Published in final edited form as:

Chemosphere. 2015 November ; 138: 751–757. doi:10.1016/j.chemosphere.2015.07.075.

Temperature dependencies of Henry's law constants for different plant sesquiterpenes

Lucian Copolovici^{1,2,*} and Ülo Niinemets^{2,3}

¹Institute of Technical and Natural Sciences Research-Development of "Aurel Vlaicu" University, Elena Dragoi 2, Arad 310330, Romania

²Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, Kreutzwaldi 1, Tartu 51014, Estonia

³Estonian Academy of Sciences, Kohtu 6, 10130 Tallinn, Estonia

Abstract

Sesquiterpenes are plant-produced hydrocarbons with important ecological functions in plant-to-plant and plant-to-insect communication, but due to their high reactivity they can also play a significant role in atmospheric chemistry. So far, there is little information of gas/liquid phase partition coefficients (Henry's law constants) and their temperature dependencies for sesquiterpenes, but this information is needed for quantitative simulation of the release of sesquiterpenes from plants and modeling atmospheric reactions in different phases. In this study, we estimated Henry's law constants (H_{pc}) and their temperature responses for 12 key plant sesquiterpenes with varying structure (aliphatic, mono-, bi- and tricyclic sesquiterpenes). At 25 °C, Henry's law constants varied 1.4-fold among different sesquiterpenes, and the values were within the range previously observed for monocyclic monoterpenes. H_{pc} of sesquiterpenes exhibited a high rate of increase, on average ca. 1.5-fold with a 10 °C increase in temperature (Q10). The values of Q10 varied 1.2-fold among different sesquiterpenes. Overall, these data demonstrate moderately high variation in H_{pc} values and H_{pc} temperature responses among different sesquiterpenes. We argue that these variations can importantly alter the emission kinetics of sesquiterpenes from plants.

Keywords

Flower and leaf volatiles; Sesquiterpenes; Henry's law constant; Partition coefficients; Temperature dependence

1 Introduction

All plant species emit different volatile organic compounds (VOC) either constitutively, or during certain ontogenetic stages or upon exposure to different stresses (Schnitzler et al., 2010; Peñaflor et al., 2011; Fineschi et al., 2013; Niinemets et al., 2013; Niinemets and Monson, 2013). Plants synthesize more than 100,000 chemical products and at least 1700 of

*corresponding author: Lucian Copolovici, Tel.: +3727313207, fax.: +3727313738, lucian.copolovici@emu.ee.

these are known to be volatile (Kesselmeier and Staudt, 1999). Around 90% of global terrestrial non-methane VOC emissions are of vegetation origin (Guenther et al., 1995; Arneth et al., 2008; Guenther et al., 2012). Among biogenic volatiles, volatile and semi-volatile terpenoids including sesquiterpenes play a major role in tropospheric chemistry due to their high reactivity with OH radicals and ozone-forming potentials (Fehsenfeld et al., 1992). Sesquiterpenes and especially their oxidation products with relatively low vapor pressure of less than 5 Pa at 25 °C are considered semi-volatiles (Hoskovec et al., 2005; Kosina et al., 2013) and have a high capacity to form and condense on solid particles, thus, playing an important role in secondary aerosol formation and in formation of cloud condensation nuclei (Huff Hartz et al., 2005; Helmig et al., 2006).

Plants under different types of stresses emit a great variety of sesquiterpenes (Beauchamp et al., 2005; Copolovici et al., 2011; Copolovici et al., 2012). The composition of the emissions depend on the stress type and on the stress severity (Niinemets et al., 2013). The induced emissions of caryophyllene, humulene, valencene etc. are usually (but not only) due to abiotic stresses such as heat, frost, drought and flooding (Copolovici et al., 2012). Biotic stresses (herbivory, fungal attacks etc) result in emissions of farnesene, and nerolidol derivative homoterpenes (Joo et al., 2011). However, it is not easy to generalize because the induced sesquiterpene emissions are species-specific and the blend of emission could be different for different stresses. Apart from stress-elicited sesquiterpene release, sesquiterpenes are constitutively emitted by a huge variety of flowers. As floral scent is the key long-distance attractant to pollinators that are often plant species specific, the composition of the scent is a characteristic trait of every plant species (Pichersky et al., 1994; Dudareva et al., 1998), and plays a major role in plant reproductive success (Pichersky and Gershenzon, 2002). For example, flowers of *Asarum* species emit α -cedrene, α -humulene, β -caryophyllene, (*E*)-nerolidol and many other oxygenated and non-oxygenated sesquiterpenes at a high level of 1000 ng g⁻¹ h⁻¹ (Azuma et al., 2010; Farré-Armengol et al., 2014), while the volatile profile of *Alstroemeria* “Sweet Laura” flowers is dominated by (*E*)- β -caryophyllene, humulene and an ocimene-like compound (Aros et al. (2012). *Arabidopsis thaliana* flowers release a complex mixture of volatile monoterpenes and sesquiterpenes with (*E*)- β -caryophyllene as the dominant component (Chen et al., 2003) whereas the formation of all sesquiterpenes found in the *Arabidopsis* floral volatile blend is due to only two terpene synthases specifically expressed in flowers (Tholl et al., 2005). Due to high emission rates during the flowering period, atmospheric sesquiterpene concentrations strongly increase during the blooming period (Baghi et al., 2012). This evidence collectively indicates that both stress-elicited emissions and constitutive flower emissions constitute an important source of atmospheric BVOC.

