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What makes a volatile organic compound a reliable indicator of insect herbivory?

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Abstract

Plants that are subject to insect herbivory emit a blend of so-called herbivore-induced plant volatiles (HIPVs), of which only a few serve as cues for the carnivorous enemies to locate their host. We lack understanding which HIPVs are reliable indicators of insect herbivory. Here, we take a modelling approach to elucidate which physicochemical and physiological properties contribute to the information value of a HIPV. A leaf-level HIPV synthesis and emission model is developed and parameterized to poplar. Next, HIPV concentrations within the canopy are inferred as a function of dispersion, transport and chemical degradation of the compounds. We show that the ability of HIPVs to reveal herbivory varies from almost perfect to no better than chance and interacts with canopy conditions. Model predictions matched well with leaf-emission measurements and field and laboratory assays. The chemical class a compound belongs to predicted the signalling ability of a compound only to a minor extent, whereas compound characteristics such as its reaction rate with atmospheric oxidants, biosynthesis rate upon herbivory and volatility were much more important predictors. This study shows the power of merging fields of plant–insect interactions and atmospheric chemistry research to increase our understanding of the ecological significance of HIPVs.

KEYWORDS

biogenic volatile organic compound (BVOC), emission, herbivore induced plant volatile (HIPV), hydroxyl radical, nitrate radical, oxidation, ozone, *Populus nigra*

1 | INTRODUCTION

Plants emit a large number of volatile organic compounds (VOCs; Mumm & Dicke, 2010; Dudareva, Klempien, Muhlemann, & Kaplan, 2013) both in stressed and non-stressed conditions. Herbivore-induced plant volatiles (HIPVs) are stress-induced VOCs de novo synthesized and/or released in higher amounts, when a plant is subjected to herbivory (Dicke, van Loon, & Soler, 2009). HIPVs are used as cues by herbivores, natural enemies of herbivores, neighbouring plants and other members of the community providing information on the infested plant (Dicke & Baldwin, 2010). For example, natural enemies of herbivores are attracted by the volatile blends emitted by herbivore-infested plants to localize their hosts (Turlings & Wäckers, 2004). Similarly, neighbouring plants prime their antiherbivore defenses in response to HIPVs (Frost et al., 2007).

The blend emitted upon herbivory typically contains tens to hundreds of compounds (Mumm & Dicke, 2010). Some compounds occur frequently irrespective of the taxon (Clavijo McCormick, Unsicker, &

Gershenzon, 2012), whereas other compounds are specific to the emitting plant genotype, cultivar or species as well as the insect species feeding on the plant (De Moraes, Lewis, Paré, Alborn, & Tumlinson, 1998; Dicke & Baldwin, 2010). In contrast to the large number of HIPVs emitted upon herbivory, the number necessary to induce a response in insects is rather small, with up to six compounds being sufficient to induce a response comparable with the full blend (De Boer, Posthumus, & Dicke, 2004; Natale, Mattiacci, Hern, Pasqualini, & Dorn, 2003; Riffell, Lei, & Hildebrand, 2009).

There is a limited number of studies identifying which HIPVs or blend of HIPVs elicit responses in receivers of the blends. Some studies show that single compounds can induce a response in insects (Becker et al., 2015; Bruce, Wadhams, & Woodcock, 2005; Clavijo McCormick, Boeckler, Köllner, Gershenzon, & Unsicker, 2014; Dicke et al., 1990) and plants (Engelberth, Alborn, Schmelz, & Tumlinson, 2004). Others have shown that combinations of compounds are needed to elicit or enhance a response (De Boer et al., 2004; Fontana et al., 2011; Hu, Ye, & Erb, 2019). Sometimes the mixtures had to be offered in specific ratios (Beyaert et al., 2010; Natale et al., 2003) or contain constitutively emitted volatiles to induce a response (Fontana et al., 2011; Mumm, Tiemann, Varama, & Hilker, 2005).

Which compounds or blends are used as cues seems context-specific, and a general pattern, either across taxa or across chemical classes, seems lacking. This makes it hard to move the field forward and design applications for agriculture (Shrivastava, Rogers, Wszelaki, Panthee, & Chen, 2010). Moreover, the number of compounds and mixtures to evaluate is potentially very large and requires a large amount of resources. Yet, the number of candidate compounds to be evaluated could be narrowed down if chemical, physical and physiological characteristics affect the reliability of a compound as indicator of herbivory.

To localize an herbivore by HIPVs, the cue needs to be reliable in time and space. Compounds whose emission rate quickly increases upon herbivory and quickly ceases after herbivory are expected to be better signalling compounds compared with compounds that are not closely connected to the herbivory event (Puente, Kennedy, & Gould, 2008). Compounds vary substantially in their emission rate upon herbivory with emission rates increasing within 1 up to 12 h after the onset of herbivory (Clavijo McCormick, Boeckler, et al., 2014; Turlings, Lengwiler, Bernasconi, & Wechsler, 1998) with green leaf volatiles usually being the first to be emitted followed by monoterpenes and sesquiterpenes (Allmann & Baldwin, 2010; Turlings et al., 1998). In addition, one would expect that compounds that are emitted in rather constant amounts overday are preferred over compounds that fluctuate strongly, although this may depend on the receiving species. Some compounds are emitted in high quantities during the night, whereas for others, nocturnal emission is close to zero (Clavijo McCormick, Boeckler, et al., 2014). The volatility of the VOC also affects the emission flux as the volatility affects to what extent the stomata exert control over the emission flux (Dudareva, Pichersky, & Gershenzon, 2004; Niinemets, Reichstein, Staudt, Seufert, & Tenhunen, 2002). Another important and widely ignored factor controlling the spatial concentration gradient of a compound is its

atmospheric lifetime. For example, compounds with a long lifetime can be dispersed over large distances in the canopy resulting in shallow concentration gradients around the infested plant (McFrederick, Kathilankal, & Fuentes, 2008). The lifetime of compounds is determined by the reactivity of a compound with oxidants such as ozone (O_3), nitrate radical ($\cdot NO_3$) and hydroxyl radical ($\cdot OH$) and varies orders of magnitude across compounds. This potentially makes one compound a better indicator of insect herbivory than others (Holopainen & Blande, 2013), although this depends on the concentrations of the oxidants as well. For example, plant–plant interactions mediated by HIPVs were impaired when O_3 concentrations increased (Blande, Holopainen, & Li, 2010). This also implies that the assessment of HIPVs in plant–insect interactions requires consideration of the role of compound dispersion inside and above canopies as well as the role of chemical degradation of these HIPVs.

In this study, we take a modelling approach to elucidate to which extent the physiological and chemical properties of an HIPV affect its ability to infer insect herbivore presence based on its concentrations in a forest canopy (Fig. 1). This ability is defined as the degree to which the presence/absence of an insect herbivore can be inferred from the volatile concentration in the canopy relative to chance. Importantly, we only consider the reliability of the cue from the perspective of the sender, but not from the receiver, as we do not consider how physicochemical characteristics affect the ability of receivers to perceive the cues. Calculating the ability of a compound to indicate insect herbivory consisted of three steps: (1) development and parameterization of a leaf-level synthesis and emission model; (2) application of the leaf-level emission flux to infer the HIPV concentrations within and outside the canopy as a function of dispersion, transport and chemical degradation of this compound. The HIPV concentration in the canopy over time and space was modelled through developing a 3-D (height, horizontal and time) multilayer canopy model; (3) statistical analysis of model-simulated canopy HIPV concentrations and presence/absence of insect herbivores.

2 | MATERIALS AND METHODS

2.1 | Model description

2.1.1 | Leaf level synthesis of herbivore induced plant volatiles

A phenomenological model was developed with the main aim to accurately describe the variability in emission dynamics that is observed among different HIPVs (Clavijo McCormick, Boeckler, et al., 2014; Fig. 1). The Guenther leaf model for volatile emission was used as starting point (Guenther, Monson, & Fall, 1991; Guenther, Zimmerman, Harley, Monson, & Fall, 1993). The Guenther model simulates the emission of a compound (E) as the product of the baseline emission E_b multiplied with a number of scaling functions ($\gamma_\bullet$). The scaling functions reflect the scaling of the baseline emission to environmental conditions of which radiation (γ_L) and temperature (γ_T) are

