn, P. R., OConnor, S., Wackers, F. L., Goulson, D., 2012. Neonicotinoid pesticide
673 reduces bumble bee colony growth and queen production. *Science* 336 (6079), 351–352.
- 674 Wright, G. A., Lutmerding, A., Dudareva, N., Smith, B. H., 2005. Intensity and the ratios
675 of compounds in the scent of snapdragon flowers affect scent discrimination by honeybees
676 (*apis mellifera*). *Journal of Comparative Physiology A* 191 (2), 105–114.
- 677 Wright, G. A., Schiestl, F. P., 2009. The evolution of floral scent: the influence of olfactory
678 learning by insect pollinators on the honest signalling of floral rewards. *Functional Ecology*
679 23 (5), 841–851.

680 **Figure captions**

681 **Figure 1.** (Top) Configuration of the Large Eddy Simulation domain and distribution of
 682 flowers releasing scents to attract insects, and (bottom) spatial distribution of scent plumes
 683 and location foraging insects.

684 **Figure 2.** Vertical variations of wind speed (top) and standard deviation of the vertical
 685 wind speed (bottom) under the influences of friction velocity (u_*) of 0.1 and 0.2 m per s.

686 **Figure 3.** Lifetimes of floral volatiles as a function of reactivity with respect to (top)
 687 ozone, (middle) hydroxyl radical, and (bottom) nitrate radical under the the influences of
 688 the oxidant levels shown on the insets (right hand side). Labels placed on top of symbols
 689 are 1: β -Caryophyllene, 2: β -Ocimene, 3: β -Myrcene, 4: Linalool, and 5: α -Pinene.

690 **Figure 4.** Three-dimensional scent plume characteristics for (top) β -myrcene and (bot-
 691 tom) β -caryophyllene under the influences of pollution scenarios (i) Sc0, (ii) Sc3, and (iii)
 692 Sc5 and friction velocity values of 0.1 m s^{-1} and 0.2 m s^{-1} . Iso-surfaces corresponding to
 693 gas mixing ratios of 0.6 pptv (blue) and 4.8 pptv (purple) are illustrated.

694 **Figure 5.** Horizontal cross sections of (left) β -myrcene and (right) β -caryophyllene time-
 695 averaged plumes for pollution scenarios (i) Sc0, (ii) Sc3, and (iii) Sc5. The friction velocity
 696 of 0.1 m per s was used in the LES. The cross section is at 1.0 m above the surface.

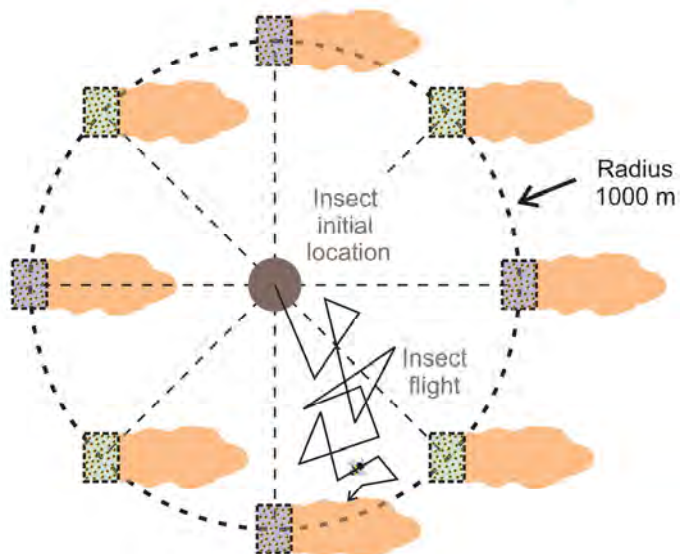
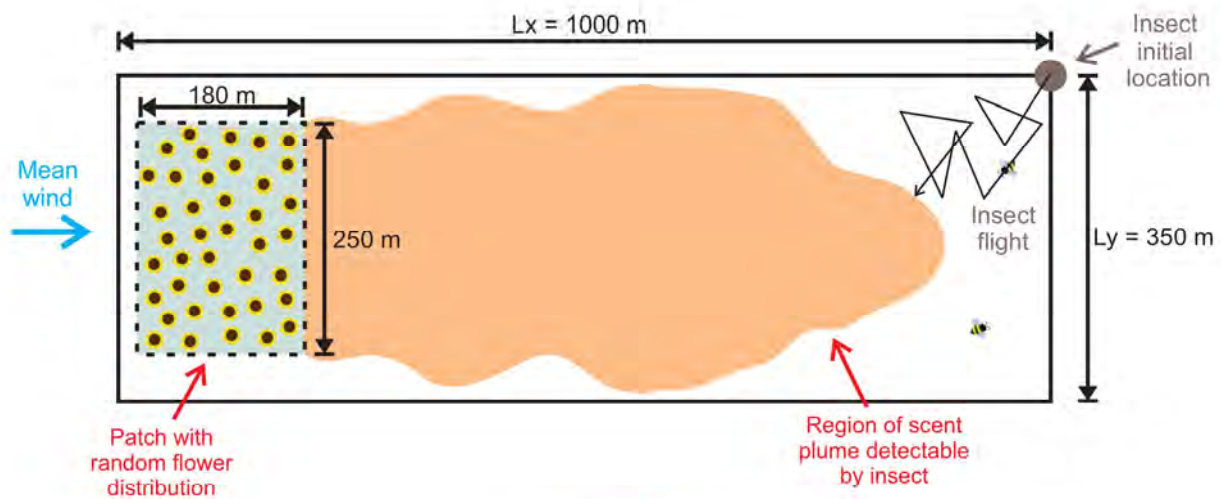
697 **Figure 6.** Horizontal cross sections of (left) β -myrcene and (right) β -caryophyllene
 698 instantaneous plumes for pollution scenarios (i) Sc0, (ii) Sc3, and (iii) Sc5. The friction
 699 velocity of 0.1 m per s was used in the LES. The cross section is at 1.0 m above the surface.