As different sesquiterpenes have widely different atmospheric rate constants for reactions with ozone and OH radicals (Arneth and Niinemets, 2010; Holopainen and Blande, 2013; Holopainen et al., 2013), predicting atmospheric reactions of sesquiterpenes requires understanding of dynamics of fractional composition of emitted sesquiterpenes. Moreover, short atmospheric lifetimes (two minutes for β -caryophyllene and α -humulene) (Richters et al., 2015) due to reactions with ozone implicate the sesquiterpenes in secondary organic aerosol formation (van Eijck et al., 2013). From the perspective of plant-insect interactions in reactive atmospheres, this information is also important for predicting the changes in

composition of sesquiterpene blend with distance from the emission source (Holopainen et al., 2013; Blande et al., 2014). The emission models can predict the fractional composition of complex compound mixtures once the physico-chemical characteristics of specific compounds are available (Niinemets and Reichstein, 2002; Niinemets et al., 2002). In particular, due to the controls of compound-physico-chemical characteristics on gas-phase transfer resistance between the leaves and the atmosphere, the kinetics of emission can importantly depend on the Henry's law constant (air–water equilibrium partition constant; H_{pc} , Pa m³ mol⁻¹) (Niinemets and Reichstein, 2002). Furthermore, temperature of leaves and flowers strongly varies through the day, and thus, there is a huge diurnal variation in the emission of sesquiterpenes due to both temperature-dependent changes in the synthesis rate and due to temperature-dependent changes in compound physico-chemical characteristics (Niinemets and Reichstein, 2003).

The temperature dependencies of equilibrium coefficients are already available for more than 5000 different compounds (Staudinger and Roberts, 1996, 2001; Sander, 2015), but few data are available for relevant plant volatiles. Recently, Henry's law constants for 10 monoterpenes (C10) (Copolovici and Niinemets, 2005; Copolovici and Niinemets, 2007) and benzenoid methyl salicylate (C8) and, methyl jasmonate (C13) (Karl et al., 2008) have been determined, but there are very few data on higher molecular mass plant volatiles compounds. As a few exceptions, the solubility of C₁₃ compound β -ionone and solubility of taxol (polyoxygenated diterpene) have been determined by Fichan (1999) and Kapoor and Mahindroo (1997) but no data are available for sesquiterpenes (C15) with the exception of farnesene (Schuhfried et al., 2015). Furthermore, there is a general lack of temperature dependencies of higher molecular mass volatiles.

In the current study, we determined the temperature dependencies of Henry's law constant (air–water equilibrium partition constant; H_{pc} , Pa m³ mol⁻¹) for 12 structurally different sesquiterpenes (β -caryophyllene, α -cedrene, α -farnesene, γ -gurjonene, α -humulene, isosativene, α -longipinene, nerolidol, α -neoclovene, β -neoclovene, γ -neoclovene, and valencene) and the monoterpene derivative bornyl acetate (C12) that is frequently emitted by many plant species as well.

2 Methods

Terpenoid standards were obtained from Sigma – Aldrich (Munich, Germany) and were all of high purity (> 98%). For the determination of Henry's law constant we used EPICS (equilibrium partitioning in closed systems) method of Gosset (1987) as applied previously (Copolovici and Niinemets, 2005; Copolovici and Niinemets, 2007). The EPICS method is based on analysis of compound partitioning in different liquid volumes of two binary solute-solvent equilibrium systems. The liquid- or gas-phase concentrations in the two systems are measured, and the ratio of these values is used to compute the dimensionless Henry's law constant (H_{cc}) using the combined mass balance equations of these two systems. Shortly, two identical glass vials (total volume, V_T , of 64.5 mL) were used. 4 mL (V_{L1}) distilled water was added to the first vial and 50 mL (V_{L2}) to the second vial. Thereafter, 0.2 μ L of given sesquiterpene was added to both vials using a 1 μ L micro-syringe (SGE International, Ltd., Victoria, Australia). After the injection, the vial was immediately sealed with a Teflon-

