Air pollution modifies floral scent trails

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Abstract

Floral hydrocarbons provide essential signals to attract pollinators. As soon as they are emitted to the atmosphere, however, hydrocarbons are destroyed by chemical reactions involving pollutants such as ozone. It is therefore likely that increased air pollution interferes with pollinator attracting hydrocarbon signals. To test this hypothesis, a Lagrangian diffusion model was used to determine the position of air parcels away from hydrocarbon sources and to estimate the rate of chemical destruction of hydrocarbons as air parcels moved across the landscape. The hydrocarbon compounds linalool, β-myrcene, and β-ocimene were chosen because they are known to be common scents released from flowers. The suppressed ambient abundances of volatile organic compounds were determined in response to increased regional levels of ozone, hydroxyl, and nitrate radicals. The results indicate that the documented increases in air pollution concentrations, from pre-industrial to present times, can lead to reductions in volatile compound concentrations insects detect as they pollinate flowers. For highly reactive volatiles the maximum downwind distance from the source at which pollinators can detect the scents may have changed from kilometers during pre-industrial times to <200 m during the more polluted conditions of present times. The increased destruction of floral signals in polluted air masses may have important implications for both pollinators and signaling plants. When patches of flowers are further apart than the visual range of pollinators, such as in fragmented landscapes, the loss of scent signals may mean that pollinators spend more time searching for patches and less time foraging. This decrease in pollinator foraging efficiency will simultaneously decrease the pollinator’s reproductive output and the amount of pollen flow in flowering plants.

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1. Introduction

It is well established that, after undergoing atmospheric chemical reactions, volatile organic compounds emitted by flowering plants contribute to the formation of free radicals, carbon monoxide, and formaldehyde (Atkinson and Arey, 2003; Fuentes et al., 2000). Additionally, in environments rich in nitrogen oxides, plant-emitted hydrocarbons can enhance the formation of ground-level ozone (O₃) via reactions with nitric oxide (NO) emitted from anthropogenic sources (Pierce et al., 1998) and secondary organic aerosols as a result of gas-to-particle portioning of the reaction products (Hoffmann et al., 1997; Ng et al., 2006).

Phytogenic hydrocarbons also play important ecological roles in plant communities. Both pollinators and herbivores exploit the attracting signals provided by hydrocarbons to locate their host plants and flowers (Thies and Raguso, 2005;
Dudareva et al., 2006). Additionally, phytogenic hydrocarbons serve as indirect plant defenses against herbivores. Natural enemies of herbivores can be attracted by hydrocarbons released by plants in response to herbivore attack (Dudareva et al., 2004). Pollinators use both vision and scent to locate flowers, and floral volatiles play an important role in pollinator attraction (Dobson, 1994). There is experimental evidence that floral volatiles attract pollinators such as orchid bees (Williams and Dodson, 1972). Volatiles such as linalool (C\textsubscript{10}H\textsubscript{18}O) are known to cause strong antennal responses in sphinx moths (Raguso and Light, 1998; Raguso et al., 1996) and to be effective attractants to honey bees (Henning et al., 1992; Wright et al., 2005). Linalool is also known to elicit feeding responses from honey bees (Blight et al., 1997). It is also known that honey bees increase their discrimination of volatile fragrances based on differing ratios of compounds such as β-myrcene (C\textsubscript{10}H\textsubscript{16}) and β-ocimene (C\textsubscript{10}H\textsubscript{16}) (Wright et al., 2005; Wright and Smith, 2004).

One relatively unexplored aspect of phytogenic hydrocarbons lies at the intersection of their atmospheric chemistry and ecological roles. As floral scent trails are transported from source sites to downwind areas they undergo chemical degradation. With the continued changes in concentrations of ground-level O\textsubscript{3} (Fiore et al., 2002) and free radicals (Prinn et al., 2005) it is likely that the modified atmospheric chemistry of phytogenic hydrocarbons can interfere with their ecological roles in plant communities. Specifically, increased levels of air pollution will weaken the phytogenic hydrocarbon chemical signals because of enhanced chemical reactions. Such chemical transformations are likely to have negative effects on both emitting plants and intended recipients of scent signals. The only study that has addressed this intersection of chemistry and ecology dealt with hydrocarbon signals to natural enemies of plant pests (Pinto et al., 2007). In this study, the volatile trails were degraded but natural enemy orientation to damaged plants was not disrupted, presumably due to the persistence of more stable volatiles or reaction products.