the most important ($E = E_b \gamma_T \gamma_L...\gamma_n$; (Grote, Monson, & Niinemets, 2013). By using established models, we adapted and extended the model in three ways to simulate the synthesis and emission of HIPVs. See Table 1 for the list of parameters and their description.
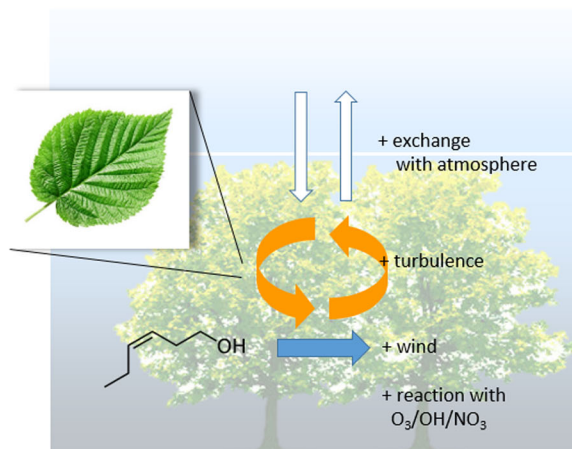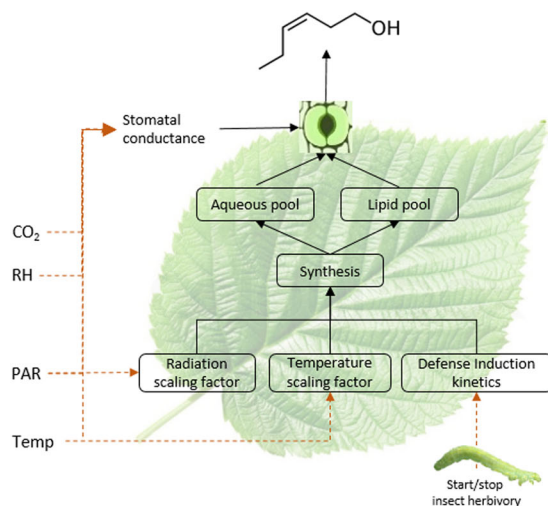
Firstly, the synthesis of HIPVs is increasing after herbivory starts and decreasing after termination of herbivory. We assumed a synthesis rate of a compound when the plant is in noninduced state (p_c ; mol/m^2 leaf s) and an increase in this synthesis rate when the plant is induced by insect herbivory (p_i mol/m^2 leaf s). The maximum synthesis rate of a HIPV is $p_c + p_i$ when all conditions are favourable. p_i is modified by a scaling function γ_H (-) that reflects the activity of the HIPV biosynthesis pathway. γ_H is calculated by an ordinary differential equation and has the standard logistic function as solution.

When herbivory starts (t_{hs}), the HIPV biosynthesis pathway increases in a sigmoidal way (Equation 1) with rate r_u (s^{-1}) followed by a decrease with rate r_d (s^{-1}) when herbivory ends (t_{he}; Equation 2). r_u and r_d together account for the time lag that has been observed between the onset and stop of herbivory and the synthesis of the compound (Dicke, 2009). Equations 1 and 2 lead to behaviour that is comparable with that described by the dynamic model for gene expression developed by Vu and Vohradsky (2007) except that we assume a sigmoidal decrease in biosynthesis pathway activity also because this results in a slightly better model fit. We assume a minimum value for γ_H of 0.0001.

If $t < t_{he}$ & $t > t_{hs}$

$$\frac{d\gamma_H}{dt} = r_u \gamma_H (1 - \gamma_H) \quad (1)$$

$$\frac{d\gamma_H}{dt} = -r_d \gamma_H (1 - \gamma_H) \quad (2)$$

Secondly, to account for the fact that nighttime emission of HIPVs can be substantial (Arimura et al., 2008; Arimura, Huber, & Bohlmann, 2004; Clavijo McCormick, Boeckler, et al., 2014; De Moraes, Mescher, & Tumlinson, 2001) the scaling function for radiation (γ_L; Guenther et al., 1993; Equation 3) was modified by a factor d_P, that describes the dependency of the synthesis of a compound driven by radiation versus stored substrates (Equation 4, see e.g. Pokhilko, Bou-Torrent, Pulido, Rodriguez-Concepcion, & Ebenhoh, 2015). PAR represent photosynthetic active radiation (µmol/m^{2}s) and c_{l1} and α are empirical constants.

$$\gamma_L = \frac{\alpha \, c_{l1} PAR}{\sqrt{1 + \alpha^2 PAR^2}} \quad (3)$$

$$\gamma_P = d_P + (1 - d_P) \, \gamma_L \quad (4)$$

Thirdly, an alternative explanation for substantial nighttime emissions of some compounds is a substantial time lag between the synthesis and emission of a compound (Niinemets et al., 2010). Niinemets and Reichstein (2002) postulated that after synthesis, compounds can be stored in two nonspecific storage pools, an aqueous and a lipid pool, respectively. The volatiles stored in the lipid pool (S_L, mol/m^2 leaf area) are released at a lower rate than volatiles stored in the aqueous pool (S_A, mol/m^2 leaf area). Assuming these two pools led to a more accurate description of volatile emission than assuming a single nonspecific storage pool, although to our knowledge, direct experimental evidence is lacking (Noe, Ciccioli, Brancaleoni, Loreto, & Niinemets, 2006).

The partitioning between the slow and fast pool and their associated rate constants (k_A, k_L) will cause variation in emission dynamics, partly explaining high nighttime emissions. The partitioning coefficient η describes which proportion of the VOCs is stored in the aqueous pool versus the lipid pool.

FIGURE 1 A conceptual diagram of the model. The HIPV concentration in the canopy over time was simulated through modelling the synthesis and emission at leaf level with radiation, temperature, insect herbivory and stomatal conductance as input (left panel). The synthesis of a compound is determined by its dependency on radiation (PAR), relative humidity (RH), temperature and the defense induction kinetics. Following Niinemets and Reichstein (2002), synthesized compounds can be stored in an aqueous and lipid pool and are released through the stomata into the canopy. Leaf-level emission flux is applied to infer the in- and above-canopy concentrations of the HIPVs as a function of dispersion, transport and chemical destruction of this compound (right panel). Finally, presence/absence of insect herbivory is predicted based on the modelled canopy concentrations

TABLE 1 Overview of the parameters and variables used in the model and their values and sources

Parameter	Description	Units	Value	Source
Photosynthesis				
V_{cmax}	Maximum rate of carboxylation at 25 C	µmol/m^{2}s	58	Casella & Ceulemans, 2002
J_{max}	Maximum rate of electron transport	µmol/m^{2}s	118	Casella & Ceulemans, 2002
R_d	Dark respiration	µmol/m^{2}s	1.8	Casella & Ceulemans, 2002
g_m	Mesophyll conductance	mol/m^{2}s	0.309	Broeckx, Fichot, Verlinden, & Ceulemans, 2014
Temperature scaling factor				
c_{T1}	Empirical constants	kJ/mol	95	Guenther et al., 1999
c_{T2}	Empirical constants	kJ/mol	230	Guenther et al., 1999
R	Gas constant	kJ/K mol	0.00831	Guenther et al., 1999
T_{opt}	Temperature at which E_{opt} occurs	K	321.5	Guenther et al., 1999
E_{opt}	Maximum normalized emission capacity		1	Guenther et al., 1999
Radiation scaling factor				
c_{l1}	Empirical constant	[–]	1.066	Guenther et al., 1993
α	Empirical constant	[m^{2}s/µmol]	0.0027	Guenther et al., 1993
Emission rate				
A/V	Leaf area to volume ratio	m^{-1}	3905	Niinemets & Reichstein, 2003
f_w	liquid volume fraction in the leaf	m^3/m^3	0.49	Niinemets & Reichstein, 2003
f_{lip}	Volumetric lipid fraction	m^3/m^3	0.029	Niinemets & Reichstein, 2003
P	Air pressure	Pa	101325	Niinemets & Reichstein, 2003
g_s	Stomatal conductance with respect to a typical VOC	m/s		Calculated from photosynthesis model and Equation 7 in Appendix S1
Compound specific values				
p_c	Maximum synthesis rate of non-induced plants	mol/m^2 leaf s		See Supporting Information Table S2
p_i	Maximum synthesis rate of induced plants	mol/m^2 leaf s		See Supporting Information Table S2
r_u	Increase in synthesis upon after herbivory	s^{-1}		See Supporting Information Table S2
r_d	Decrease in synthesis rate when herbivory stops	s^{-1}		See Supporting Information Table S2
d_P	Dependency of synthesis on photosynthesis	-		See Supporting Information Table S2
η	Partition coefficient aqueous vs. lipid pool	-		See Supporting Information Table S2
H	Henry's law constant	Pa m^3/mol		See Supporting Information Table S1.1
$K_{o/w}$	Octanol/water partition coefficient	-		See Supporting Information Table S1.1
k_{O3}	Rate constant for ozone	cm^3/molecule s		See Supporting Information Table S1.1
k_{OH}	Rate constant for the hydroxyl radical	cm^3/molecule s		See Supporting Information Table S1.1
k_{NO3}	Rate constant for nitrate radical	cm^3/molecule s		See Supporting Information Table S1.1
Canopy characteristics				
PAR	Photosynthetic active radiation	µmol/m^2/s		Calculated by MLC-CHEM[a]
RH	Relative humidity	%		Calculated by MLC-CHEM
Ca	CO$_2$ partial pressure	µbar		Calculated by MLC-CHEM
T_{air}	Air temperature	K		Calculated by MLC-CHEM
K_H	Eddy diffusivity for heat	m^2/s		Calculated by MLC-CHEM
u	Wind speed	m/s		Calculated by MLC-CHEM
O$_3$	Ozone concentration	molecules/m^3		Calculated by MLC-CHEM
NO$_3$	Nitrate concentration	molecules/m^3		Calculated by MLC-CHEM
OH	Hydroxyl concentration	molecules/m^3		Calculated by MLC-CHEM
Other				
t_{hs}, t_{he}	Onset and end of herbivory	days	7, 14	

Note: Parameters indicated in bold are varied in the model.