coated silicone septum, vigorously shaken and ultrasound until the organic phases has been completely dissolved. The vials were equilibrated in a thermostatic water bath at desired temperature for 3 h. According to our work in the previous study (Copolovici and Niinemets, 2005) the phase equilibrium was reached in ca. 2 h after the injection. The headspace was further sampled for GC analyses using a multibed steel cartridges filled with different Carbotrap fractions as described previously (Niinemets et al., 2010; Kännaste et al., 2014). The cartridges were analyzed with a Shimadzu 2010 Plus Gas Chromatograph Mass Spectrometer with a TD20 thermodesorption system. The method and chromatographic programs have been described in detail in (Copolovici et al., 2009; Toome et al., 2010).

Given the presence of phase-equilibria in both vials, the Henry's law constant was calculated according to Gosset (1987). Under equilibrium conditions, the same amount of sesquiterpene injected into both vials 1 and 2 is partitioned among the gas and liquid phases as:

$$C_{L1} V_{L1} + C_{G1} V_{G1} = C_{L2} V_{L2} + C_{G2} V_{G2} \quad (1)$$

where C_{L1} is the equilibrium sesquiterpene liquid-phase concentration in vial 1 and C_{L2} the liquid-phase concentration in vial 2, C_{G1} is the equilibrium sesquiterpene gas-phase concentration in vial 1 and C_{G2} the concentration in vial 2, V_{G1} is the equilibrium gas-phase (headspace) volume in vial 1 and V_{G2} the gas-phase volume in vial 2. We assume that liquid-phase volumes remain constant during equilibration in both vials. From equation 2,

the dimensionless Henry's law constant ($H_{cc} = \frac{C_{G1}}{C_{L1}} = \frac{C_{G2}}{C_{L2}}$) is given as:

$$H_{cc} = \frac{V_{L2} - V_{L1} \frac{C_{G1}}{C_{G2}}}{\frac{C_{G1}}{C_{G2}} (V_T - V_{L1}) - (V_T - V_{L2})} \quad (2)$$

where $V_T = V_{L1} + V_{G1} = V_{L2} + V_{G2}$ is the total vial volume. The compound concentration in the headspace, C_G , is proportional to the signal peak area (A_1 for the first vial and A_2 for the second vial) from the gas chromatogram:

$$\frac{C_{G1}}{C_{G2}} = \frac{A_1}{A_2} \quad (3)$$

Combining Equations 2 and 3, H_{cc} is ultimately given as:

$$H_{cc} = \frac{V_{L2} - V_{L1} \frac{A_1}{A_2}}{\frac{A_1}{A_2} (V_T - V_{L1}) - (V_T - V_{L2})} \quad (4)$$

The data were finally converted to units $\text{Pa m}^3 \text{ mol}^{-1}$, i.e. presented as H_{pc} values (gas-phase vapor pressure to liquid-phase concentration ratio). $H_{\text{pc}} = H_{\text{cc}}RT$, where R is the gas constant ($\text{Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$) and T the absolute temperature (K). The determinations of H_{pc} were conducted at temperatures 25, 32, 38, 45, 50 °C. At each temperature, average Henry's law constant was calculated for three to four independent determinations.

Over a relatively small temperature range, H_{pc} temperature response can be fitted as (Dewulf et al., 1999; Görgényi et al., 2002):

$$\ln H_{\text{pc}} = -\frac{\Delta H_{\text{vol}}}{RT} + C, \quad (5)$$

where H_{vol} is the enthalpy of volatilization and C is a compound-specific constant. Thus, H_{vol} was derived for each compound as the slope of $\ln H_{\text{pc}}$ vs. $1/T$ relationship. In addition, Q10 values (van't Hoff equation) were also calculated.

3 Results

For all studied sesquiterpenes, Henry's law constants were of the same order of magnitude varying from 2548 - 3505 $\text{Pa m}^3 \text{ mol}^{-1}$ at 25 °C (Table 1) with an average $\pm$ SE (standard error of the mean) value for all sesquiterpenes of $3135 \pm 84 \text{ Pa m}^3 \text{ mol}^{-1}$. The H_{pc} value for the monoterpene derivative bornyl acetate was within the range of H_{pc} values observed for sesquiterpenes (Table 1).

Simplified temperature response (Eq. 5) fitted well the temperature relation of H_{pc} over the entire temperature range of 25 - 50 °C for all compounds studied ($r^2 > 0.98$, on average 0.989 ± 0.005 ; Figures 1-2). The enthalpy of volatilization (H_{vol}) varied ca. 1.6-fold from 25.7–40.5 kJ mol^{-1} among sesquiterpenes with an average ($\pm$ SE) of $34.2 \pm 1.4 \text{ kJ mol}^{-1}$, corresponding to an average Q10 value of 1.512 ± 0.027 (Table 1). Both H_{vol} and Q10 were lower for oxygenated monoterpene derivative bornyl acetate (Table 1).