In this manuscript, we evaluate the hypothesis that increases in levels of air pollutants are modifying hydrocarbon signaling trails, specifically the trails emitted by flowers to attract pollinators. We determined the chemical degradation rate of selected hydrocarbons as air parcels carried scent trails away from floral hydrocarbon sources. To estimate the rate of chemical destruction of linalool, β-myrcene, and β-ocimene as air parcels traveled away from scent sources, we included atmospheric chemical reactions in a Lagrangian diffusion model (Baldocchi, 1997; Strong et al., 2004). We chose the selected hydrocarbons because they are known to be common scents released from flowers (Dudareva and Pichersky, 2000; Knudsen et al., 2006) and they attract bees (Wright et al., 2005). The suppressed ambient abundances of volatile organic compounds were determined in response to increased regional levels of O\textsubscript{3}, hydroxyl radicals (HO), and nitrate radicals (NO\textsubscript{3}). One important conclusion derived from this study is that suppressed levels of scents may become undetectable by pollinators foraging at distances  >200 m away from volatile sources. Therefore, the decreased insect attractant levels may interfere with pollinator detection of floral resources. These hydrocarbon–air pollution processes are likely operating in landscapes such as the eastern United States where summertime air pollution levels can become substantially higher than the ones observed in the rural atmosphere away from anthropogenic influences. Additionally, these processes may increase the search time of pollinators, which would likely lead to lower brood production and diminished pollination services, especially in landscapes where floral patches are separated by distances greater than the visual range of pollinators, such as fragmented urban habitats.

2. Chemistry of hydrocarbons

The hydrocarbon species included in this study are transported from their sources and react rapidly with O\textsubscript{3}, HO, and NO\textsubscript{3}. In the lower atmosphere, O\textsubscript{3} sources include transport from the stratosphere and photochemical production involving the reaction of molecular oxygen (O\textsubscript{2}) with the atomic oxygen (O), which is produced from the photolysis of nitrogen dioxide (NO\textsubscript{2}) (R1). During the daytime, O\textsubscript{3} molecules undergo photolysis to form excited oxygen atoms (O(\textsuperscript{1}D)) (R3) which can then quickly react with water vapor (H\textsubscript{2}O) to form HO (R4). The other major tropospheric source of HO is formaldehyde (CH\textsubscript{2}O) photolysis, which produces hydroperoxy radicals (HO\textsubscript{2}) (R5). The HO\textsubscript{2} radicals undergo subsequent reaction with NO (R6) to form HO and NO\textsubscript{2}. Moreover, the reactions of O\textsubscript{3} with alkenes can produce HO (Finlayson-Pitts and Pitts, 1999). In the case of NO\textsubscript{3} its source comes from the reaction of O\textsubscript{3} molecules with NO\textsubscript{2} ((R7); Atkinson and Arey, 2003).
The thermal decomposition of dinitrogen pentoxide (N$_2$O$_5$) can generate NO$_3$ (R8). Under favorable meteorological conditions and in areas with abundant nitrogen oxides (NO$_X$ = NO + NO$_2$), these three compounds—O$_3$, HO, and NO$_3$—can contribute to the destruction of phytoenic hydrocarbons.