[a]These variables are output from a multi-layer canopy chemistry model (MLC-CHEM), see main text for details.

The above modifications lead to the following description of the aqueous and lipid pool dynamics (Equations 5 and 6):

$$\frac{dS_A}{dt} = \eta \, \gamma_P \gamma_T (p_c + p_i \gamma_H) - k_A S_A \tag{5}$$

$$\frac{dS_L}{dt} = (1 - \eta) \, \gamma_P \gamma_T (p_c + p_i \gamma_H) - k_L S_L, \tag{6}$$

with γ_T representing the scaling function for temperature (Guenther et al., 1999; Equation 7), c_{T1}, c_{T2} representing empirical scaling constants (kJ/mol), T_{leaf} leaf temperature (K), T_{opt} the temperature (K) at which E_{opt} is reached and R being the gas constant (kJ/mol K).

$$\gamma_T = \frac{E_{opt} c_{T2} e^{(c_{T1} x)}}{c_{T2} - c_{T1} (1 - e^{c_{T2} \, x})} \text{ with } x = \frac{\left(\frac{1}{T_{opt}} - \frac{1}{T_{leaf}} \right)}{R} \tag{7}$$

2.1.2 | Leaf-level emission of volatile organic compounds

It has been suggested that the majority of the VOCs are released into the atmosphere through the stomata (Niinemets & Reichstein, 2003). Volatiles stored in the lipid and the aqueous pool can diffuse to the substomatal cavities from which they are released through the stomata into the atmosphere. We adopted the simplified dynamic emission model as presented by Noe et al. (2006) and assumed further that the emission from the lipid and aqueous pool occur independent of each other and that the amount of HIPVs that are released from the wound sites is negligible compared with the amount of HIPVs that are produced systemically. The emission flux, E, (mol m^{-2}s^{-1}) is modelled as the sum of $k_A S_A$ and $k_L S_L$ (Equation 8):

$$E = k_A S_A + k_L S_L, \tag{8}$$

with k_A being a function of the conductance from the aqueous phase to substomatal cavities (m/s), the gas-phase diffusion conductance (mol m^{-2}s^{-1}) and a compound-specific parameter describing the gas/water partitioning constant (i.e. the Henry's law constant, H, Pa m^3/mol) and k_L being a function of the conductance from the lipid phase to substomatal cavities, the gas-phase diffusion conductance, and a compound-specific parameter describing the octanol-to-water partition coefficient ($K_{o/w}$–) and Henry's law constant. The gas-phase diffusion conductance is the inverse of the resistances of stomatal conductance (g_s; m/s) and the gas-phase conductance from the outer surface of cell walls to substomatal cavities. A detailed description of k_A, k_L and g_s is presented in Appendix S1 in the Supporting Information. Henry's law constant is the dominant factor in determining to what extent the stomata exert control over the emission of that compound. In addition, volatiles with a relatively large octanol/water partition coefficient result in a smaller conductance from the lipid phase, which leads to a lower emission rate from the lipid pool.

2.2 | Dispersion, transport and chemical destruction of HIPVs in the canopy

To calculate the concentration of HIPVs (C) in the canopy, we discretize the canopy into a number of layers in which radiation (PAR; μmol/m^{2}s), turbulence (K_H, m^2/s), wind speed (u, m/s) and concentrations of CO_2, O_3, ·NO_3 and ·OH (mol/m^3) change with canopy height. In this first assessment of HIPV production and exchange, we assumed for simplicity that temperature and relative humidity are constant across the canopy profile. Furthermore, we assumed that the leaf-level emission can be scaled up to a layer emission flux multiplying the leaf-level emission with the leaf area index (LAI) of that particular canopy layer (Equation 9). Volatiles that are released in the canopy get vertically dispersed by turbulence (K_H) ultimately being ventilated into the overlaying atmospheric boundary layer. In addition, there is also horizontal dispersion to neighbouring trees as a function of the wind speed (u). In addition, HIPVs are degraded through oxidation by ozone (O_3), the hydroxyl radical (·OH) and nitrate (·NO_3; Holopainen & Blande, 2013). The efficiency of oxidation of a HIPV depends on the concentrations of O_3, ·OH and ·NO_3 (mol/m^3) and the respective oxidation rate constants k_{O3}, k_{OH} and k_{NO_3} (cm^3/molecule s; Atkinson & Arey, 2003). Note that in this study, we assume that simulated HIPV concentrations do not affect the oxidant concentrations.

$$\frac{\partial C}{\partial t} = \text{LAI } E - u \left(\frac{\partial C}{\partial x} \right)$$
$$+ K_H \left(\frac{\partial^2 C}{\partial z^2} \right) - k_{O3} C \, [O_3] - k_{OH} C [OH] - k_{NO_3} C [NO_3] \tag{9}$$

2.3 | Statistical model to infer herbivore presence/absence from the volatile concentration in the canopy

To infer the presence/absence of insect herbivore feeding based on the concentration of the HIPVs (molecules/m^3) in the canopy, a generalized linear model with binomial error distribution (for presence/absence of herbivores) was used. The model predicts a probability that the herbivore is present based on the volatile concentration. Herbivore feeding started at t_{hs} and stopped at t_{he}. The model ran for 20 days with a 0.5 hourly output. One-half of this dataset was used to fit a relationship between the HIPV concentration and the presence/absence of herbivores, whereas the other half was used to predict the presence/absence of insect herbivores based on the volatile concentration. The proportion of correctly predicted instances was corrected for chance, using a κ coefficient (Douma, Cornwell, & Bodegom, 2017). Compounds with a κ = 0 do not perform better than chance, and compounds with κ = 1 are perfectly able to predict when the herbivore is present or absent.

2.4 | Parameterization

A detailed dataset on *Populus nigra* (black poplar) plants infested with gypsy moth (*Lymantria dispar*) caterpillars was available with diurnal emission measurements of 31 HIPVs for induced and noninduced plants during 96 h (see Clavijo McCormick, Boeckler, et al., 2014 for details). The model was parameterized to optimally reproduce these measurements on this tree species (Appendix S1 for details on parameterization). To allow for variation in emission dynamics among HIPVs, six parameters, $p_c, p_i\, r_u,\, r_d, d_P$ and η, were estimated for each compound specifically. Other parameters were assumed to be constant across HIPVs. The observed emission flux was calculated from an average of 8–10 plants.

Datasets providing simultaneous information on O_3, $\cdot NO_3$ and $\cdot OH$ concentrations in the canopy as well as radiation, CO_2 concentration, wind speed and turbulence are lacking. For this reason, we used the extensively evaluated Multi-Layer Canopy CHEmistry Model (MLC-CHEM; Ganzeveld, Lelieveld, Dentener, Krol, & Roelofs, 2002, Yáñez-Serrano et al., 2018) to obtain realistic values for O_3, $\cdot NO_3$ and $\cdot OH$ concentrations inside and above the vegetation canopy. MLC-CHEM considers the processes that affect the diurnal cycle and vertical gradients in O_3, $\cdot NO_3$ and $\cdot OH$ concentrations, such as biogenic emissions, dry deposition, in-canopy photolysis and chemical transformations and turbulent transport inside and above the canopy in the atmospheric mixed layer. MCL-CHEM is set-up using six equidistant canopy layers and an atmospheric mixed layer of variable size (mixed layer depth). The latter is essential to consider the large contrasts between the nocturnal shallow (~100 m) and daytime deep (~1500 m) mixed layer. The model was run being constrained with micrometeorological parameters and atmospheric surface layer O_3 concentrations being measured above a broadleaved forest site in the United States (e.g. Seok, Helmig, Ganzeveld, Williams, & Vogel, 2013) for 20 consecutive days in summer 2016 (https://www2.acom.ucar.edu/news/prophet-amos-field-campaign). The canopy structure is defined by a canopy height of 22 m, an assumed surface roughness for momentum of 1 m, an LAI of 4.15 (m^2/m^2) and assuming a leaf area density distribution with most of the leaf biomass (~80%) being concentrated in the top three canopy layers. The output variables of MLC-CHEM were used in a 2-D reaction-diffusion model with seven vertical layers and 30 boxes in the x-direction. We assumed that each box has a size of 1 m in the x-direction and that a single tree is 3 m wide and 22 m tall, with in total 10 trees in the x-direction.