The enthalpy of volatilization varied significantly among the neoclovene isomers which differ in the location of the double bond in the molecule. The enthalpy of volatilization was 25.7 kJ mol^{-1} for α -neoclovene and 26.3 kJ mol^{-1} for γ -neoclovene that have the double bond located within the hydrogenated indene scaffolding, while H_{vol} was 38.5 kJ mol^{-1} for β -neoclovene that has the double bond in the methylene group attached to the hydrogenated indole scaffolding (Table 1). The enthalpy of volatilization was not significantly different ($p = 0.94$) between two aliphatic sesquiterpene α -farnesene and nerolidol, which is surprising given that nerolidol has an OH group in its structure (Table 1).

4 Discussion

Henry's law constants of sesquiterpenes at 25 °C

Due to greater molecular size of sesquiterpenes compared with monoterpenes, the saturated vapor pressure (P_v) and, aqueous solubility (S) are expected to be much smaller for sesquiterpenes than for monoterpenes. In fact, saturated vapor pressure of non-oxygenated

sesquiterpenes is more than two orders of magnitude less than that in non-oxygenated monoterpenes (Hoskovec et al., 2005; Kosina et al., 2013). Compared with monoterpenes, the values of H_{pc} for sesquiterpenes are somewhat lower than those observed for bicyclic monoterpenes α -pinene and β -pinene and monocyclic monoterpenes α - and β -phellandrene, but they are of the same order of magnitude than H_{pc} values in other studied monocyclic monoterpenes (Copolovici and Niinemets, 2005), and in the monoterpene derivative bornyl acetate studied here (Table 1). Given that $H_{pc} = P_v/S$, this evidence suggests that lower P_v of sesquiterpenes is associated with analogous reductions in S compared with monoterpenes.

In the recent work Schuhfried et al. (2015) determined the H_{pc} for farnesene using another method based on on-line PTR-MS measurements in non-equilibrium conditions. There are no data on aqueous solubility of sesquiterpenes, but Fichan et al. (1999) demonstrated that the C13 oxygenated compound β -ionone had a much lower aqueous solubility and vapor pressure at 25 °C than the C10 oxygenated monoterpenes fenchol, linalool, borneol, and α -pinene and limonene oxides.

Temperature responses of Henry's law constants for sesquiterpenes

We determined the temperature dependencies of H_{pc} for important plant volatile sesquiterpenes which are elicited in response to different abiotic and biotic stresses. These estimations are, to our knowledge, the first determinations of temperature characteristics of equilibrium coefficients for plant volatile sesquiterpenes. The average ($\pm$ SE) enthalpy of volatilization determined for 204 different compounds by Staudinger and Robert (2001) was 39.1 ± 2.3 kJ mol⁻¹, while our average value for 12 sesquiterpenes of 34.2 ± 1.2 kJ mol⁻¹ is in the same range. On the other hand, previous estimations of monoterpene volatilization enthalpies have yielded an average value of 36.5 ± 0.4 kJ mol⁻¹ for non-oxygenated monoterpenes and 17.8 ± 0.4 kJ mol⁻¹ for oxygenated monoterpenes (Copolovici and Niinemets, 2005). Thus, the volatility of sesquiterpenes is expected to increase more with temperature than the volatility of oxygenated monoterpenes. In contrast, the temperature responses of H_{pc} for non-oxygenated monoterpenes and sesquiterpenes are expected to be similar.

Although the values of the volatilization enthalpy were similar among most compounds, still a significant variation in temperature responses, ca. 1.2-fold (and 1.6-fold when also considering bornyl acetate) was observed across the compounds (Table 1). This variability is currently difficult to explain as similar H_{pc} values were observed for aliphatic compounds. Even for isomers differing in the location of the double bonds such as neoclovene isomers (Fig. 2), important variability was observed (Table 1). We suggest that future studies with more sesquiterpenes and with experimental characterization of additional compound physico-chemical characteristics such as saturated vapor pressure, aqueous solubility and molar volume are needed to gain an insight into variation in H_{pc} at a given temperature and into H_{pc} temperature responses among different sesquiterpenes.