\[
\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \quad (\lambda < 420 \text{ nm})
\]  
\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (\text{M} = \text{O}_2 \text{ or nitrogen (N$_2$))}
\]  
\[
\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}^{(1D)} \quad (\lambda < 320 \text{ nm})
\]  
\[
\text{O}^{(1D)} + \text{H}_2\text{O} \rightarrow \text{HO} + \text{HO}
\]  
\[
\text{CH}_2\text{O} + h\nu(+\text{O}_2) \rightarrow \text{CO} + 2\text{HO}_2 \quad (\lambda < 360 \text{ nm})
\]  
\[
\text{HO}_2 + \text{NO} \rightarrow \text{HO} + \text{NO}_2
\]  
\[
\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2
\]  
\[
\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_3 + \text{NO}_2 + \text{M} \quad (\text{M} = \text{O}_2 \text{ or N$_2$})
\]

The reactions of hydrocarbons with O$_3$, HO, and NO$_3$ lead to the formation of O$_3$, carbonyl containing organic compounds, and other degradation products such as carbon monoxide and formaldehyde (Atkinson and Arey, 2003). As noted in Table 1, the reactions of hydrocarbons with HO and NO$_3$ have greater rate parameters than the O$_3$ reactions. For the reaction of linalool with HO the main reaction products include acetone, 6-methyl-5-hepten-2-one, and 4-hydroxy-4-methyl-5-hexenal. The associated yields are 0.505, 0.068, and 0.46 for the three reaction products listed above (R9), respectively (Shu et al., 1997). Meanwhile the reaction of linalool with NO$_3$ only produces acetone and 4-hydroxy-4-methyl-5-hexenal, with corresponding yields of 0.225 and 0.191 (R10), respectively. This reaction (R10) can produce major but unquantifiable amounts of nitrooxycarbonyls (Shu et al., 1997). The reaction of linalool with O$_3$ is more complex and produces acetone, formaldehyde, 4-hydroxy-4-methyl-5-hexen-1-al, and 5-ethylyldihydro-5-methyl-2-furanone (C$_7$H$_{10}$O$_2$) with associated yields of 0.211, 0.360, 0.850, and 0.126, respectively (Shu et al., 1997) (R11).

Table 1
Characteristics of the volatiles included in the present study (Reissell et al., 2002; Shu et al., 1997)

<table>
<thead>
<tr>
<th>Volatile</th>
<th>Chemical structure</th>
<th>Molecular weight</th>
<th>Life time (min)$^a$</th>
<th>HO reactivity (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>HO</td>
<td>NO$_3$</td>
</tr>
<tr>
<td>$\beta$-Ocimene</td>
<td><img src="image1" alt="Chemical structure" /></td>
<td>136.24</td>
<td>13.2</td>
<td>3.0</td>
</tr>
<tr>
<td>$\beta$-Myrcene</td>
<td><img src="image2" alt="Chemical structure" /></td>
<td>136.24</td>
<td>15.5</td>
<td>5.2</td>
</tr>
<tr>
<td>Linalool</td>
<td><img src="image3" alt="Chemical structure" /></td>
<td>154.25</td>
<td>22.2</td>
<td>6.0</td>
</tr>
</tbody>
</table>

$^a$The lifetime ($\tau$) was estimated as $\tau = 1/\sqrt{w}k$, where $\sqrt{w}$ represents the concentration of O$_3$ (= 50 ppbv = 1.23 x 10$^{12}$ molecules cm$^{-3}$), HO (= 5.0 x 10$^6$ radicals cm$^{-3}$), or NO$_3$ (= 2.5 x 10$^8$ radicals cm$^{-3}$); and $k$ denotes the associated reaction rate constant.
The reactions involving \( \beta \)-myrcene and \( \beta \)-ocimene with HO and \( O_3 \) produce three common compounds: acetone, 4-vinyl-4-pentanal, and 4-methyl-3,5-hexadienal. In the case of \( \beta \)-myrcene, its reaction with HO produces acetone (with a yield of 0.36), 4-methyl-3,5-hexadienal (0.45), and 4-vinyl-4-pentenal (0.19) (R12). The reaction of \( \beta \)-myrcene with \( O_3 \) produces acetone (0.21), 4-methyl-3,5-hexadienal (0.21), and 4-vinyl-4-pentanal (0.70) (R13). The reactions of \( \beta \)-ocimene with HO only produce acetone (0.18) and 4-vinyl-4-pentanal (0.20) (R14). The reactions of \( \beta \)-ocimene with \( O_3 \) are more complex and generate acetone (0.21), 4-methyl-3,5-hexadienal (0.33), and 4-vinyl-4-pentenal (0.24) ((R15); Reissell et al., 2002).