700 **Figure 7.** Fraction of (a) β -myrcene and (b) β -caryophyllene remaining as a function
 701 of downwind distance traveled from the source after reacting with hydroxyl radicals, ozone,
 702 and nitrate radicals for the four scenarios considered in the modeling study using friction
 703 velocity values of 0.1 m per s and 0.2 m per s. The values are averaged at 1.0 m above the
 704 surface.

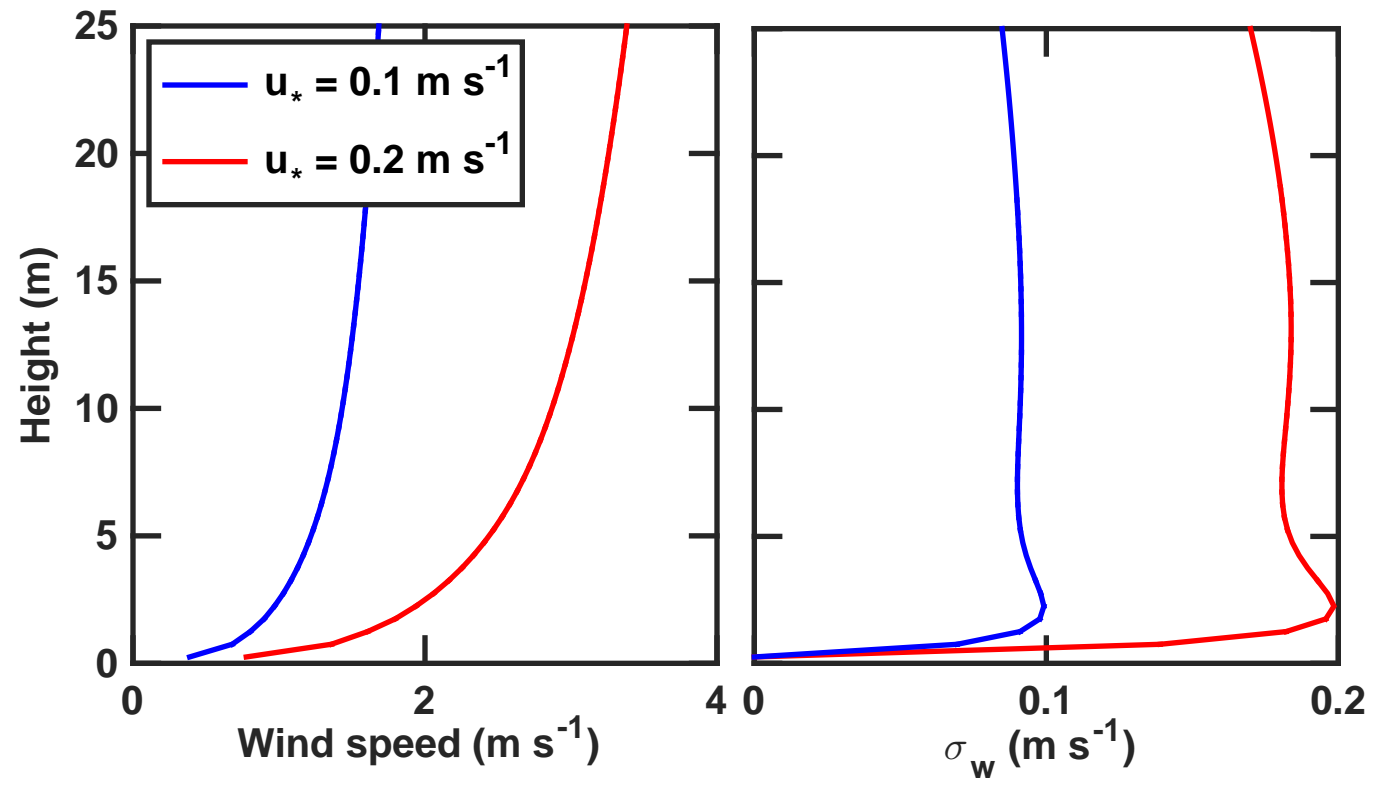
705 **Figure 8.** Modification of plume composition as compounds travel and react from sources
 706 to downwind areas for (i) no pollution, (ii) 60 ppb of ozone, and (iii) 120 ppb of ozone using
 707 u_* of 0.1 m per s. (B) Modification of scents as compounds travel and react from sources to