The compound-specific parameters, Henry's law constant (*H*), the octanol/water partitioning coefficient ($K_{o/w}$), and the rate constants, k_{O3}, k_{OH}, k_{NO_3} of the HIPVs measured in (Clavijo McCormick, Boeckler, et al., 2014) were obtained from the literature (see Supporting Information Table S1.1), and if not available, they were estimated based on structure–activity relationships or expert judgement (Pfrang, King, Canosa-Mas, & Wayne, 2006, AOPWIN part of EPIsuite U.S. Environmental Protection Agency, 2010). In every simulation run, a single HIPV is modelled and we assume that this HIPV gets oxidized as a function of the prescribed concentrations of O_3, $\cdot NO_3$ and $\cdot OH$ but also assuming that the HIPV does not affect those oxidant concentrations in turn.
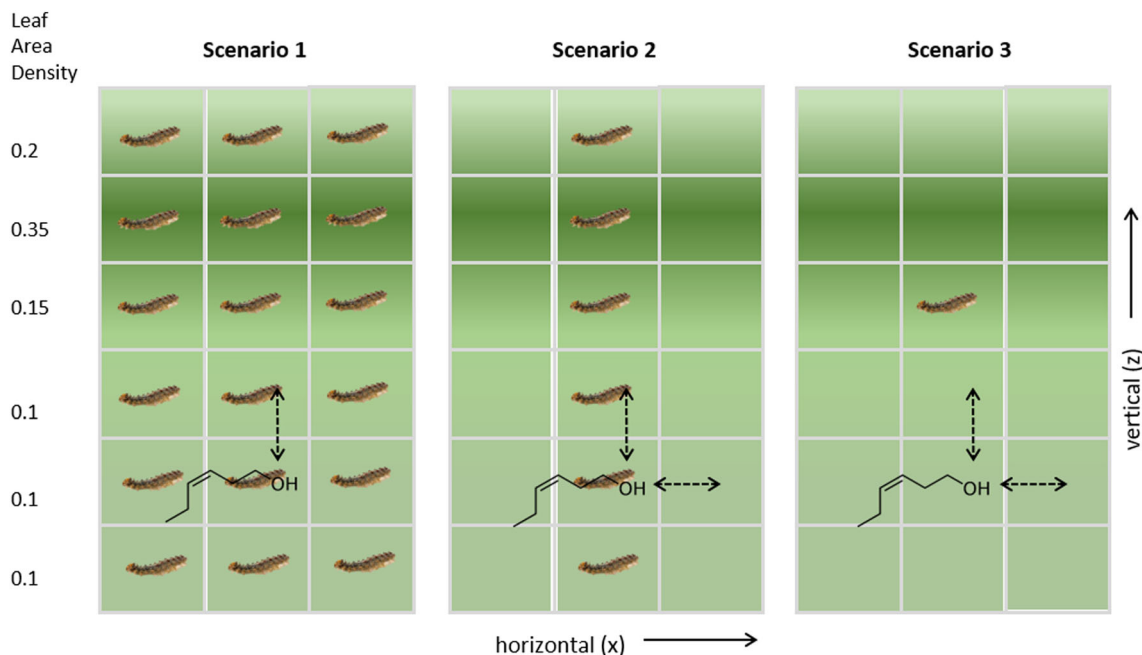
2.5 | Scenarios

We explored four scenarios to analyse how the ability of HIPVs to indicate herbivory is affected by their characteristics. In the first three scenarios, we explored the ability of 31 HIPVs emitted by poplar to indicate insect herbivory for three different scenarios: (1) with insect feeding in all trees but without considering HIPV horizontal transport (Fig. 2). This scenario gives insight in the ability of the HIPV to be an indicator of herbivory when all trees are equally infested (outbreak). In addition, we analysed if the ability of HIPVs to indicate herbivory increases when a pair of two HIPVs is used (465 combinations in total); (2) with horizontal transport of the HIPV and insect feeding in one tree in all canopy layers. This scenario gives insight in the ability of the HIPV to indicate insect herbivory when only one tree is infested and surrounded by non-infested trees; and (3) with horizontal transport of the HIPV and insect feeding in only the fourth canopy layer of one tree. This scenario was used to further explore the spatial concentration gradient of compounds with different characteristics. Finally, to get insight in how the characteristics of a HIPV determine its ability to indicate insect herbivory, we simulated a large number of artificial HIPVs that vary in their characteristics. To systematically explore the effect of compound parameters on the ability of an HIPV to indicate insect herbivory, we divided all HIPV-specific leaf synthesis/emission and chemical parameters (11) into five groups of parameters that are somehow related (Supporting Information Table S1.2). Within each group, those parameters were varied over a realistic range, whereas the other parameters were kept constant. In the five groups the following sets of parameters were varied (1) the maximum synthesis rate of a compound in a noninduced, control (p_c) and induced state (p_i); (2) the rate at which HIPVs are synthesized after herbivory (r_u) and stop being synthesized after herbivory stops (r_d); (3) Henry's law constant (H), the octanol/water partitioning coefficient ($K_{o/w}$) and the partitioning coefficient (η). Because *H* and $K_{o/w}$ are strongly correlated on a log-scale (Pearson $r = 0.84$), we generated correlated parameter values; (4) reactivity constants with respect to ozone (k_{O3}), nitrate (k_{NO3}) and the hydroxyl radical (k_{OH}); and (5) the extent to which the synthesis of a compound depends on photosynthesis or stored substrates (d_p). The default values were set at p_i=1.170, p_c=0.0530, r_d=0.0397, r_u= 0.1849, d_p= 0.3327, η=0.8137, H=68, mw=141, and $K_{o/w}$=2574.

3 | RESULTS

3.1 | Leaf-level emission of HIPVs

The leaf-level emission model developed in this paper and parameterized for 31 HIPVs emitted by poplar (Clavijo McCormick, Boeckler, et al., 2014) describes the experimentally established diurnal emission

FIGURE 2 Schematic representation of three scenarios to explore the ability of HIPVs emitted by poplar to indicate insect herbivory [(Z)-3-hexenol is shown as example]. Scenario 1 simulates a situation when all trees in a canopy are infested in all layers (three trees per scenario are shown). HIPVs are transported vertically through turbulence (vertical dotted arrow). Scenario 2 simulates a situation when only one tree in the canopy is infested in all layers; HIPVs are transported through turbulence and wind (horizontal dotted arrow). Scenario 3 represents a situation when one tree in the canopy is infested in only one layer, HIPVs are transported through turbulence and wind. The fraction of total leaf area in each layer (Leaf Area Density) is indicated in the left column [Colour figure can be viewed at wileyonlinelibrary.com]

dynamics of the different compounds quite well (Fig. 3 & Supporting Information Table S2 for the estimated parameter values and Supporting Information Fig. S2 for the diurnal dynamics). The explained variance of the emission fluxes of the induced plants ranged from 0.42–0.91 with an average of 0.80. No systematic variation in the explained variance was observed among compound classes. However, the model did not fit well for a few compounds, such as (Z)-3-hexenal, that exhibit higher nighttime emission than daytime emission. This could be explained because gypsy moth (Lymantria dispar) caterpillars also feed at night.

Parameterizing the leaf-level emission model to the 31 HIPVs showed that these varied substantially in the rate of increase upon herbivory (r_u, $1.03e^{-4}$-5.10) and decrease after herbivory (r_d, $1.85e^{-9}$-1.12). In addition, compounds differed in their dependency on radiation (d_p, 0-1) and the partitioning from the lipid to aqueous pool (η, 0-1; Supporting Information Table S2 for all estimated parameters). Some of the parameters varied consistently across compound class. For example, the biosynthesis of green leaf volatiles [e.g. (Z)-3-hexenal, (Z)-3-hexenol, (Z)-3-hexenylacetate] and aromatic compounds (e.g. salicylaldehyde, benzylbenzoate, and benzaldehyde) was found to cease significantly faster after herbivory compared with monoterpenoids (r_d). Likewise, the synthesis of nitrogenous compounds was found to be less dependent on variation in radiation compared with monoterpenes (d_p). Yet, variation in parameter values could be substantial within a compound class. For example, some monoterpenoids were among the fastest to be biosynthesized after herbivory (sabinene, limonene), whereas other monoterpenes were among the slowest (camphene, α-pinene).

3.2 | HIPVs as indicators of herbivory presence

The differences in the emission dynamics and the reactivity of a compound affected its ability to indicate insect herbivory based on its concentration in the canopy. This ability varied from hardly better than random (κ= 0) to almost perfect (κ = 1; Table 2). Figure 4 illustrates the emission dynamics for six representative HIPVs out the 31 released by poplar and their resulting concentrations in the canopy as a result of differences in reactivity with O_3, •NO_3 and •OH (see Supporting information Fig. S3 for all 31 compounds). •OH is the main daytime oxidant as it requires radiation to be formed, whereas the O_3 and •NO_3 are more important for nocturnal oxidation. For a decrease in reactivity, the longer lifetime reduces the concentration gradients around the source (Fig. 5) through more efficient dispersion but which differs largely between day and night.