More discussion about the volatile reaction products is provided in Section 4. The reactions listed above (R9)–(R15) are included in the numerical model described below.

The lifetimes of hydrocarbons may be decreasing over the years in response to temporal increases in ground-level \( O_3 \) since the late 1800s (Marceno et al., 1994). As a result, their lifetimes now can range from 3 to 32 min (Table 1). During the last two decades, in the United States \( O_3 \) concentrations in the rural atmosphere (away from anthropogenic influences) have increased in response to greater global precursor emissions and long-range transport (Fiore et al., 2002). Although there are no long-term trends in HO levels during the last century.
(Lelieveld et al., 2004), large inter-annual variability in ambient HO concentrations are possible due to changes in air pollution emissions and forest fires (Prinn et al., 2005). There is also evidence that the HO levels have varied during the last two decades (Prinn et al., 2001). Taken together, the overall consequence of the changes in ambient HO and O$_3$ levels has been to alter the rates of atmospheric photochemical reactions associated with the destruction of phytogenic hydrocarbons.

3. Numerical modeling

A Lagrangian model was applied to estimate the changes in ambient hydrocarbon concentrations as the hydrocarbons traveled from the hydrocarbon source to downwind locations. The atmospheric turbulence data required as input for the Lagrangian diffusion model were obtained at the Blandy Experimental Farm in Virginia (39.06°N, 78.07°W, elevation of 183 m above mean sea level) from a 10-ha successional field (Emanuel et al., 2006). The chosen site had a mixture of grass and shrub canopy that was 1.0 m tall and had a leaf area index (LAI) of 2.0. The friction velocity ($u^*$) information, which was obtained using a three-dimensional sonic anemometer (model CSAT3, Campbell Scientific Inc., Logan, UT) deployed above the plant canopy, was segregated based on the wind direction to obtain averaged quantities. The $u^*$ data were grouped in several bins, each of 5°, to estimate average $u^*$ values from all the wind directions influencing the research site during the months of June–August 2002. Additionally, the average temperature data required to estimate the rate of production of the volatile hydrocarbons were processed in a similar manner as the $u^*$ information (Fig. 1).

Monoterpene emissions do not usually depend on light and are largely controlled by temperature (Fuentes et al., 2000). Therefore, emission rates of monoterpines from flowers were estimated using a temperature-dependent relationship (Tingey, 1980),

$$E_{\text{mono}} = E_s \exp[\beta(T_1 - T_s)]. \quad (1)$$

The $E_{\text{mono}}$ represents the emission of monoterpenes, $E_s$ is the basal emission rate at a nominal temperature, $T_s = 303$ K, $\beta$ is a constant taken as 0.06, and $T_1$ is the temperature of flowers. Relationship (1) was originally derived to determine monoterpene emissions from intact leaves. Here the assumption is made that similar processes govern monoterpene emissions from flowers. The flower temperature was assumed to be the same as air temperature. In the model, the source of hydrocarbons came from snapdragon plants (Antirrhinum majus), which are known to be strong emitters of the volatiles considered in this study (Wright et al., 2005). A hypothetical 1 m$^3$ patch with 10 snapdragon plants was considered in the model, each plant with five spikes of 10 flowers, for a total of 500 florets. Reported basal emissions (Wright et al., 2005) and LAI data were used to determine the hydrocarbon emissions on a per unit ground area. The estimated maximum emission rates for $\beta$-ocimene reached 82 nmoles m$^{-2}$ min$^{-1}$ whereas the maximum emission rates for $\beta$-myrcene were 25 nmoles m$^{-2}$ min$^{-1}$ (Fig. 2). Linalool emissions followed a similar pattern as that for $\beta$-myrcene and $\beta$-ocimene (data not shown), with maximum emission rates reaching 6.5 nmoles m$^{-2}$ min$^{-1}$. The estimated diurnal emission rates were determined using relationship (1), which