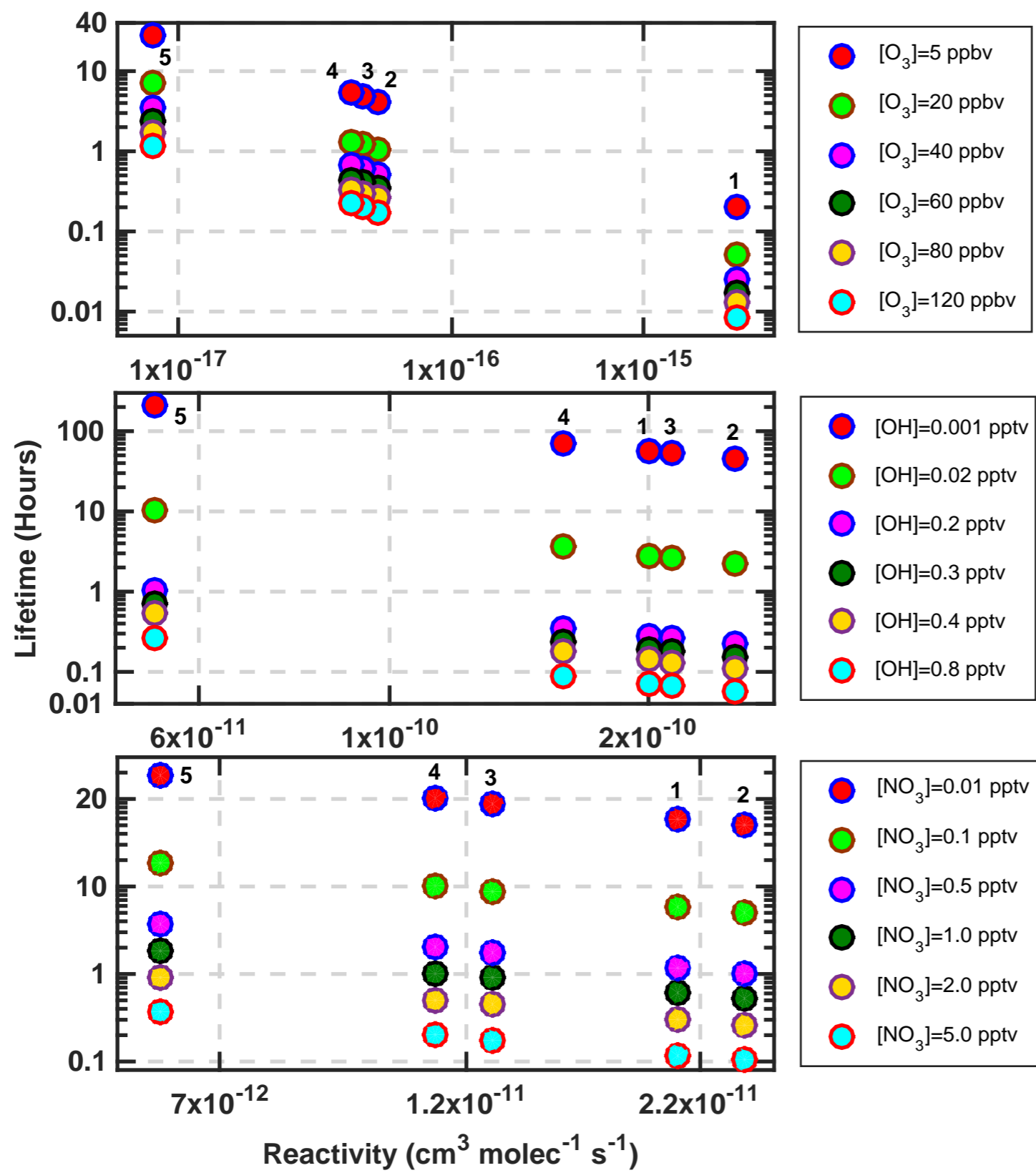
708 downwind areas for (i) no pollution, (ii) 60 ppb of ozone, and (iii) 120 ppb of ozone using u_*
709 of 0.2 m per s. The values are averaged at 1.0 m above the surface.

