Estimating Terpene and Terpenoid Emissions From Conifer Oleoresin Composition

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A B S T R A C T

The following algorithm, which is based on the thermodynamics of nonelectrolyte partitioning, was developed to predict emission rates of terpenes and terpenoids from specific storage sites in conifers:

$$E_i = x_{or}^i \gamma_{or}^i p_i^\circ$$

where E_i is the emission rate ($\mu\text{g C gdw}^{-1} \text{ h}^{-1}$) and p_i° is the vapor pressure (mm Hg) of the pure liquid terpene or terpenoid, respectively, and x_{or}^i and γ_{or}^i are the mole fraction and activity coefficient (on a Raoult's law convention), respectively, of the terpene and terpenoid in the oleoresin. Activity coefficients are calculated with Hansen solubility parameters that account for dispersive, polar, and H-bonding interactions of the solutes with the oleoresin matrix. Estimates of p_i° at 25°C and molar enthalpies of vaporization are made with the SIMPOL.1 method and are used to estimate p_i° at environmentally relevant temperatures. Estimated mixing ratios of terpenes and terpenols were comparatively higher above resin-acid- and monoterpene-rich oleoresins, respectively. The results indicated a greater affinity of terpenes and terpenols for the non-functionalized and carboxylic acid containing matrix through dispersive and H-bonding interactions, which are expressed in the emission algorithm by the activity coefficient. The correlation between measured emission rates of terpenes and terpenoids for *Pinus strobus*

and emission rates predicted with the algorithm were very good ($R = 0.95$). Standard errors for the range and average of monoterpene emission rates were $\pm 6 - \pm 86\%$ and $\pm 54\%$, respectively, and were similar in magnitude to reported standard deviations of monoterpene composition of foliar oils ($\pm 38 - \pm 51\%$ and $\pm 67\%$, respectively).

Keywords: Terpenes; Terpenoids; conifer oleoresin; Biogenic volatile organic compound (BVOC) emissions

1. Introduction

About 90% of reduced carbon emissions to the global troposphere ($1000 \pm 600 \text{ Tg C a}^{-1}$) are attributed to biogenic volatile organic compounds (BVOCs; Guenther et al. 1995; Kanakidou et al. 2005). The BVOCs are rapidly photooxidized and form secondary organic aerosol (SOA; Kulmala et al., 2004). The SOA are the most abundant fine particle in the global troposphere and are hydrophilic making the aerosol effective at scattering light and forming clouds, which increases albedo and cools the atmosphere. Emissions of terpenes and terpenoids (i.e., oxygen-containing terpenes) from coniferous forests are one of the principal sources of BVOCs (Helmig et al., 2007); however, considerable uncertainty exists in developing emission inventories.

Emission factors for vegetation like conifers that accumulate terpenes and terpenoids in specialized storage tissues within leaves have been developed for many species through measurement of emission rates under various environmental conditions (Ortega et al., 2008). The emission factors are used in models to derive plant-specific emission inventories (Geron et al., 2000; Guenther et al., 2012). The monoterpene emission algorithm for specific storage tissues is based on evaporation and diffusion from the storage site (Tingey et al., 1980; Guenther et al., 1991, 1993; Geron et al., 1994). Emission rates are scaled to an emission factor determined at a standard leaf temperature and are predicted to increase

exponentially with temperature via an emission coefficient in a manner similar to monoterpene vapor pressure. Compilations of emission factors and coefficients, which are empirically derived from measurements of emission rates, indicate the values are likely characteristic of the species of vegetation (Guenther et al., 1993; 1994). However, monoterpene emission rates are jointly regulated by synthesis and volatility of the chemical species (Niinemets et al., 2010) and are typically greater than rates predicted by changes in monoterpene vapor pressure with temperature.

Conifer oleoresins, which are synthesized by many plant organs and stored in secretory cells, cavities, canals, or glands, are composed of a volatile mixture of monoterpenes, monoterpenoids, sesquiterpenes, sesquiterpenoids and the less volatile diterpenes and diterpenoic acids (Langeheim, 2003; Zulak and Bohlmann 2010). Here, in referring to terpenoids, we do not include terpenoic acids. Composition of conifer oleoresins varies with taxonomy, phenology and age, and biotic and abiotic stresses (see, e.g., Flores, 2013), which is the reason emission factors and coefficients can vary significantly for the same species of conifer (Litvak et al., 1999; Hakola et al., 2006; Holzke et al., 2006). Terpenes and terpenoids are emitted from foliage and the stems and bole of conifers via resin blisters and induction of traumatic resin ducts by herbivore and pathogen infestations (Martin et al., 2002). Resin ducts or glands in foliage are distinct from the series of ducts in stems and the bole of the tree (Jeffrey, 1925; Hanes, 1927; Roller, 1966; Suzuki, 1979). Thus, terpenes and terpenoids are emitted from conifers (1) by exhalation from foliage stomata and (2) through evaporation from resin blisters and traumatic resin ducts on the bole of the tree.