The overall increase in the rate of enzymatic reactions and integrated biological processes for a 10 °C rise in temperature (Q10, Table 1) is in the range of 1.5 to 3 (Nobel, 1991). The value of Q10 for physical processes such as diffusion is typically low, on the order of 1.05-1.1 (Gates, 1980; Niinemets and Reichstein, 2003). However, the volatility increase

across the sesquiterpenes studied, ca. 1.5-fold for a 10 °C rise in temperature, is very large for a non-biological process. From a biological perspective, there are two important implications of this large Q10 value for sesquiterpenes. First, it is well-known that leaves release sesquiterpenes in the stress conditions (Niinemets, 2010). Due to their semivolatile character, their emission level is typically quite low. Due to their high enthalpy of volatilization, emission rates can be strongly enhanced with rising temperatures. This needs to be considered when predicting plant volatile emission responses when stress occurs at different temperatures. The second aspect is the involvement of sesquiterpenes in pollinator attraction (e.g., Tholl et al., 2005; Nieuwenhuizen et al., 2009). Increases in temperature, e.g. even long-term increases such as due to global warming, can importantly enhance the flower attraction for pollinators due to facilitated sesquiterpene release (Valterova et al., 2007; Farré-Armengol et al., 2014). However, flower volatiles are often characterized by a high fraction of oxygenated monoterpenes and phenolic compounds known to be perceived by pollinator insects (Dudareva et al., 1996; Dudareva et al., 1998; Nagegowda et al., 2008). Because these compounds have lower Q10 values, flower detection by pollinators attracted to these oxygenated volatiles might be hindered due to the increased odor background of non-oxygenated mono- and sesquiterpenes. We also emphasize that although the role of sesquiterpenes is generally neglected in air quality estimations due to low rates of emissions in cool conditions, these emissions are expected to become gradually more important in warmer atmospheres, especially given their high potential to produce ozone and secondary organic aerosols (Huff Hartz et al., 2005; Helmig et al., 2006).

Acknowledgements

Funding for this study has been provided by the Estonian Ministry of Science and Education (institutional grant IUT-8-3), the European Commission through the European Regional Fund (the Center of Excellence in Environmental Adaptation), the European Research Council (advanced grant 322603, SIP-VOL+), and the European Commission and the Romanian Government (project POSCCE 621/2014).

References

- Arneth A, Monson RK, Schurgers G, Niinemets Ü, Palmer PI. Why are estimates of global isoprene emissions so similar (and why is this not so for monoterpenes)? *Atmos Chem Phys*. 2008; 8:4605–4620.
- Arneth A, Niinemets Ü. Induced BVOCs: how to bug our models? *Trends Plant Sci*. 2010; 15:118–125. [PubMed: 20071208]
- Aros D, Gonzalez V, Allemann RK, Mueller CT, Rosati C, Rogers HJ. Volatile emissions of scented *Alstroemeria* genotypes are dominated by terpenes, and a myrcene synthase gene is highly expressed in scented *Alstroemeria* flowers. *J Exp Bot*. 2012; 63:2739–2752. [PubMed: 22268153]
- Azuma H, Nagasawa J-i, Setoguchi H. Floral scent emissions from *Asarum yaeyamense* and related species. *Biochem System Ecol*. 2010; 38:548–553.
- Baghi R, Helmig D, Guenther A, Duhl T, Daly R. Contribution of flowering trees to urban atmospheric biogenic volatile organic compound emissions. *Biogeosciences*. 2012; 9:3777–3785.
- Beauchamp J, Wisthaler A, Hansel A, Kleist E, Miebach M, Niinemets Ü, Schurr U, Wildt J. Ozone induced emissions of biogenic VOC from tobacco: relations between ozone uptake and emission of LOX products. *Plant Cell Environ*. 2005; 28:1334–1343.
- Blande JD, Holopainen JK, Niinemets Ü. Plant volatiles in polluted atmospheres: stress responses and signal degradation. *Plant Cell Environ*. 2014; 37:1892–1904. [PubMed: 24738697]
- Chen F, Tholl D, D'Auria JC, Farooq A, Pichersky E, Gershenzon J. Biosynthesis and emission of terpenoid volatiles from *Arabidopsis* flowers. *Plant Cell*. 2003; 15:481–494. [PubMed: 12566586]