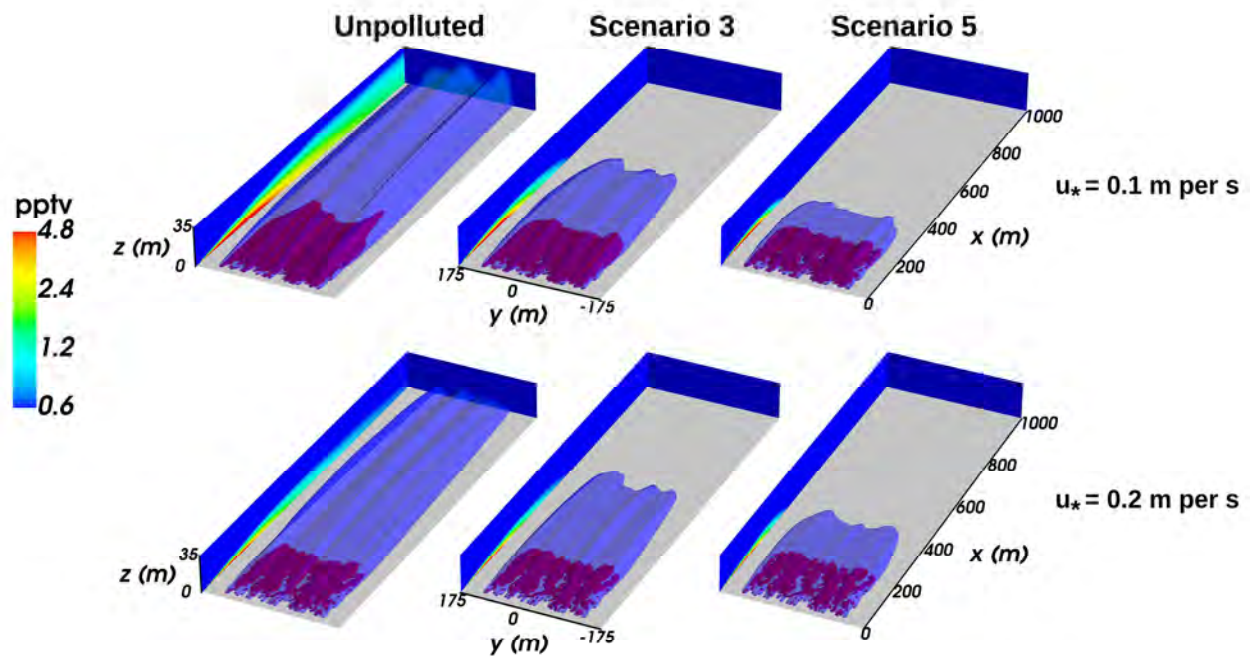
710 **Figure 9.** Cumulative distribution function of the foraging times required for insects to
711 locate scent plumes in a landscape with scarce resources (solid lines) and rich in resources
712 (dashed lines). Pollution scenarios are represented by different colors: Sc0 (black), Sc1 (red),
713 Sc2 (green), Sc3 (blue), Sc4 (gray), and Sc5 (orange). Each figure (e.g., Figure A) reports
714 the cumulative distribution function of foraging times for insects with a given threshold
715 detection of α -pinene, β -myrcene, and β -caryophyllene.