Resin canals in conifer foliage are embedded in the mesophyll tissue that is immersed in the apoplastic fluid, which is a complex mixture of organic and inorganic electrolytes (i.e., amino acids and salts, respectively) and neutral organic compounds (i.e, sugars) (Canny, 1995; Lohaus et al., 2001). Terpenes and terpenoids diffuse from specific storage sites containing foliar oleoresin through the mesophyll into intercellular airspaces and through the substomatal cavity that is located proximal to the stoma. Cortical

oleoresins rise to the surface of conifer stems and the bole and evaporate directly into the atmosphere from blisters or traumatic resin ducts. Compositions of foliar and cortical oleoresins from *Abies magnifica* and *Picea sitchensis* are distinct during the first 25 years of growth and become similar in the oldest branches (Zavarin, 1968; Hrutfiord et al., 1974). Signatures of foliar oleoresins of *Picea glauca* vary dramatically with phenology during the first year of growth and are invariant in mature foliage (von Rudloff, 1972).

Here we propose a new algorithm that is based on thermodynamics of nonelectrolyte partitioning to estimate terpene and terpenoid emissions from physicochemical properties and conifer oleoresin composition. Chemical potentials (μ) of solutes in all phases of multiphase systems like foliar tissue are identical at equilibrium for constant temperature and pressure. Chemical potentials are expressed relative to some arbitrary reference state, and thus, calculating chemical potentials of solutes in various phases is not particularly useful. Conceptually, the fugacity (f) of a solute in a phase is closely linked to pressure and is directly related to μ by the relation, $(d\mu = RT \ln f)_T$, and thus, fugacity can be used as a criterion to define equilibrium (Thibodeaux, 1996; Prausnitz et al., 1999). If the rate of partitioning of some terpenes and terpenoids between phases in foliage and the bole of the tree is rapid relative to the time required to attain equilibrium, an algorithm based on thermodynamics is suitable for estimating emission rates.

Similarities between the monoterpene emission algorithm and the Clausius-Clapeyron equation are discussed and a new algorithm for estimating emission rates of some terpenes and terpenoids from conifers is presented. Emission fugacities for specific storage sites are derived for an oleoresin with high monoterpene and resin acid contents to illustrate effects of oleoresin composition on emission fugacities of terpenes and terpenoids. Measurements of oleoresin composition and foliar emissions from the same species of tree are few. We use the average terpene and terpenoid composition of foliar extracts of *Pinus strobus* reported by Toma and Bertman (2012) as the measured molar composition of foliar oils, estimate emissions from the oleoresin composition, and compare with measurements of foliar emissions from

Pinus strobus reported by Ortega et al. (2008). Both investigations were conducted at the University of Michigan Biological Station (UMBS) in Pellston, Michigan.

2. Methods

Emission fugacities are estimated for α -pinene, germacrene D, and germacrene D-4-ol, which were 3 of the most abundant terpenes and terpenoids isolated from foliar oils of *Pinus strobus* at UMBS over a 3-yr period (Toma and Bertman, 2012). α -Terpineol was not reported; however, the chemical species was one of the more abundant monoterpenols reported by Yatagai and Sato (1986) in foliar oils of *Pinus strobus* and is the value used in the subject study. Molar compositions of the foliar oils were used to determine mole fractions of terpenes and tepenoids. Essential oil of *Pinus strobus* contains primarily monoterpenes and resin acids, which comprise an average of 25% and 75%, respectively, of the oleoresin (Mirov, 1961). Foliar oil composition was converted to oleoresin composition by multiplying the chemical species composition in mole fraction by the average yield of essential oil from oleoresin. Molar composition of cortical oleoresin of *Pinus strobus* has not been reported; however, comprehensive analysis of *Abies magnifica* and *Picea sitchensis* (Zavarin, 1968; Hrutfiord et al., 1974) indicates foliar and cortical oleoresin compositions are distinct within the first 25 years of growth and become similar thereafter. Foliar and cortical oleoresin compositions were assumed equal for the subject study.