![Fig. 1. Average air temperature (a) and friction velocity (b) determined as a function of wind direction experienced at the Blandy Experimental Farm, Boyce, Virginia during June–August 2002. The shaded region represents the standard deviations.](image-url)
required as input the average temperature data reported in Fig. 1.

A Lagrangian diffusion model was adopted to estimate the displacement of air parcels released from the level of hydrocarbon emissions to downwind areas. Air parcel vertical displacement (dz) was estimated based on the vertical velocity ($w$) and the travel time increment (dt) as shown in Eq. (2).

$$dz = w \, dt.$$  

Changes in the released air parcel vertical velocity (dw) were estimated with the Langevin relationship (Baldocchi, 1997) as in Eq. (3).

$$dw = a_w(z, t, w)dt + b_w(z, t, w)d\xi.$$  

Additionally, the changes in air parcel horizontal position (dx) and horizontal velocity (du) were estimated based on relationships (4a) and (4b).

$$dx = (\bar{u} + u')dt,$$  

$$du = a_u(z, t, u')dt + b_u(z, t, u')d\xi,$$

where $\bar{u}$ is the mean horizontal wind speed and $u'$ is the deviation from the mean air flow. In Eqs. (3)–(4b), the coefficients $a_w$ and $a_u$ represent nonlinear functions of the air parcels’ momentum and atmospheric turbulence statistics. Both $b_u$ and $b_w$ coefficients were multiplied by a Gaussian term ($d\xi$) to include the random nature of the air parcel motions. The $a_w$ and $a_u$ were defined in Baldocchi (1997) and the random forcing terms in relationships (3), (4a), and (4b) were estimated according to Eq. (5).

$$b_u = b_w = \sqrt{\frac{2\sigma_w^2}{T_L}}.$$  

In Eq. (5), $\sigma_w^2$ represents the standard deviation of the vertical wind speed and $T_L$ denotes the Lagrangian time scale. In this study, $T_L$ was determined based on turbulence statistics and friction velocity as described in Eq. (6) (Baldocchi, 1997; Strong et al., 2004).

$$T_L = 2\frac{(w')^2}{\epsilon}.$$  

The $w'$ represents the deviation of $w$ from average conditions (the overbar represents average conditions) and $\epsilon$ denotes the average rate of turbulent kinetic energy dissipation. The values for $\epsilon$ were determined by $w' / 0.4z$ (Strong et al., 2004), where $z$ is the altitude above ground. Atmospheric turbulence within and above the canopy were estimated with the model described by Massman and Weil (1999) and appropriately modified to the field conditions of the present study (Strong et al., 2004; Tiwary et al., 2007).

With the model described above, it was possible to estimate the vertical profiles of $T_L$, turbulence statistics (e.g., $\sigma_w^2$), wind speed within the canopy, and momentum transfer using as input atmospheric turbulence data obtained above the plant canopy. To model the turbulent statistics within the canopy, we assumed that the canopy had a uniform leaf area distribution and the spatial modeling domain had plants with a uniform leaf area distribution. The model was executed for each of the average $u_*$ values corresponding to all wind directions (Fig. 1). For each wind direction, 5000 marked air parcels were released from 1.0 m above the ground. In the model, we assumed that volatile organic hydrocarbons released by plants were from the top of the canopy. We allowed marked air parcels to move according to the nature of turbulent characteristics as described by the turbulence model. The movement of air parcels was not constrained, but marked air parcels were recorded in a vertical and horizontal domain of 10 and 1500 m, respectively. We considered this horizontal extent to include the foraging range of most pollinators, as estimates of foraging distances for strong fliers such as bumble bees range up to and beyond 1500 m (Walther-Hellwig and Frankl, 2000) and additionally assumed that most pollinator movement will be near ground level.
As air parcels moved from the volatile source site to the downwind areas we estimated the reactions of hydrocarbons with HO, O₃, and NO₃. For each compound (i.e., linoolool, β-myrcone, and β-octimene) the three reactions included in Table 2 were considered as the only destruction mechanism. Therefore, the overall rate of each hydrocarbon (\(z\)) chemical destruction is determined by