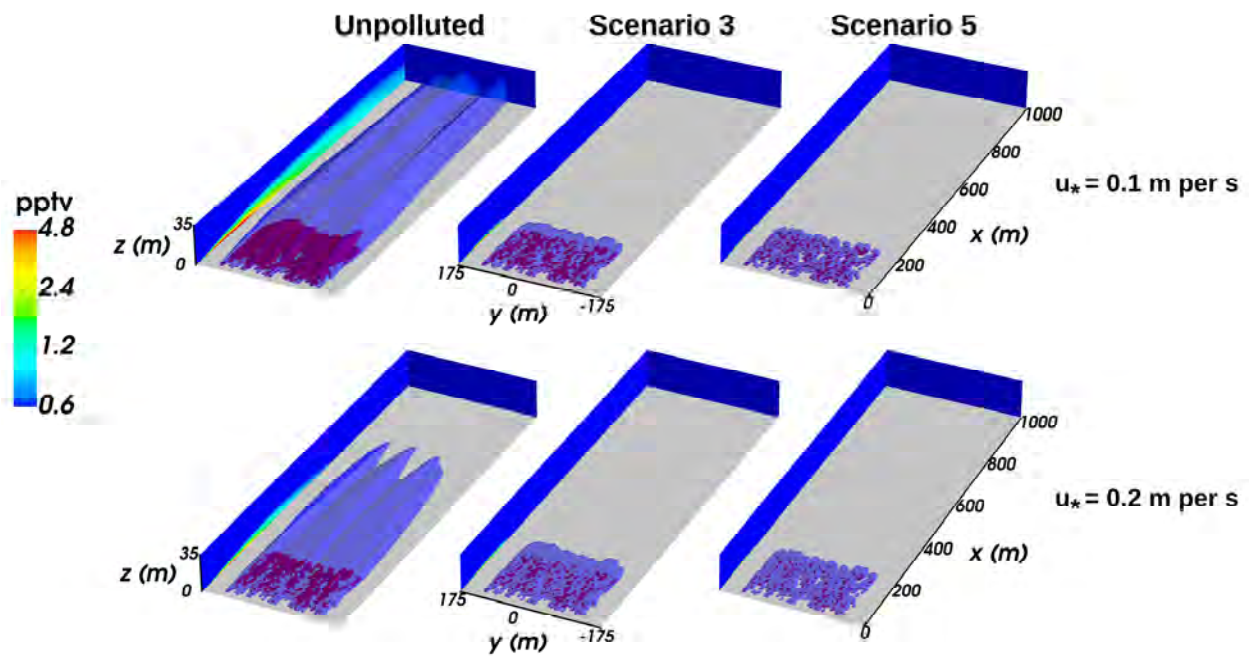
ACCEPTED

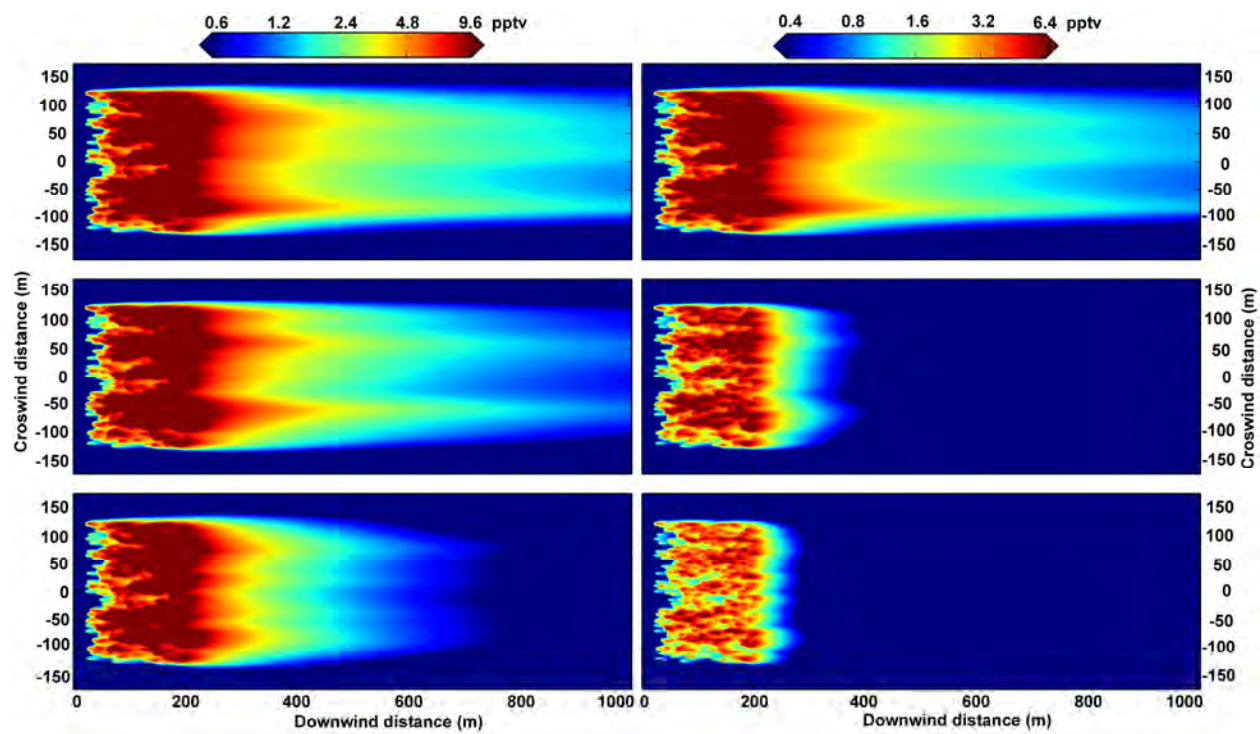




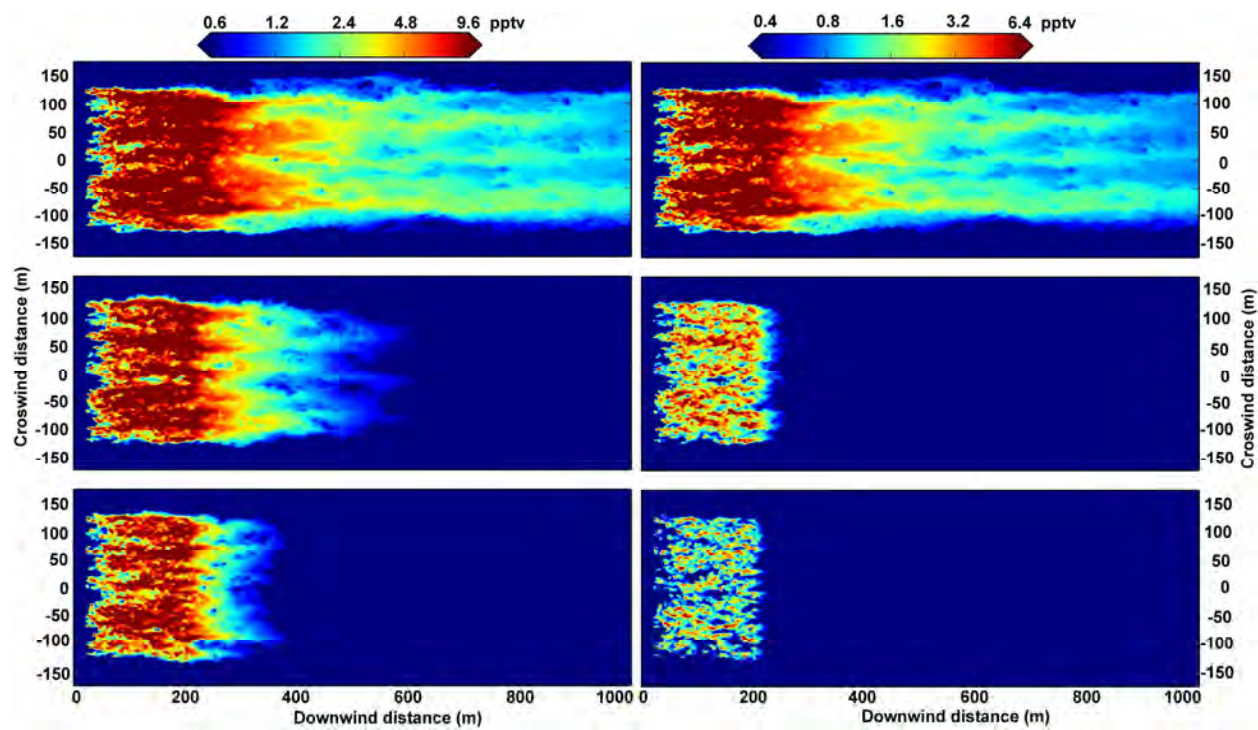


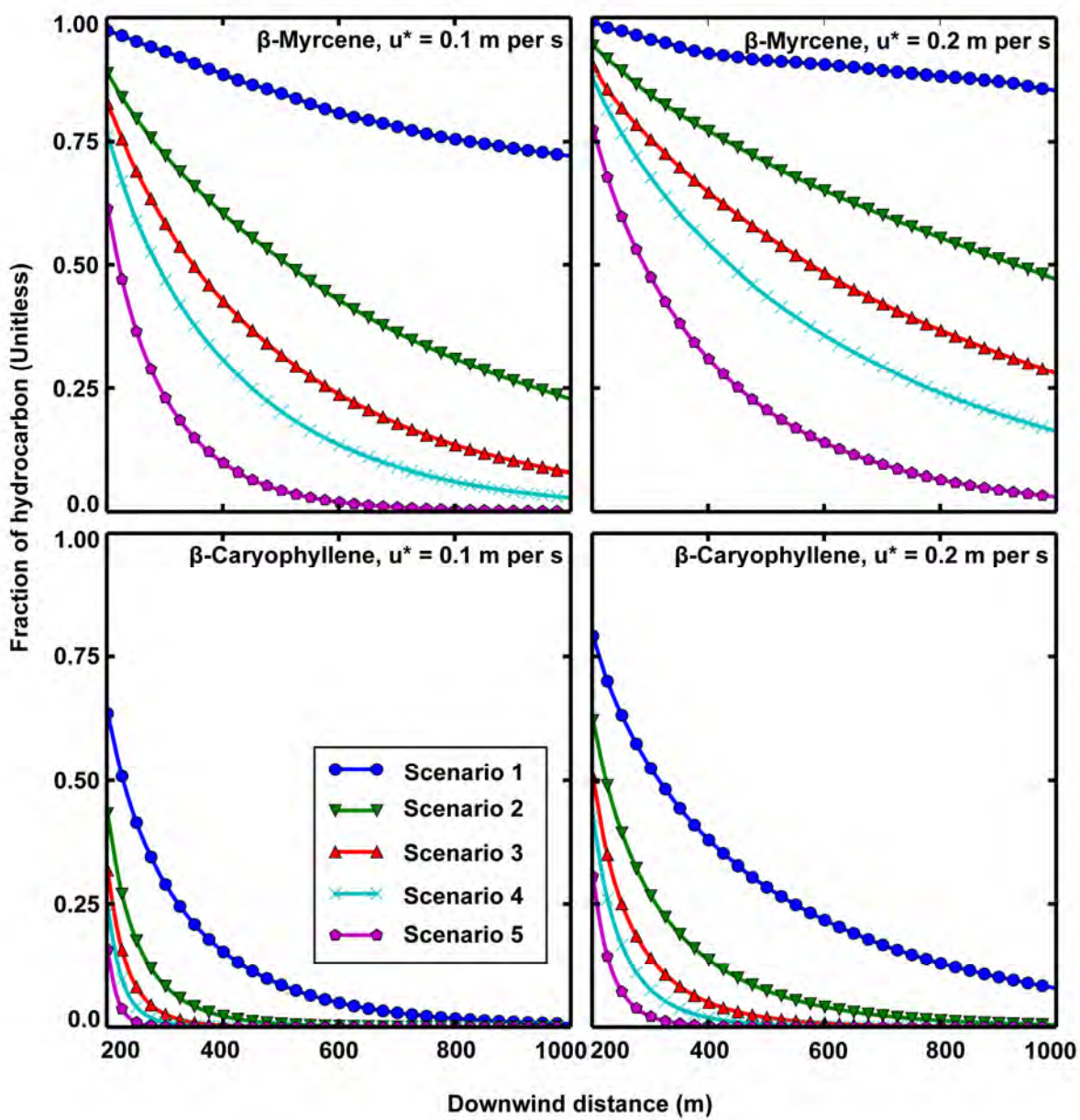
ACCEPTED MANUSCRIPT

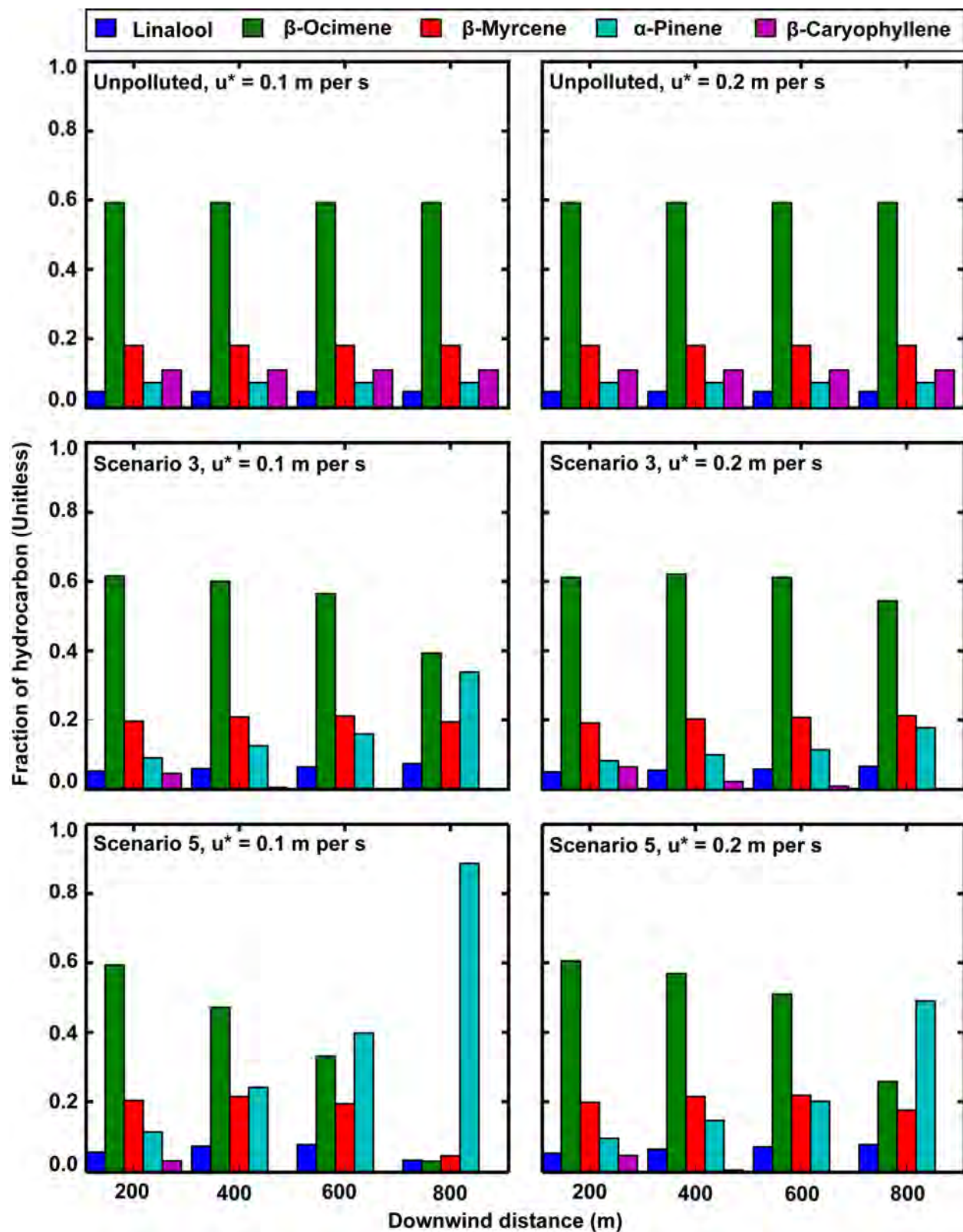