The top five HIPVs from which herbivore presence could be inferred based on the emission flux were three green leaf volatiles [(Z)-3-hexenal, (Z)-3-hexenol and (Z)-3-hexenylacetate], an aromatic compound (salicylaldehyde) and a nitrogenous compound (2-methylbutyraldoxime). When inferring herbivore presence based on the canopy concentration in a scenario without horizontal dispersion, the top six best compounds were the green leaf volatiles, (Z)-3-hexenal, (Z)-3-hexenol and (Z)-3-hexenylacetate, a homoterpenoid [(E)-4,8-dimethylnona-1,3,7-triene, DMNT] and an aromatic compound (salicylaldehyde). The top five compounds in the scenario considering the horizontal dispersion contribution and one tree infested in the canopy consisted of one green leaf volatile (Z)-3-hexenylbenzoate, three
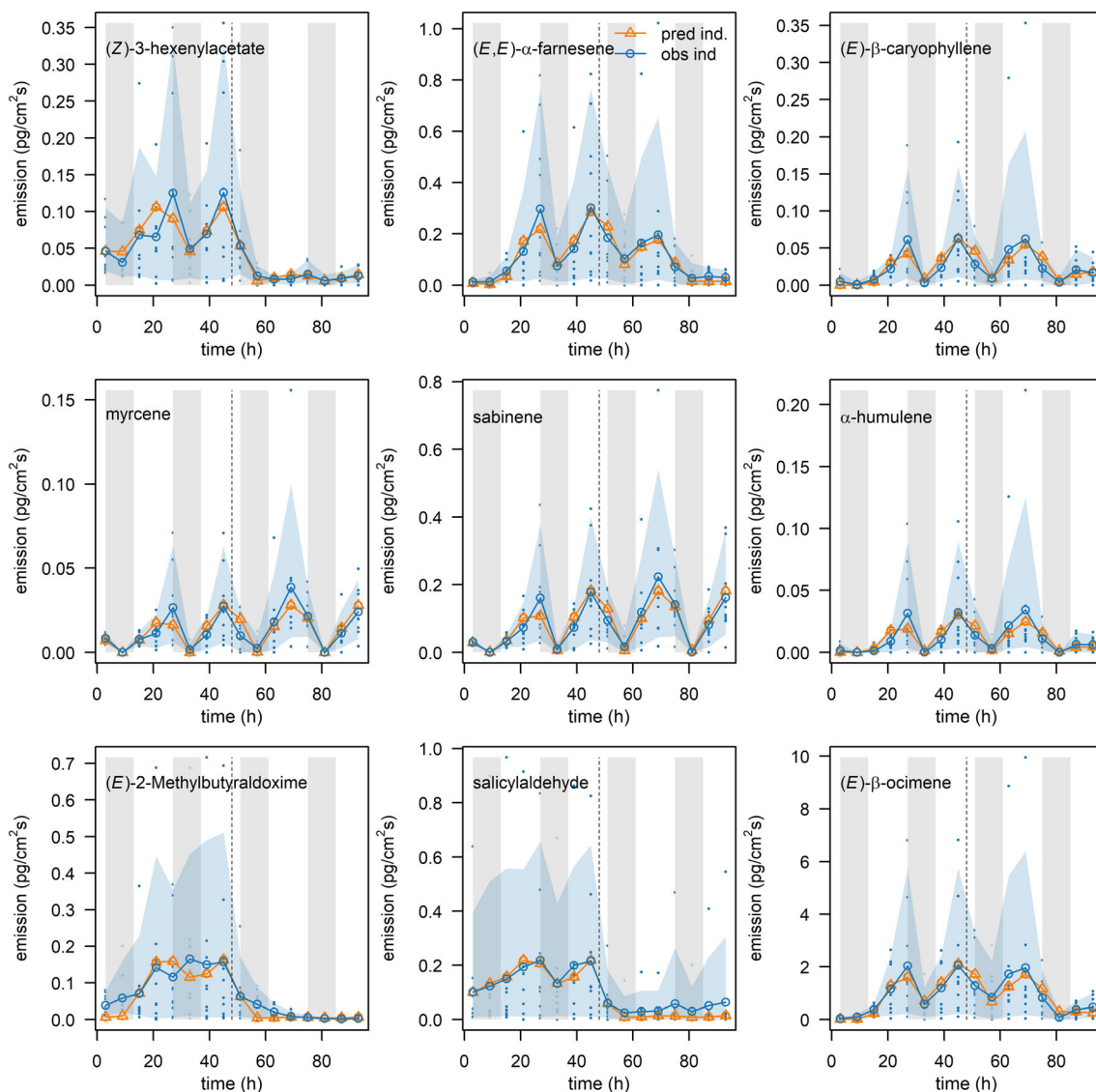
FIGURE 3 The emission fluxes (pg/cm² leaf s) as observed (blue) and predicted (orange) of six different herbivore induced plant volatiles ranging in their ability of indicate insect herbivory (Table 2). The blue shaded area shows the 95% quantiles of observed emission of individual plants and the dots represent the measurement of the individual plants. Gypsy moth caterpillars were placed on the plants shortly before the measurements started and were taken off after 48 hours (dotted line). Day/night is indicated by the white/grey background. Note the different scaling on the y-axis [Colour figure can be viewed at wileyonlinelibrary.com]

nitrogenous compounds (3-methylbutyraldoxime, phenylnitroethane) an aromatic compound (benzaldehyde) and one sesquiterpene alcohol (nerolidol).

Green leaf volatiles were on average rather good indicators of herbivory, whereas aromatics were among the poorest indicators. However, within a compound class there is large variation in the ability to indicate insect herbivory. For example, some monoterpenoids were rather good indicators of herbivory [(E)-β-ocimene and linalool], whereas others were poor indicators (α-pinene, myrcene). Furthermore, the ability of a compound to indicate insect herbivory dropped when its degradation under natural conditions is taken into account and dropped even further when assuming horizontal dispersion within the canopy with one infested tree surrounded by noninfested trees.

The above scenarios assumed that a single compound can be used to indicate insect herbivory. When two HIPVs were used to infer insect

herbivory, it appeared that the ability of this pair of HIPVs to indicate insect herbivory was hardly better than the best-performing HIPV in that pair. Thus, not much additional information is gained by mixing best-performing compounds, but some combinations of moderately performing compounds indicate insect herbivory rather well (e.g. a combination of 2-methylbutyraldoxime and benzylcyanide). HIPVs that do well in combination seemed to be the compounds that did poorly in the scenario when all trees were infested (no advection) but did well in the scenario with a single tree is infested and advection (Appendix S4).

3.3 | Factors affecting the ability of a HIPV to indicate insect herbivory

The above analyses showed that compounds vary substantially with respect to their ability to indicate the presence/absence of insect

TABLE 2 The ability of 31 HIPVs to serve as reliable indicator of insect herbivory

| Compound name	Km emis	Km no advection	Km with advection
Aromatics			
salicylaldehyde	**0.96**	**0.75**	0.26
benzylbenzoate	0.73	0.17	0.64
benzylalcohol	0.66	0.31	0.13
benzaldehyde	0.65	0.29	0.16
benzenethanol	0.52	0.19	0.08
Green leaf volatiles			
(Z)-3-hexenal	**0.97**	**0.89**	0.61
(Z)-3-hexenol	**0.95**	**0.76**	0.43
(Z)-3-hexenylacetate	**0.94**	**0.77**	0.26
(Z)-3-hexenylbenzoate	0.81	**0.75**	**0.66**
Homoterpenoid			
(E)-4,8-dimethylnona-1,3,7-triene (DMNT)	0.82	**0.76**	0.63
Monoterpenoids			
(E)-β –ocimene	0.71	0.64	0.61
(Z)-β –ocimene	0.7	0.63	0.6
linalool	0.69	0.65	0.56
α-pinene	0.16	0.29	0.05
sabinene	0.12	0.24	0.05
camphene	0.09	0.21	0.03
borneol	0.03	0.11	0.04
limonene	0.03	0.06	0.01
myrcene	0.02	0.07	0.02
Nitrogenous			
(E)-2-methylbutyraldoxime	**0.87**	0.25	0.24
(Z)-2-methylbutyraldoxime	0.83	0.24	0.4
Indole	0.79	0.59	0.61
(Z)-3-methylbutyraldoxime	0.76	0.22	**0.72**
2-phenylnitroethane	0.73	0.11	**0.67**
benzyl cyanide	0.73	0.02	**0.65**
Sesquiterpenoids			
nerolidol	0.77	0.7	**0.70**
(E,E)-α-farnesene	0.72	0.66	0.63
δ-cadinene	0.62	0.55	0.54
(E)-β-caryophyllene	0.59	0.52	0.55
germacrene D	0.56	0.6	0.51
α-humulene	0.45	0.4	0.43

Note: The reliability of the compound is expressed relative to chance agreement (κ=1 perfect agreement, 0 = no better than chance). The predictability differs substantially between HIPVs ranging from almost perfect agreement to hardly better than chance. The k-values were calculated based on the leaf emission flux, the concentration in the canopy without and with wind (+ advection) and sorted by compound class and the performance of the compound in relation to its emission flux. The top six best performing compounds are highlighted in bold. The colour scale reflects the predictability (k=1 dark green, k=0 dark red).