\[
\frac{dz}{dt} = -k_1[\text{[HO]}] - k_2[\text{[O₃]}] - k_3[\text{[NO₃]}].
\] (7)

The quantities in brackets, \([z]\), represent the hydrocarbon concentrations and \(k_j\) for the \(j\)th reaction (see Table 2). Assuming relatively short time steps (e.g., 10% of the Lagrangian time scale), the temporal variations in HO, O₃, and NO₃ concentrations can be assumed relatively invariant and then relationship (7) can be treated as a system of first-order simultaneous reactions. The overall result is described by Eq. (8).

\[
[z]_t = [z]_0 \exp(\frac{-k_1[\text{[HO]}]t}{t}) \exp(\frac{-k_2[\text{[O₃]}]t}{t}) \exp(\frac{-k_3[\text{[NO₃]}]t}{t}).
\] (8)

The \([z]_0\) indicates the hydrocarbon concentration at the initial time, \(t_0\). The subscript \(t\) was the time required for air parcels to travel each assigned incremental distance (\(dz\)). We estimated the reaction rates described in Eqs. (7) and (8) for each incremental distance traveled by air parcels. This permitted the determination of the hydrocarbon concentration in a given air parcel at each estimated location as the parcel moved across the landscape. Thus, the hydrocarbon concentration of a particular air parcel was estimated as the hydrocarbon reacted with pollutants at different distances from the source. We obtained hydrocarbon concentration and distance traveled by air parcels for each direction class (Fig. 1).

We considered four different scenarios to determine the change in hydrocarbon concentration as a function of air parcel traveled distance away from volatile sources (Table 3). The first scenario included the levels of 0.02 part per trillion on a volume basis (pptv) \(\left(= 5.0 \times 10^3 \text{ radicals cm}^{-3}\right)\), 20 ppbv, and 0 pptv for HO, O₃, and NO₃, respectively. This scenario may be viewed as the air pollutant levels prevailing during the 1800s. The second scenario involved the levels of 0.2 pptv \(\left(= 5.0 \times 10^6 \text{ radicals cm}^{-3}\right)\), 40 ppbv, and 1 pptv for HO, O₃, and NO₃, respectively. The third scenario required the levels of 0.41 pptv \(\left(= 1.0 \times 10^7 \text{ radicals cm}^{-3}\right)\), 80 ppbv, and 2 pptv for HO, O₃, and NO₃, respectively. The fourth scenario necessitated the levels of 0.81 pptv \(\left(= 2.0 \times 10^7 \text{ radicals cm}^{-3}\right)\), 120 ppbv, and 5 pptv for HO, O₃, and NO₃, respectively. We chose these HO, O₃, and NO₃ levels to reflect the broad ranges in these compounds from pre-industrial times (Marceno et al., 1994; Prinn et al., 2001) to current summertime conditions in eastern United States where maximum O₃ levels can sometimes exceed 120 ppbv (Fiore et al., 2002). For simplicity and convenience, the ambient mixing ratios for HO, O₃, and NO₃ remained constant in time and space throughout the course of model simulations. Additionally, all simulated scenarios applied to daytime conditions.