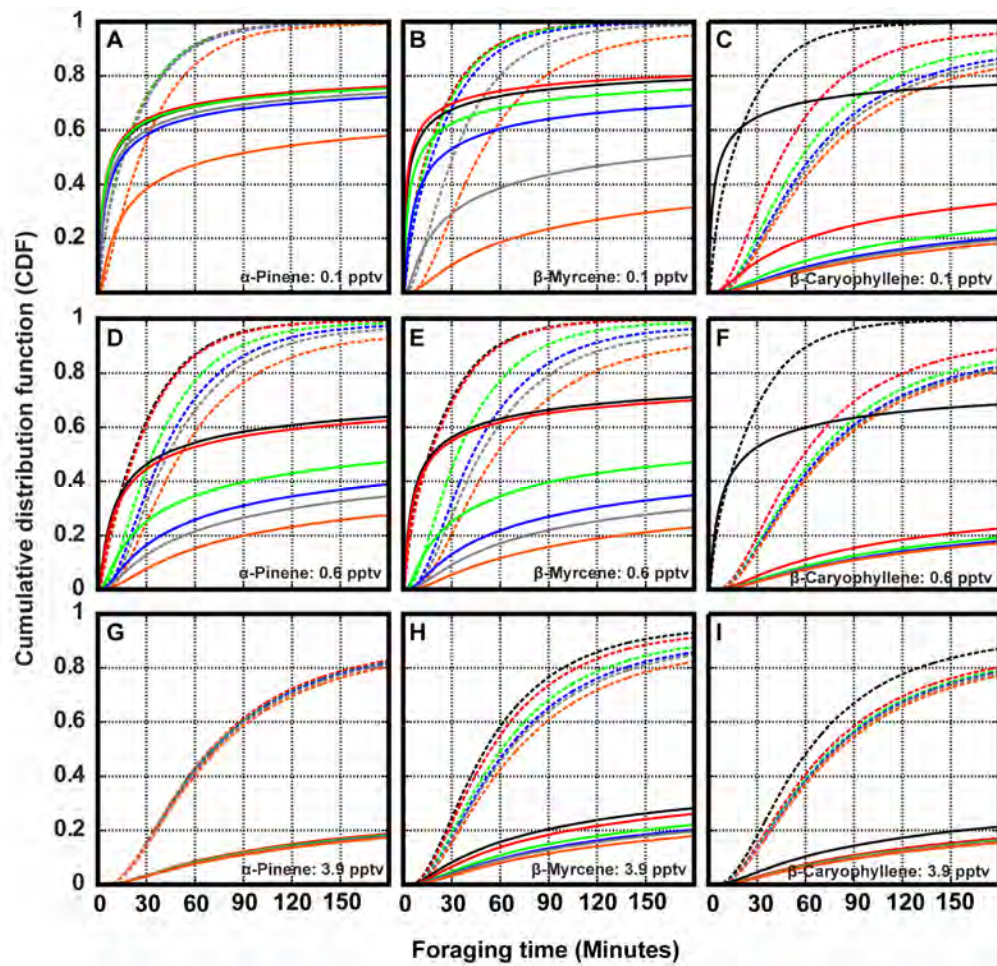


ACCEPTED MANUSCRIPT









Highlights

- Pollutants such as ozone, nitrate radical, and hydroxyl radical react with floral scents, modifying their chemical composition downwind of sources.
- Ozone mixing ratios greater than 60 parts per billion on a per volume basis can substantially reduce the downwind footprint of floral scents, depending on the reactivity of the chemical constituents of the floral plume.
- Insects increase the time to encounter target floral plumes in polluted air masses due to the modified chemical composition of floral scents.
- Plant-pollinator interactions could be sensitive to changes in floral scent composition, especially if insects are unable to adapt to the modified scentscape.