- Copolovici L, Kaennaste A, Pazouki L, Niinemets U. Emissions of green leaf volatiles and terpenoids from *Solarium lycopersicum* are quantitatively related to the severity of cold and heat shock treatments. *J Plant Physiol.* 2012; 169:664–672. [PubMed: 22341571]
- Copolovici L, Kännaste A, Niinemets U. Gas chromatography-mass spectrometry method for determination of monoterpene and sesquiterpene emissions from stressed plants. *Studia Univ Babes-Bolyai Chemia.* 2009; 54:329–339.
- Copolovici L, Kännaste A, Remmel T, Vislap V, Niinemets Ü. Volatile emissions from *Alnus glutinosa* induced by herbivory are quantitatively related to the extent of damage. *J Chem Ecol.* 2011; 37:18–28. [PubMed: 21181243]
- Copolovici L, Niinemets U. Salting-in and salting-out effects of ionic and neutral osmotica on limonene and linalool Henry's law constants and octanol/water partition coefficients. *Chemosphere.* 2007; 69:621–629. [PubMed: 17462701]
- Copolovici LO, Niinemets Ü. Temperature dependencies of Henry's law constants and octanol/water partition coefficients for key plant volatile monoterpene compounds. *Chemosphere.* 2005; 61:1390–1400. [PubMed: 15967478]
- Dewulf J, Van Langenhove H, Graré S. Sediment/water and octanol/water equilibrium partitioning of volatile organic compounds: temperature dependence in the 2 - 25 °C range. *Water Research.* 1999; 33:2424–2436.
- Dudareva N, Cseke L, Blanc VM, Pichersky E. Evolution of floral scent in *Clarkia*: novel patterns of s-linalool synthase gene expression in the *C. breweri* flower. *Plant Cell.* 1996; 8:1137–1148. [PubMed: 8768373]
- Dudareva N, Raguso RA, Wang JH, Ross EJ, Pichersky E. Floral scent production in *Clarkia breweri* - III. Enzymatic synthesis and emission of benzenoid esters. *Plant Physiol.* 1998; 116:599–604. [PubMed: 9489012]
- Farré-Armengol G, Filella I, Llusà J, Niinemets Ü, Peñuelas J. Changes in floral bouquets from compound-specific responses to increasing temperatures. *Glob Change Biol.* 2014; 20:3660–3669.
- Fehsenfeld F, Calvert J, Fall R, Goldan P, Guenther AB, Hewitt CN, Lamb B, Liu S, Trainer M, Westberg H, Zimmerman P. Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry. *Glob Biogeochem Cycle.* 1992; 6:389–430.
- Fichan I, Larroche C, Gros JB. Water solubility, vapor pressure, and activity coefficients of terpenes and terpenoids. *J Chem Eng Data.* 1999; 44:56–62.
- Fineschi, S., Loreto, F., Staudt, M., Peñuelas, J. Diversification of volatile isoprenoid emissions from trees: evolutionary and ecological perspectives. *Biology, controls and models of tree volatile organic compound emissions.* Niinemets, Ü., Monson, RK., editors. Springer; Berlin: 2013. p. 1-20.
- Gates, D. *Biophysical Ecology.* Springer-Verlag; New York: 1980.
- Görgényi M, Dewulf J, Van Langenhove H. Temperature dependence of Henry's law constant in an extended temperature range. *Chemosphere.* 2002; 48:757–762. [PubMed: 12201206]
- Gossett JM. Measurement of Henry's Law Constants for C1 and C2 Chlorinated Hydrocarbons. *Environ Sci Technol.* 1987; 21:202–208.
- Guenther A, Hewitt CN, Erickson D, Fall R, Geron C, Graedel T, Harley P, Klinger L, Lerdau M, McKay WA, Pierce T, et al. A global model of natural volatile compound emissions. *J Geophys Res.* 1995; 100:8873–8892.
- Guenther AB, Jiang X, Heald CL, Sakulyanontvittaya T, Duhl T, Emmons LK, Wang X. The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions. *Geosci Model Dev.* 2012; 5:1471–1492.
- Helmig D, Ortega J, Guenther A, Herrick JD, Geron C. Sesquiterpene emissions from loblolly pine and their potential contribution to biogenic aerosol formation in the Southeastern US. *Atmos Environ.* 2006; 40:4150–4157.
- Holopainen JK, Blande JD. Where do herbivore-induced plant volatiles go? *Front Plant Sci.* 2013; 4:185. [PubMed: 23781224]
- Holopainen, JK., Nerg, A-M., Blande, JD. Multitrophic signalling in polluted atmospheres. *Biology, controls and models of tree volatile organic compound emissions.* Niinemets, Ü., Monson, RK., editors. Springer; Berlin: 2013. p. 285-314.