herbivores. To explore which characteristics of HIPVs contribute to the reliability of using the compound as indicator of herbivory, we simulated a large number of compounds varying in characteristics. This analysis showed that (1) the ability of a compound to indicate insect herbivory increases when the emission of that compound is low in noninfested trees (p_c) and high in infested trees (p_i, Fig. 6). (2) The
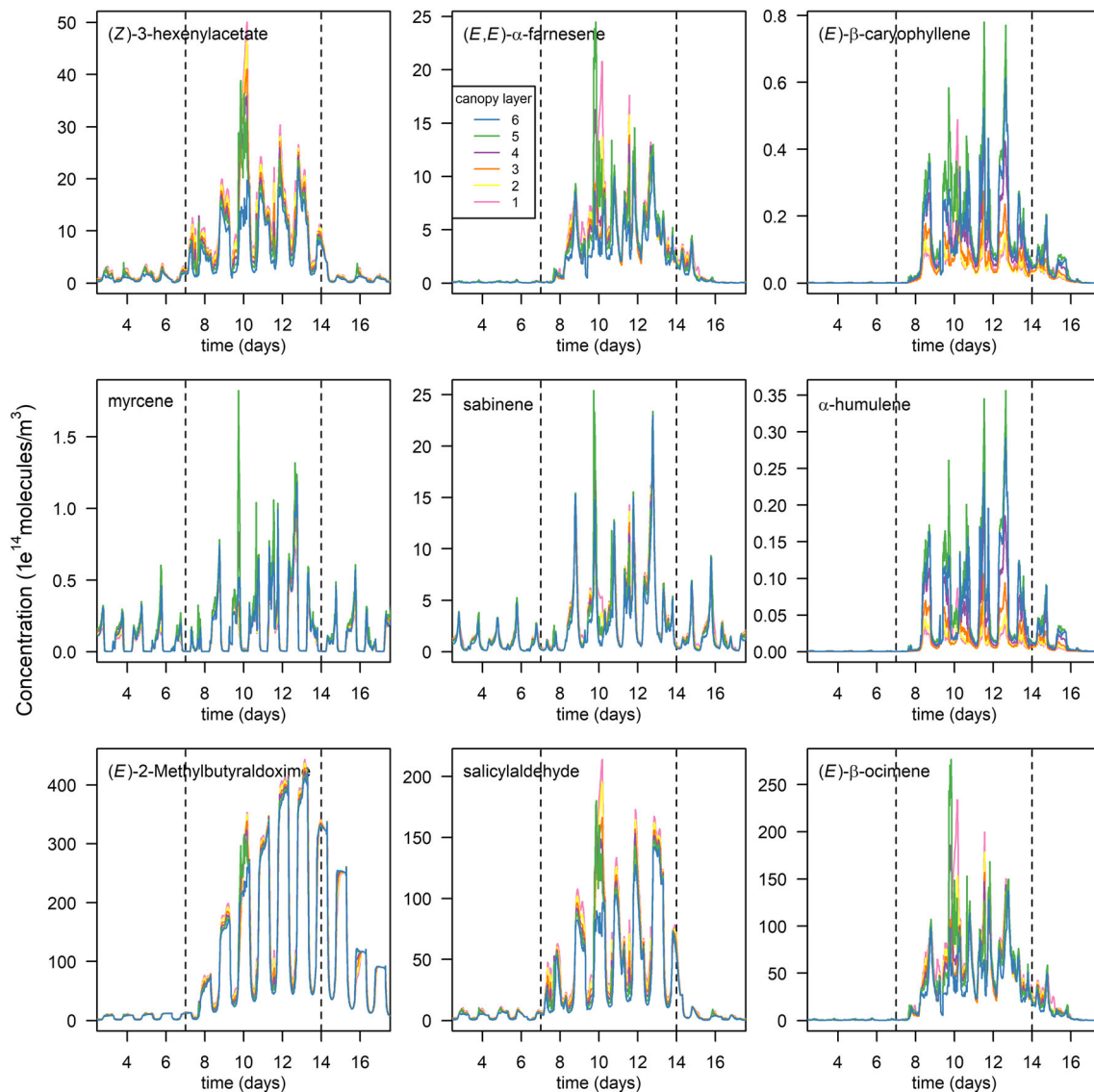
FIGURE 4 The simulated volatile concentrations in the canopy for six different HIPVs and six canopy layers (coloured lines, 1=lowest, 6=highest) under assumption that all trees are infested in all canopy layers. Herbivory started at day 7 and stopped at day 14 (vertical dotted lines). Note that different scales on the y-axis [Colour figure can be viewed at wileyonlinelibrary.com]
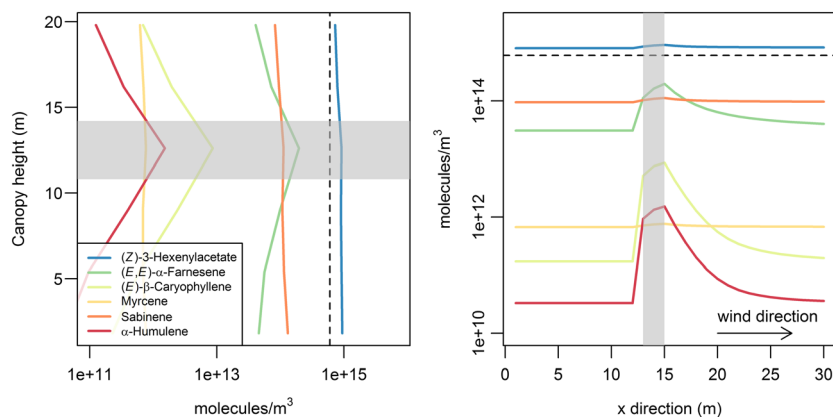
FIGURE 5 Concentration profile over canopy height (m; left panel) and along the x-direction (right panel) for 6 compounds varying in reactivity with O_3, ●NO_3 and ●OH. The dotted line represents a threshold concentration of $6e^{14}$ molecules/m^3 (based on (Shiojiri, Ozawa, Matsui, Sabelis, & Takabayashi, 2012) . The grey shaded area represents the vertical layer of the tree where herbivory took place (left panel) and the infested tree among non-infested trees (right panel). The concentration profile in the x-direction is asymmetric because of the downwind transport of the volatiles [Colour figure can be viewed at wileyonlinelibrary.com]

ability of a compound to indicate insect herbivory is affected by the rates at which HIPVs are synthesized after herbivory (r_u) and stop being synthesized after herbivory stops (r_d). High values of r_u and r_d imply that the volatile biosynthesis closely follows the herbivore event. (3) Compounds with very small Henry's law constant (e.g. $H <$ 0.1 Pa m^3/mol) are less reliable as cue because the stomata exert control over the emission of these compounds leading to more dynamic emission patterns and hence making it more difficult to infer insect

herbivory from the concentration in the canopy. In addition, compounds with a large $K_{o/w}$ are less reliable as indicator of herbivory because those compounds dissolve easily in the lipid pool and are, therefore, released at a lower rate from the lipid storage pool into the intracellular airspace, leading to a delay in emission compared with the moment the compound was synthesized. As a consequence, such compounds are less able to follow the presence/absence of herbivores. (4) HIPVs that are more reactive are generally better indicators
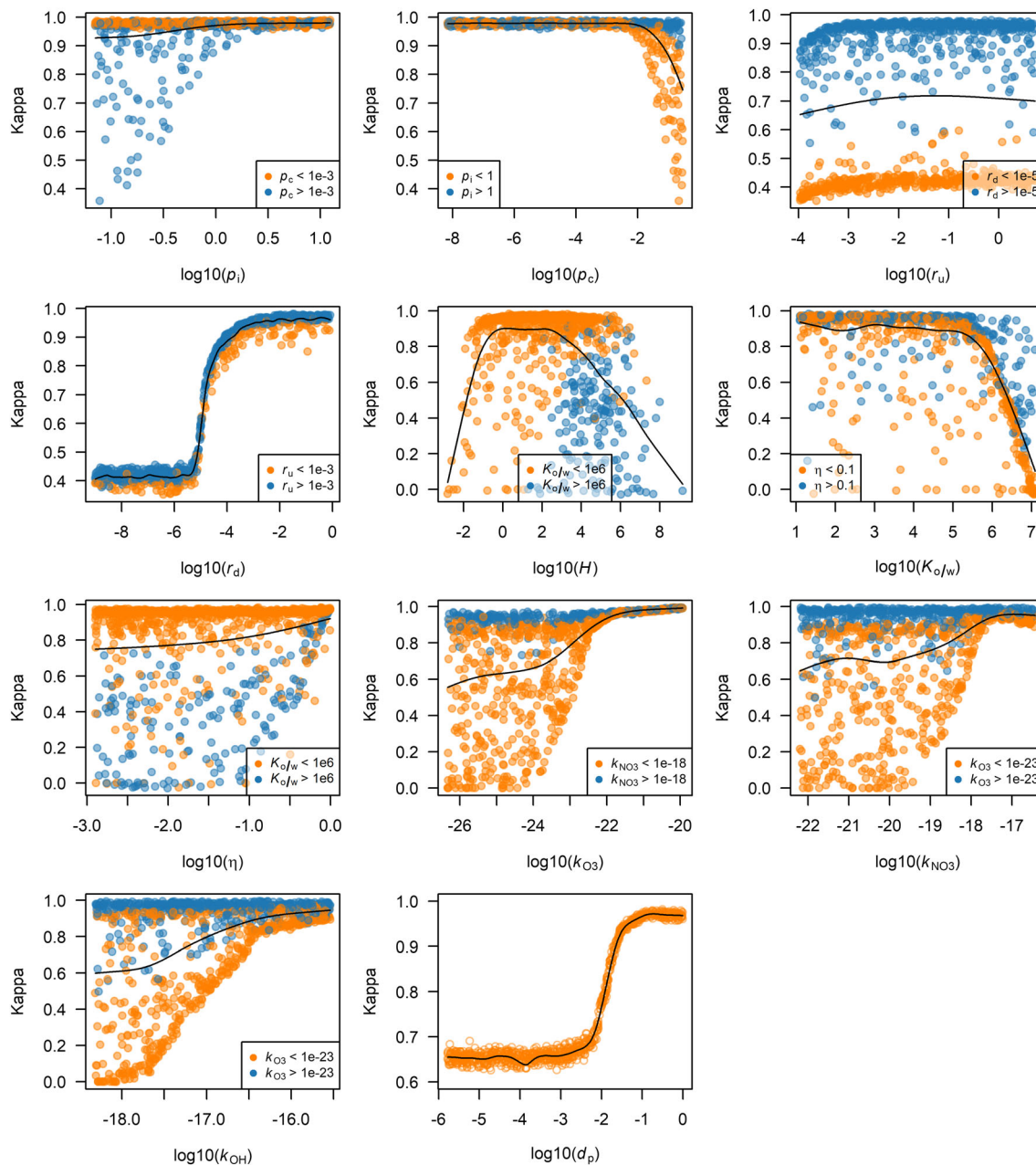
FIGURE 6 The relationship between the properties of an HIPV and its ability to indicate insect herbivory (κ, κ=1 perfect agreement, 0 = no better than chance). Each dot represents an artificial HIPV having a realistic combination of properties (simulated within the parameter range that was observed in the 31 HIPVs emitted by Poplar). Different colours represent different parameter values that were changed simultaneously. Abbreviations: p_i maximum HIPV synthesis rate of induced plants, p_c maximum HIPV synthesis rate of non-induced plants, r_u increase in synthesis upon after herbivory, r_d decrease in synthesis rate when herbivory stops, d_p dependency of synthesis on photosynthesis, H Henry's law constant, $K_{o/w}$ octanol/water partition coefficient, η partition coefficient aqueous vs. lipid pool, k_{O3} Rate constant for ozone, k_{OH} Rate constant for the hydroxyl radical, k_{NO3} Rate constant for nitrate radical [Colour figure can be viewed at wileyonlinelibrary.com]

