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Emissions of monoterpenes linalool and ocimene respond differently to environmental changes due to differences in physico-chemical characteristics

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Abstract

We investigated the ^{13}C-labeling kinetics of the emission of two major monoterpenes emitted by needles of Mediterranean conifer *Pinus pinea* L., monoterpene alcohol linalool and non-oxygenated monoterpene *trans*-β-ocimene. These data were further used to develop and parameterize a dynamics monoterpene emission model, predicting the emissions of monoterpenes with contrasting physico-chemical properties to environmental changes. All monoterpenes emitted were labeled by ^{13}C in short pulse-labeling experiments. ^{13}C-labeling experiments further indicated for these two monoterpenes comprising 77% of total emissions that a major part of the emissions of these two monoterpenes relied on recently synthesized carbon not on specific storage compartments within the resin ducts. However, labeling kinetics suggested existence of transient storage pools, located within the needle aqueous and lipid phases. For linalool, we found half-lives of 13 min for the aqueous phase storage and 3 h for the lipid phase while *trans*-β-ocimene exhibit an aqueous phase half-life of 2 and 15 min for the lipid phase, overall indicating that the transient storage due to limited monoterpene volatility can significantly alter the emission dynamics. The key physico-chemical characteristics determining the time constants of the transient storage pools were the Henry's law constant (liquid/gas phase partition coefficient) and the octanol/water (lipid/liquid) phase partition coefficient. As monoterpene Henry's law constants vary over four orders of magnitude and octanol/water partition coefficients over three orders of magnitude, the capacity for non-specific storage, and damping of the effects of rapidly changing environmental conditions is expected to strongly vary among different monoterpenes. Overall, our study suggests that non-specific storage due to limited volatility is a common phenomenon of common of plant-emitted compounds.

Keywords: ^{13}C-labeling; Monoterpene emissions; Henry's law constant; Octanol/water partition coefficient; Dynamic model; *Pinus pinea*

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1. Introduction

Emissions of monoterpenoids by plants constitute a major source of volatile organic compounds (VOC) in the atmosphere (Guenther et al., 2000; Guenther et al., 1994; Tingey et al., 1991). Because volatile compounds play a major role in tropospheric chemistry, in particular in ozone-generating reactions and as condensation nuclei of secondary aerosol formation (Chameides et al., 1988; Fuentes et al., 2000; Kulmala et al., 2004), considerable effort has been made towards measuring and predicting monoterpenoid emission rates from plant foliage (Guenther et al., 2000).

While many studies have focused on the biochemical synthesis of monoterpenoids (Gershenzon and Croteau, 1993; Lichtenthaler, 1999; Lichtenthaler et al., 1997) and their changes due to environmental factors and stress response (Bertin and Staudt, 1996; Fischbach et al., 2002; Loreto et al., 2001; Staudt et al., 2000), much less is known about the biophysics of monoterpenoid emissions. Environmental factors, such as light, temperature or air humidity for instance, affect directly the monoterpene emissions via changes in the rates of synthesis, and also indirectly via alternations in physico-chemical properties of monoterpenes. In many species, the rates of monoterpene synthesis are dependent on light similarly to carbon assimilation (Schuh et al., 1997; Shao et al., 2001; Tarvainen et al., 2005). This suggests that the emitted monoterpenes rely on a small pool of immediately assimilated carbon, especially in species without specific storage pools such as resin ducts or oil glands (Staudt et al., 1997). Even for species with extensive monoterpene storage pools in resin ducts such as conifers, monoterpene emissions often exhibit a light-dependent emission pattern (Bäck et al., 2005; Janson, 1993; Kesselmeier and Staudt, 1999; Shao et al., 2001; Staudt et al., 1997).

Fumigation experiments with non-emitting species (Delfine et al., 2000) and emissions from darkened leaves of terpene emitting species like *Quercus ilex*, that do not possess specific storage pools (Loreto et al., 2000b), have yielded evidence that 'non-specific' storage pools are present in leaves. Monoterpene emission from terpene-fumigated leaves in non-emitting species are measurable for more than 12 h after the fumigation (Delfine et al., 2000). Darkened leaves, in which the monoterpene synthesis rate is expected to be zero, are also capable of prolonged emissions (Loreto et al., 2000b). This evidence collectively demonstrates that even leaves in species without specific storage compartments have a significant capacity for monoterpene storage.

Previous model studies suggest that the magnitude of these 'non-specific' storage pools can be linked to physico-chemical characteristics of the emitted compounds (Niinemets et al., 2004; Niinemets and Reichstein, 2002). The correlation of the compound physico-chemical properties with the model time constants of the proposed 'non-specific' storage pools suggests that the compounds are located in the leaf aqueous and lipid phases. Thus, the overall capacity of storage and emission dynamics can be described by the compound water solubility, given by Henry's law constant (H), and the solubility of the compound in the lipid phase (octanol/water partition coefficient, $K_{O/W}$). Depending on physico-chemical monoterpene characteristics, emissions of monoterpenes can also be controlled by stomatal conductance, affecting the gas-phase transfer resistance between the leaf substomatal cavities and the atmosphere (Niinemets and Reichstein, 2003b; Niinemets et al., 2002a).

In this study, we used ^{13}C-labeling to demonstrate that the emissions of two major monoterpenes emitted by needles of Mediterranean conifer *Pinus pinea* L., linalool and *trans*-β-ocimene, mostly rely on a recently synthesized pool of monoterpenes rather than the emission flux from the resin ducts. We further use a dynamic monoterpene emission model that combines the approaches of Niinemets and Reichstein (2002, 2003b) and Niinemets et al. (2002a) to demonstrate that non-specific storage of monoterpenes in leaf aqueous and liquid pools can importantly modify the responses of emission rates to rapidly changing environmental drivers such as light and temperature. In particular, (a) parameters of the time constants for the aqueous and lipid phase storage pools were obtained, and empirical monoterpene leaf/atmosphere partition coefficients were derived. (b) Effects of changes in H and $K_{O/W}$ to the time constants were investigated. (c) The impact of changes in stomatal conductance and monoterpene production rates on the emission pattern were predicted. The monoterpene alcohol linalool and non-oxygenated monoterpene *trans*-β-ocimene have widely differing physico-chemical characteristics allowing us to make generalizations of the overall influence of non-specific storage of emission dynamics for the range of chemically divergent monoterpenes emitted by plants.