- Hoskovec M, Grygarová D, Cvačka J, Streinz L, Zima J, Verevkin SP, Koutek B. Determining the vapour pressures of plant volatiles from gas chromatographic retention data. *J Chromatogr A*. 2005; 1083:161–172. [PubMed: 16078703]
- Huff Hartz KE, Rosenørn T, Ferchak SR, Raymond TM, Bilde M, Donahue NM, Pandis SN. Cloud condensation nuclei activation of monoterpene and sesquiterpene secondary organic aerosol. *J Geophys Res Atmos*. 2005; 110:D14208. doi:10.1029/2004JD005754.
- Joo E, Dewulf J, Amelynck C, Schoon N, Pokorska O, Simpraga M, Steppe K, Aubinet M, Van Langenhove H. Constitutive versus heat and biotic stress induced BVOC emissions in *Pseudotsuga menziesii*. *Atmos Environ*. 2011; 45:3655–3662.
- Kännaste, A., Copolovici, L., Niinemets, Ü. Gas chromatography mass-spectrometry method for determination of biogenic volatile organic compounds emitted by plants. *Plant isoprenoids: methods and protocols*. Rodríguez-Concepción, M., editor. Vol. 1153. Humana Press; New York: 2014. p. 161-169.
- Kapoor VK, Mahindroo N. Recent advances in structure modifications of Taxol (Paclitaxel). *Indian J Chem Sect B*. 1997; 36:639–652.
- Karl T, Guenther A, Turnipseed A, Patton EG, Jardine K. Chemical sensing of plant stress at the ecosystem scale. *Biogeosciences*. 2008; 5:1287–1294.
- Kesselmeier J, Staudt M. Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology. *J Atmos Chem*. 1999; 33:23–88.
- Kosina J, Dewulf J, Viden I, Pokorska O, Van Langenhove H. Dynamic capillary diffusion system for monoterpene and sesquiterpene calibration: quantitative measurement and determination of physical properties. *Intern J Environ Anal Chem*. 2013; 93:637–649.
- Nagegowda DA, Gutensohn M, Wilkerson CG, Dudareva N. Two nearly identical terpene synthases catalyze the formation of nerolidol and linalool in snapdragon flowers. *Plant J*. 2008; 55:224–239. [PubMed: 18363779]
- Nieuwenhuizen NJ, Wang MY, Matich AJ, Green SA, Chen X, Yauk Y-K, Beuning LL, Nagegowda DA, Dudareva N, Atkinson RG. Two terpene synthases are responsible for the major sesquiterpenes emitted from the flowers of kiwifruit (*Actinidia deliciosa*). *J Exp Bot*. 2009; 60:3203–3219. [PubMed: 19516075]
- Niinemets Ü. Mild versus severe stress and BVOCs: thresholds, priming and consequences. *Trends Plant Sci*. 2010; 15:145–153. [PubMed: 20006534]
- Niinemets Ü, Copolovici L, Hüve K. High within-canopy variation in isoprene emission potentials in temperate trees: implications for predicting canopy-scale isoprene fluxes. *J Geophys Res - Biogeosciences*. 2010; 115 G04029.
- Niinemets Ü, Kännaste A, Copolovici L. Quantitative patterns between plant volatile emissions induced by biotic stresses and the degree of damage. *Front Plant Sci*. 2013; 4:262. [PubMed: 23888161]
- Niinemets, Ü., Monson, RK., editors. *Biology, controls and models of tree volatile organic compound emissions*. Springer, Dordrecht - Heidelberg; New York - London: 2013.
- Niinemets Ü, Reichstein M. A model analysis of the effects of nonspecific monoterpenoid storage in leaf tissues on emission kinetics and composition in Mediterranean sclerophyllous *Quercus* species. *Glob Biogeochem Cycle*. 2002; 16:1110. DOI 10.1029/2002GB001927.
- Niinemets Ü, Reichstein M. Controls on the emission of plant volatiles through stomata: sensitivity or insensitivity of the emission rates to stomatal closure explained. *Journal of Geophysical Research - Atmospheres*. 2003; 108:4208. doi:10.1029/2002JD002620.
- Niinemets Ü, Reichstein M, Staudt M, Seufert G, Tenhunen JD. Stomatal constraints may affect emission of oxygenated monoterpenoids from the foliage of *Pinus pinea*. *Plant Physiol*. 2002; 130:1371–1385. [PubMed: 12428002]
- Nobel, PS. *Physicochemical and environmental plant physiology*. Academic Press, Inc; San Diego - New York - Boston - London - Sydney - Tokyo - Toronto: 1991.
- Peñaflor MFGV, Erb M, Miranda LA, Werneburg AG, Bento JMS. Herbivore-induced plant volatiles can serve as host location cues for a generalist and a specialist egg parasitoid. *J Chem Ecol*. 2011; 37:1304–1313. [PubMed: 22170346]