### 4. Results and discussion

Ambient volatile hydrocarbon abundances depend upon rates of emissions from sources, the atmospheric turbulence intensity, and reaction rates. We included these processes in the numerical model to determine the chemical degradation of hydrocarbons as they moved away from scent...
sources. We estimated the scent trails from sources by running the Lagrangian dispersion model for all wind directions, and plotted the fraction (expressed in percentage) of hydrocarbon compounds remaining after chemical degradation of the amounts emitted by flowers as a function of distance away from scent sources (Figs. 3–5). In effect, the resulting contour plots of dispersion for the floral scents provided information on the effective source ‘footprint’ of a particular floral patch. The three compounds in consideration exhibited similar chemical degradation patterns in response to the four pollution scenarios considered in this study (Table 3). We ascribed this result to the somewhat similar reaction rates of linalool, β-ocimene, and β-myrcene with O₃, HO, and NO₃ (Table 2). For unpolluted (pre-industrial) conditions (scenario I, Figs. 3a–5a), chemical reactions had negligible effects in destroying the hydrocarbon compounds. At distances >1000 m downwind from hydrocarbon sources, approximately 20% of volatiles were destroyed by chemical reactions. In addition, hydrocarbon abundance gradients between source sites and 1000 m downwind from floral scents amounted to 15–20% loss (Fig. 3). The effect of pollution in the destruction of volatiles was amplified by even slight increases in ambient O₃ and HO levels. For example, for conditions ordinarily observed in the current rural atmosphere (scenario II, Table 3) >40% of the originally emitted linalool, β-ocimene, and β-myrcene was destroyed at distances >500 m from floral sources. The results were even more pronounced when polluted conditions were considered. For highly polluted conditions (scenario IV, Table 3), only approximately 25% of the original biogenic hydrocarbons remained within a radius of 200–300 m downwind from floral sources (Figs. 3d–5d). Based on these results, it is concluded that increasing levels of pollution may impair the detection of floral scents by pollinators and lead to decreased pollination rates by insects.

To determine the levels of volatiles as they traveled across the landscape, we plotted the

![Contour plots of the fraction of linalool remaining as a function of downwind distance traveled from the source after reacting with hydroxyl radicals, ozone, and nitrate radicals for four scenarios considered in this study. Contour plots represent scenario I (a), scenario II (b), scenario III (c), and scenario IV (d) (see Table 3 for details).](image-url)
Fig. 4. The same as in Fig. 3 but for β-ocimene.

Fig. 5. The same as in Fig. 3 but for β-myrcene.
fraction of hydrocarbon compounds remaining after chemical degradation along transects representing the most pronounced volatile gradients away from sources (Fig. 6). The decreases in volatile abundances away from sources followed exponential declines, with steeper decreases in the remaining fraction of hydrocarbons with increasing levels of pollution. In unpolluted air masses, volatiles showed nearly linear decreases and remained above 80% of their original levels after diffusing and reacting with O₃, HO, and NO₃ within a radius of 1000 m away from volatile sources. In the most polluted air masses, compounds such as β-ocimene decreased exponentially and only 25% of the original concentration remained within a radius of 250 m from sources (Fig. 6). In all scenarios examined, the results demonstrated that concentrations of the studied volatile compounds decrease in response to increasing levels of air pollutants.

These results highlight a potentially detrimental consequence of air pollution that has heretofore received little attention. Pollinators assess reward availability based on both sight and smell (Galen and Kevan, 1980; Goulson, 2003). For most bees, smell has been shown to be most important within a meter of a flower, while sight is more important on the scale of several meters (Dobson, 1994). Bees, however, have poor visual acuity (Chittka and Raine, 2006). Therefore, scents may provide important signals when bees are flying between patches of flowers, outside the range that the flowers could be visually detected. Data on the distances at which bees can detect floral scents are sparse, though it has been noted that male euglossine bees have been attracted from at least 1 km to volatile bait stations (Dobson, 1994). Many pollinators, such as moths and orchid bees, rely heavily on scents to orient to floral rewards (Dobson, 1994). In polluted air masses, these pollinators are likely to spend more time searching for forage, which could lead to a decrease in their reproductive fitness. If bees are using scent trails as a long distance cue, their fitness will be directly affected as they use pollen collected from flowers to provision their young.