of herbivory because reactive compounds have a shorter lifetime and get less dispersed in the canopy and transported to the atmosphere. However, when assuming that a minimum VOC concentration is needed for detection, very reactive compounds become poor indicators, as their lifetime is too short to reach concentrations beyond the perception limit (Supporting Information Fig. S5). (5) Compounds that depend less on radiation for their synthesis are better indicators of herbivory. Those compounds can be released in rather constant amounts during day and night, and thus may lead to more stable concentrations over time. This finding has to be interpreted with care because night–day contrasts in mixing conditions and chemistry might exert a much more dominating influence on the actual diurnal cycles in HIPV concentrations.

4 | DISCUSSION

In this study we took a modelling approach to explore to what extent the reliability of a volatile compound to act as an indicator of herbivory is affected by the physicochemical and physiological properties of that compound. The results suggest that there is large variation in the ability of compounds to serve as a cue of herbivory and that this ability depends on the physiological and chemical properties of the compound in interaction with the canopy conditions and only to a minor extent to the chemical class the compound belongs to.

4.1 | Large variation in ability of HIPVs to indicate insect herbivory and interaction with canopy conditions

Large variation was observed in the ability of HIPVs emitted by poplar in response to gypsy moth caterpillars to serve as reliable cues of caterpillar herbivory. The compounds that performed best in indicating insect herbivory consisted of green leaf volatiles such as (Z)-3-hexenal, (Z)-3-hexenol, the homoterpene DMNT and nitrogenous compounds such as (Z)-3-methylbutyraldoxime and benzylcyanide. These compounds are known to play an important role in the insect community associated with black poplar. For example, gypsy moth caterpillars are attracted to (Z)-3-hexenol (naïve caterpillars) and DMNT (experienced caterpillars; Clavijo McCormick, Reinecke, Gershenzon, & Unsicker, 2016). In addition, 2- and 3-methylbutyraldoxime and (Z)-3-hexenol attract the parasitoid *Glyptapanteles liparidis* that attacks the gypsy moth caterpillar (Clavijo McCormick et al., 2012). Furthermore, field data shows that under natural conditions, GLVs and nitrogenous compounds are emitted in substantially higher amounts upon experimental herbivory (Clavijo McCormick et al., 2019). Thus, data from controlled experiments and the field qualitatively support our model predictions, although rigorous field experiments are needed for further verification. For example, field experiments comparing blends composed of compounds that are predicted to be good *versus* poor signalling compounds could be used to verify model predictions (Clavijo McCormick et al., 2014; Turlings, Tumlinson, Heath, Proveaux, & Doolittle, 1991). Furthermore, concentrations of volatile organic compounds in the field could be measured with a proton transfer reaction mass spectrometer (PTR-MS) – a device used in the field of atmospheric chemistry to measure vertical VOC concentration gradients in and above forest canopies (e.g. Park et al., 2013), the installation of Polydimethylsiloxane (PDMS) tubes (Kallenbach et al., 2014) at multiple distances and directions from the source or comparable traps such as twisters (e.g. Gerstel GmbH & Co. KG, Mülheim an der Ruhr, Germany).

A compound can be a good indicator of insect herbivory if its properties are favourable, but if one property is unfavourable, its ability to indicate insect herbivory drops. For example, a compound whose synthesis quickly starts after herbivory but slowly stops after herbivory has ended, will still be a poor indicator of herbivory (e.g. borneol in poplar). This explains why the variation in the ability to indicate insect herbivory within the different compound classes emitted by poplar was large, because even though some parameter values were rather similar between compounds from one class, other parameters did vary orders of magnitude within this class. As each parameter contributes to the ability to indicate insect herbivory, a change in one of the parameters can negatively affect the ability to indicate insect herbivory.

The ability of a compound to indicate insect herbivory interacted with the canopy conditions. When assuming a rather homogeneous environment in which all trees are infested in all layers (similar to an outbreak situation), the temporal variability in HIPV concentrations determine the predictability of a compound. Temporal variability in HIPV emissions is largely driven by differences in emission patterns. However, when one infested tree is surrounded by noninfested trees, the spatial concentration gradient around the source becomes an important determinant of the predictability of a compound and an important determinant of the concentration gradient around the source is the lifetime of the compound. A short lifetime will lead to larger concentration gradients around the source because the compound is short-lived and will not be dispersed very far. The role of the short lifetime explains the higher performance of (Z)-3-hexenylbenzoate relative to (Z)-3-hexenol or (Z)-3-hexenylacetate in the scenario considering horizontal dispersion. However, 3-metylbutyraldoxime (3-MBA) performed better compared with a very similar compound, 2-metylbutyraldoxime (2-MBA), whereas their reactivities were estimated to be similar. The observation that 2-MBA is produced in relatively higher quantities, albeit low in absolute terms, by noninfested trees compared with 3-MBA (Clavijo McCormick, Boeckler, et al., 2014) leading to more shallow concentration gradients around the infested tree may explain the difference between the two compounds.

4.2 | Towards predicting which HIPVs are reliable cues of insect herbivory

The quest for the identification of which HIPVs could serve as reliable cues of insect herbivory can benefit from a better description of the HIPVs in terms of their emission dynamics and fate in the canopy. For example, the rate at which synthesis of the compound increases

upon herbivory and the rate at which the synthesis drops when herbivory is terminated were found to be important determinants of the ability to indicate insect herbivory. Yet, HIPV emission is rarely measured over time even though the dynamics differ substantially between compounds. In addition, compounds that are effectively oxidized by O_3, •OH and •NO_3 are better indicators of herbivory. A steep gradient may be better for localization close to the target, whereas a shallow gradient may be better for long distance signalling. When assuming that a threshold concentration should be reached before detection by plants or insects is possible, an optimum reactivity was found (Appendix S5). There is haphazard evidence for minimum concentrations to which plants and insects respond. Shiojiri and colleagues (Shiojiri et al., 2012) showed that pulses resulting in mixing ratios being reached of less than 24-140 ppt(!) are sufficient to induce a response in plants, whereas when mixing ratios as large as 7091-11003 ppm were needed for the parasitic wasp *Microplitis croceipes* to induce a response within 10 sec (Rains, Tomberlin, D'Alessandro, & Lewis, 2004). The lower threshold for plants compared with the parasitic wasp contradicts evidence from field experiments that show that parasitoids can respond to odours at larger distances compared with plants (Aartsma et al., 2019; Karban, Shiojiri, Huntzinger, & McCall, 2006; Runyon, Mescher, & De Moraes, 2006). The importance of a compound's lifetime in being a reliable indicator of insect herbivory calls for studies that quantify minimum detection thresholds to improve knowledge of how the reactivity of a compound affects its function as infochemical, although other aspects of the chemical composition that affect the minimum threshold should be taken into account as well (Aartsma, Bianchi, van der Werf, Poelman, & Dicke, 2017).