- Pichersky E, Gershenzon J. The formation and function of plant volatiles: perfumes for pollinator attraction and defense. *Curr Opin Plant Biol.* 2002; 5:237–243. [PubMed: 11960742]
- Pichersky E, Raguso RA, Lewinsohn E, Croteau R. Floral scent production in *Clarkia* (Onagraceae) .1. Localization and developmental modulation of monoterpene emission and linalool synthase activity. *Plant Physiol.* 1994; 106:1533–1540. [PubMed: 12232428]
- Richters S, Herrmann H, Berndt T. Gas-phase rate coefficients of the reaction of ozone with four sesquiterpenes at 295 +/- 2 K. *Phys Chem Chem Phys.* 2015; 17:11658–11669. [PubMed: 25866852]
- Sander R. Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmos Chem Phys.* 2015; 15:4399–4981.
- Schnitzler J-P, Louis S, Behnke K, Loivamäki M. Poplar volatiles – biosynthesis, regulation and (eco)physiology of isoprene and stress-induced isoprenoids. *Plant Biol.* 2010; 12:302–316. [PubMed: 20398237]
- Schuhfried E, Aprea E, Märk TD, Biasioli F. Refined measurements of Henry's Law Constant of terpenes with inert gas stripping coupled with PTR-MS. *Water Air Soil Pollut.* 2015; 226:120.
- Staudinger J, Roberts PV. A critical review of Henry's law constants for environmental applications. *Crit Rev Env Sci Tec.* 1996; 26:205–297.
- Staudinger J, Roberts PV. A critical compilation of Henry's law constant temperature dependence relations for organic compounds in dilute aqueous solutions. *Chemosphere.* 2001; 44:561–576. [PubMed: 11482643]
- Tholl D, Chen F, Petri J, Gershenzon J, Pichersky E. Two sesquiterpene synthases are responsible for the complex mixture of sesquiterpenes emitted from *Arabidopsis* flowers. *Plant J.* 2005; 42:757–771. [PubMed: 15918888]
- Toome M, Randjärv P, Copolovici L, Niinemets Ü, Heinsoo K, Luik A, Noe SM. Leaf rust induced volatile organic compounds signalling in willow during the infection. *Planta.* 2010; 232:235–243. [PubMed: 20419383]
- Valterova I, Kunze J, Gumbert A, Luxova A, Liblikas I, Kalinova B, Borg-Karlson A-K. Male bumble bee pheromonal components in the scent of deceit pollinated orchids; unrecognized pollinator cues? *Arthropod-Plant Interact.* 2007; 1:137–145.
- van Eijck A, Opatz T, Taraborrelli D, Sander R, Hoffmann T. New tracer compounds for secondary organic aerosol formation from beta-caryophyllene oxidation. *Atmos Environ.* 2013; 80:122–130.

Fig. 1.

Temperature dependencies of Henry's law constants (H_{pc} , $\text{Pa m}^3 \text{mol}^{-1}$) of different sesquiterpenes and bornyl acetate. Data were fitted by Eq. (5) to derive the enthalpy of vaporization (Table 1). All determinations were replicated three times, and the error bars provide $\pm$ SE.

Fig. 2.

Temperature dependencies of Henry's law constants (H_{pc} , $\text{Pa m}^3 \text{ mol}^{-1}$) of key plant sesquiterpenes. Data were fitted by Eq. (5) to derive the enthalpy of vaporization (Table 1). All determinations were replicated three times, and the error bars provide $\pm$ SE.

Table 1

Henry's law constants (H_{pc}) at 25 °C, corresponding enthalpies of volatilization and Q10 values for 12 studied sesquiterpene species (C15) and for monoterpene derivative bornyl acetate (C12)

Compound	Chemical structure	H_{pc} (Pa m ³ mol ⁻¹)	H_{vol} (kJ mol ⁻¹)	Q10
β -caryophyllene		2731±21 ^a	37.08±0.26	1.58
α -cedrene		3510±70 ^b	40.5±0.8	1.64
α -farnesene		2960±50 ^{ac}	35.7±0.5	1.54
α -humulene		3410±41 ^b	38.7±1.1	1.60
γ -gurjunene		3052±13 ^c	30.8±0.5	1.45
isosativene		2548±22 ^a	29.7±0.6	1.42

Compound	Chemical structure	H_{pc} (Pa m ³ mol ⁻¹)	H_{vol} (kJ mol ⁻¹)	Q10
α -longipinene		2960±50 ^a	34.01±0.43	1.52
α -neoclovene		3410±41 ^b	25.7±0.8	1.36
β -neoclovene		3415±6 ^b	38.5±0.9	1.58
γ -neoclovene		3421±16 ^b	26.3±0.8	1.36
nerolidol		3120±80 ^d	35.8±1.2	1.53
valencene		3090±140 ^d	37.2±0.9	1.56
bornyl acetate		2650±14 ^a	14.54±0.38	1.19

Data are averages $\pm$ SE (standard error of the mean) of three independent determinations. The atomic formulas of all sesquiterpenes are C₁₅H₂₄, except for nerolidol C₁₅H₂₆O. The atomic formula for bornyl acetate is C₁₂H₂₀O₂