Diminished scent trails are also likely to lead to decreased pollinator efficiency, which could cascade down to affect plant fitness. Flowering plant reproduction is usually pollinator mediated, and reduced pollinator efficiency could result in greater pollinator limitation. In highly polluted environments, one expected outcome of the loss of scent trails would be the eventual shift to a community dominated by self-compatible or wind-pollinated plants.

The scents analyzed here do not occur alone, as the scent trails flowers emit to attract pollinators are mixtures of hydrocarbon compounds. One aspect of scent discrimination by honey bees may be the ratio in which these hydrocarbons occur in the atmosphere, especially at high floral scent emissions.

Fig. 6. Fraction of linalool (a), β-ocimene (b), and β-myrcene (c) remaining as a function of downwind distance traveled from the source after reacting with hydroxyl radicals, ozone, and nitrate radicals for the four scenarios considered in the modeling study.
Air pollutants likely alter the signature bouquet of floral fragrances because different hydrocarbons are destroyed at different rates by air pollutants. Additionally, O$_3$ and HO$_2$ levels fluctuate throughout the day, peaking during 15:00 to 17:00 local hours (Fuentes et al., 2006). These fluctuating pollutant levels indicate that the ratio of compounds in a floral scent trail will change throughout the course of the day. This daily variation in scent may add a layer of complexity to the negative effects of pollutants on floral hydrocarbons as scents likely play a crucial role in pollinator floral constancy (the level of fidelity of a pollinating insect to one plant species) (Chittka et al., 1999). If diurnal variations in pollution levels change floral scent profiles it may be more difficult for a pollinator to follow the scent trails of one species of flower throughout the day.

Finally, the results presented here apply to the parent volatiles. The products of hydrocarbon-pollutant reactions (R9)--(R15) have a high degree of volatility and are themselves odorous compounds. This raises two different possibilities. In air masses that are filled with a multitude of hydrocarbon scent trails, it is likely that the unique hydrocarbon signal of one species of emitter will be lost. This is because different parent volatiles converge on similar reaction products. For example, reactions of $\beta$-myrcene and $\beta$-ocimene with pollutants produce 4-vinyl-4-pentanal and 4-methyl-3,5-hexadienal as reaction products (R12)--(R15). Hence, specialist pollinators in polluted environments will no longer be able to hone in on the unique floral signal of their host plant, as what was a unique signal in the 1800s has become a general signal. On the other hand, individual volatile signals will become more complex during episodes of high pollution. This is because the parent compounds break up into several reaction products (R9)--(R15). Pollinators will have to be able to discern several reaction products for every parent volatile. An interesting line of research would be to determine if there are differences in the olfactory receptor neurons of pollinating insects in polluted versus unpolluted environments, indicating pollution mediated chemical receptor evolution.

5. Conclusion and significance of results

The results presented here indicate that the documented increases in air pollution concentrations, from pre-industrial to present times, can lead to substantial reductions in the concentrations of volatile compounds insects use to detect flowering plants. For highly reactive volatiles the persistence of the scent trail may have changed from kilometers during pre-industrial times to $<200$ m during the more polluted conditions of present times. The lower concentrations of volatiles in scent trails and shorter distances that volatiles diffuse across landscapes indicate that pollinators need to travel longer distances before detecting a scent trail that they can follow to the source of emissions.

The implications of this result may be exacerbated in patchy or fragmented landscapes, where scent trails are likely to be important in leading pollinators between isolated flower patches. Pollinators in polluted air masses may be spending more time searching for patches of flowers. This elongation of foraging times may lead to decreased pollinator fitness. The decrease in pollinator foraging efficiency may simultaneously lower obligate outcrossing plant fitness. Finally, the daily fluctuations in pollutant levels may lead to fluctuating floral scents, leading to decreased floral constancy by pollinators. Though not explored here, increased air pollution likely affects other airborne scent trails, such as pheromone trails emitted by animals for defense or mate attraction and plant volatiles other than floral hydrocarbons such as those that are emitted to attract natural enemies of plant pests.

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