Even though the model simulations show that compound characteristics affect the ability to be a reliable indicator of herbivory, it remains to be tested to what extent this is an innate characteristic of the compound and whether it can be generalized across species. We expect some consistency in which compounds can be used as infochemical because biosynthetic pathways may be quite similar across species (Dudareva et al., 2013). Furthermore, the physicochemical characteristics of the compounds are derived from their chemical structure and therefore independent of the plant species that emits the compound (k_{O3}, k_{OH}, k_{NO_3}, H and $K_{O/W}$). However, a large number of parameters that affected the signalling ability of a compound such as increase and decrease in synthesis rate upon herbivory, vary within and among plant species (see Fig. 3 and Turlings, Lengwiler, et al., 1998) which renders the signalling ability of a compound to be species-specific. A compound's value as indicator of insect herbivory could potentially be further narrowed down when taking the constraints of the receiver into account (Frost, Mescher, Carlson, & De Moraes, 2008). For example, physicochemical properties, such as the lipid solubility of a compound ($K_{o/w}$) or the electrophility of a compound, may affect how easily a compound binds to the antennae of parasitoids (Arsene, Schulz, & Van Loon, 2002) or how easily a compound induces a response in the plasma membrane of plant cells (Asai, Nishioka, Takabayashi, & Furuichi, 2009; Zebelo, Matsui, Ozawa, & Maffei, 2012).

4.3 | Insect herbivory can be inferred from a single compound

Many studies indicate that organisms respond to a blend of volatiles (e.g. De Boer et al., 2004; Fontana et al., 2011; Kappers et al., 2005). Yet, our model simulations showed that presence/absence of insect herbivory can be inferred from within canopy concentrations of a single HIPV. The difference can be explained because in our model, the compounds are produced by a one herbivore–plant species combination, but, in reality, the same compound can be produced by multiple plant species–insect species combinations (Aartsma et al., 2017; Clavijo McCormick et al., 2012). It has been suggested that a single compound may serve as a reliable indicator of feeding activity in general (i.e. indicating leaf damage), but others provide the necessary context-specific information to discriminate between different insect and plant species (De Boer et al., 2004; Frost et al., 2008; Gouinguené, Pickett, Wadhams, Birkett, & Turlings, 2005).

Green leaf volatiles were predicted to be on average rather good indicators of herbivory which corroborates experimental evidence that shows that GLVs are attractive to and/or can be perceived by a broad range of natural enemies of insect herbivores (Gouinguené et al., 2005; Halitschke, Stenberg, Kessler, Kessler, & Baldwin, 2008; Loughrin, Potter, & Hamilton-Kemp, 1995; Natale et al., 2003; Shiojiri et al., 2006) and plants (Engelberth, Contreras, Dalvi, Li, & Engelberth, 2013; Kessler, Halitschke, Diezel, & Baldwin, 2006). As GLVs are produced in response to any leaf damage, parasitoids need additional information on which herbivore incurred the damage. This information may be provided by HIPVs that were found to be poor(er) indicators of herbivory. Such an HIPV should be quickly released upon herbivory to accompany the feeding-related cue, but it does not need to level off quickly when insect herbivory stops (δ-cadinene could be such a HIPV in poplar; Clavijo McCormick, Boeckler, et al., 2014). Interestingly, variation in the biosynthetic rate of HIPVs upon herbivory is three orders of magnitude smaller compared with the rate at which the biosynthesis of the compound drops after herbivory stops. If our hypothesis holds, then, for compounds that serve as host or insect ID, there would be relatively strong selection on a quick release of HIPVs but a weaker selection on the decrease in synthesis after herbivory. Yet, costs, such as energy required for biosynthesis of a compound, may select for stopping synthesis as soon as herbivory stops. Furthermore, the host-plant identity could be represented by a constitutively emitted VOC unique to the host plant, which may explain why some organisms more strongly respond to a blend containing at least a VOC that is constitutively emitted (Fontana et al., 2011; Mumm & Hilker, 2005).

Some studies report that HIPVs need to be present in specific ratios to elicit a response in natural enemies (Beyaert et al., 2010; Junker et al., 2018; Natale et al., 2003) as the ratio of compounds is discriminative for infested and noninfested trees. The present study offers an alternative explanation why specific ratios may elicit a stronger response than others. As the lifetimes of the compounds can differ substantially between compounds, this will lead to different concentration gradients in the canopy (Fig. 5). As a result, the ratio between

two compounds can provide information how close the organism is to the source. However, the ratio in which compounds occur is not only a function of space, but it may also vary over time especially given the different reactivities of compounds with respect to O_3, $\bullet NO_3$ and $\bullet OH$ (McFrederick et al., 2008) and strong diurnal contrasts in oxidation concentrations and mixing conditions inside and above the canopy.

4.4 | Strengthening the link between the fields of plant-insect relations, micro-meteorology and atmospheric chemistry

This study links leaf-level emission to their canopy concentrations to assess the ability of HIPVs to be reliable indicators of herbivory. The finding that the lifetime of the compound – which also depends on diurnal contrasts in canopy chemistry and mixing conditions – is an important determinant of the compound's ability to indicate insect herbivory, stresses the need to connect studies on plant responses to insect herbivory to studies on micro-meteorology and atmospheric chemistry (Holopainen, Nerg, & Blande, 2013; McFrederick et al., 2008). Connecting these fields can be reinforcing in both directions. First, expertise and techniques in the field of atmospheric chemistry to measure microclimate and vertical BVOC gradients in and above canopies could be used to measure horizontal volatile gradients and compare these with model predictions (e.g. Park et al., 2013). Second, HIPV emissions can constitute an important part of the total emissions from vegetation (Bergström, Hallquist, Simpson, Wildt, & Mentel, 2014; Llusià & Peñuelas, 2001; Staudt & Lhoutellier, 2007) and an accurate description of the leaf-level biosynthesis and emission of HIPVs from vegetation is critical to accurately predict total VOC emissions from vegetation and their subsequent impact on secondary aerosol formation, cloud formation and albedo (Ghimire et al., 2017; Yli-Pirilä et al., 2016; Zhao et al., 2017). An accurate prediction of HIPV emissions hinges on quantitative relationships between emission and leaf damage, defence induction, stress duration and light and temperature (Arneth & Niinemets, 2010; Maja et al., 2014; Niinemets, Kännaste, & Copolovici, 2013). To our knowledge, the model presented in this study is the first applied to a broad range of HIPVs. The model shows a good fit to the observed emission fluxes for a large number of compounds suggesting that relevant processes were included. Nevertheless, to study model behaviour at shorter time scales and to obtain insight in how temperature and radiation affect HIPV emission and to what extent that differs from constitutively emitted plant VOCs, in particular for compounds that have substantially high night-time emissions (De Moraes et al., 1998), high time-resolution measurements are needed. This is also of large relevance given the large temperature and radiation gradients that may occur within especially dense canopies.

Once the modelling approach has been applied to and tested on multiple species it could be used to find the optimal spatial configurations of push-pull systems (Khan, Midega, Bruce, Hooper, & Pickett, 2010; Stenberg, Heil, Åhman, & Björkman, 2015) or cultivar mixes that differ in attractiveness to natural enemies (Aartsma et al., 2019). Furthermore, candidate compounds identified by the model could be targeted in breeding programs (Stenberg et al., 2015).

5 | CONCLUSIONS

This study shows that HIPVs vary enormously in their ability to indicate presence/absence of insect herbivore feeding. Experimental and field tests are needed to verify the model predictions. Yet, the current approach highlights the power of combining the field of plant–insect interactions with micrometeorology and atmospheric chemistry to increase our understanding of the ecological significance of HIPVs. The significance of HIPVs to atmosphere fluxes is yet another unexplored promising avenue at the intersection of these fields.

AUTHOR CONTRIBUTIONS

J.C.D conceived the idea. J.C.D., L.G., S.B.U. and M.D. designed the study and the scenarios. J.C.D. and L.G. developed the model. A.B. and S.B.U. provided the data of poplar. All authors contributed substantially to discussions and to the writing of the manuscript.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

Appendix S1 Detailed description and parameterization of the leaf emission and canopy model

Appendix S2 Estimated model parameters and observed and predicted diurnal emission for 31 herbivore-induced plant volatiles of *Populus nigra*, infested with caterpillars of *Lymantria dispar*

Appendix S3 Simulated in-canopy volatile concentration of 31 herbivore-induced plant volatiles emitted by *Populus nigra*, infested with caterpillars of *Lymantria dispar*

Appendix S4 Predictability of combinations of two herbivore-induced plant volatiles

Appendix S5 Relationship between the reactivity of a compound with respect to ozone, the nitrate radial and the hydroxyl radical when assuming a threshold concentration for detection