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

Lucian Copolovici [a,b,*], Ülo Niinemets [b,c]

[a] Institute of Technical and Natural Sciences Research-Development of "Aurel Vlaicu" University, Elena Dragoi 2, Arad 310330, Romania
[b] Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, Kreutzwaldi 1, Tartu 51014, Estonia
[c] Estonian Academy of Sciences, Kohtu 6, 10130 Tallinn, Estonia

HIGHLIGHTS

- We studied the sesquiterpenes temperature dependences of Henry's law constants.
- At 25 °C Henry's law constants varied 1.4-fold among different sesquiterpenes.
- We demonstrate moderately variation in Henry's law constants temperature responses.

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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.

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 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, 2012; Arneth et al., 2008). 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, 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

* Corresponding author at: Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, Kreutzwaldi 1, Tartu 51014, Estonia.
E-mail address: lucian.copolovici@emu.ee (L. Copolovici).

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(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 pant 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 m^3 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, 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 C_{13} compound β-ionone and solubility of taxol (polyoxygenated diterpene) have been determined by Fichan et al. (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 m^3 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 Gossett (1987) as applied previously (Copolovici and Niinemets, 2005, 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 μL of given sesquiterpene was added to both vials using a 1 μL 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 Gossett (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 Eq. (2), the dimensionless Henry's law constant ($H_{cc} = \frac{C_{G1}}{C_{L1}} = \frac{C_{G2}}{C_{L2}}$) is given as:

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