Measurements of foliar emissions from *Pinus strobus* (Ortega et al., 2008) were converted to mole fraction to compare with estimates based on oleoresin composition. Foliar emissions are typically measured by monitoring the change in mixing ratio of the chemical species (vol chemical species vol⁻¹ of air) in an enclosure containing the live branch of a tree. Emission measurements are reported as mass of chemical species (or carbon equivalent) per mass of foliar dry weight per time. Ortega et al. (2008) report seven

measurements of the foliar emissions ($\mu\text{g C gdw}^{-1} \text{ hr}^{-1}$) of total and individual terpenes and terpenoids from *Pinus strobus*. We divided emission rates of individual terpenes and terpenoids on a mole basis by the sum of the emission rates of the total terpenes and terpenoids on a mole basis to derive the mole fraction of terpenes and terpenoids in the emissions. Assuming the terpene and terpenoid vapors act as ideal gases, the product of the mole fraction and the total pressure is the partial pressure and is equivalent to the mixing ratio via the ideal gas law.

2.1. Fugacity of the Foliar Emission Pathway

The monoterpene emission algorithm for specific storage tissues is as follows (Tingey et al., 1980; Guenther et al., 1991, 1993; Geron et al., 1994):

$$\ln(E_i) = \beta_i(T_i - T_s) + \ln(E_{si}) \quad (1)$$

where E_i is the emission rate ($\mu\text{g C gdw}^{-1} \text{ h}^{-1}$) at leaf temperature T_i (K), E_{si} is an emission factor ($\mu\text{g C gdw}^{-1} \text{ h}^{-1}$) that is E_i normalized to the leaf temperature T_s (303 K), and β_i (K^{-1}) is an emission coefficient.

Resin ducts in foliage, which are the specific storage tissues of the monoterpenes, are located in the mesophyll that is immersed in apoplastic fluid containing a mixture of electrolytes and sugars.

Intercellular airspaces connect the mesophyll to the substomatal cavity. Terpenes and terpenoids are in a dynamic equilibrium between oleoresin, apoplastic fluid, the mesophyll, and air in the substomatal cavity and fugacities of chemical species in all phases are equal at equilibrium. The fugacity of a pure liquid terpene or terpenoid in equilibrium with pure water is given by the following:

$$f_{A3} = x_{A3}\gamma_{A3}f_{A3}^{\circ} = x_{A2}\gamma_{A2}f_{A2}^{\circ} = f_{A2} \quad (2)$$

where f_{A3} and f_{A2} are fugacities of the pure liquid solute and water, respectively, x_{A3} is the mole fraction of the pure liquid solute (which is assumed to contain a negligible amount of water, and thus, the value is 1), x_{A2} is the mole fraction of the pure liquid solute in pure water, γ_{A3} is the activity coefficient (on a Raoult's law convention) of the pure liquid solute (which is a pure liquid, and thus, the value is 1), γ_{A2} is the activity coefficient (on a Raoult's law convention) of the pure liquid solute in pure water, and f_{A3}^o and f_{A2}^o are reference fugacities of the pure liquid solute and pure liquid solute in water, which by definition are the vapor pressure of the pure liquid solute. Conventions for subscripts are as follows: the letter designates the chemical species and numerals 1, 2, 3, and 4 designate the phases, which are air, water, pure liquid solute, and oleoresin, respectively.

For a pure liquid solute in equilibrium with pure water Eq. (2) reduces to the following:

$$\gamma_{A2} = \frac{1}{x_{A2}} \quad (3)$$

The relationship between the activity coefficient and the mole fraction of a pure solute in pure water is as follows (Acree, 1984):

$$\ln \gamma_i = K(1 - x_i)^2 \quad (4)$$

where K is a constant that is a function of the solute. Many nonelectrolytes like the terpenes and terpenoids are sparingly soluble in water, and thus, x_i is much less than 1 and γ_i is not proportional to concentration and instead approaches a constant value (e^K). Thus, activity coefficients (on a Raoult's law convention) for many non-electrolytes can be calculated as follows:

$$\gamma_{A2} = \frac{1}{x_{A2}^o} \quad (5)$$

where x_{A2}^o is the aqueous solubility of the liquid solute (on a mole fraction basis).

Activities of terpenes and terpenoids in the apoplastic fluid, which contains a mixture of electrolytes and sugars, are related to the aqueous solubility as follows:

$$a_{A2*} = \gamma_{A2*} c_{A2}^o \quad (6)$$

where a_{A2*} and γ_{A2*} are the activity and activity coefficient (on a Henry's law convention) of the substance in the apoplastic fluid, respectively, and c_{A2}^o is the aqueous solubility (mol m^{-3}) of a sparingly soluble, nonelectrolyte like a terpene or terpenoid. Values of γ_{A2*} are sensitive to the electrolyte and non-electrolyte composition of the apoplastic fluid. Setschenow (1889) developed the following empirical relationship that can be used to describe the effect of added salt on solute solubility:

$$\log\left(\frac{\gamma}{\gamma_0}\right) = \log\left(\frac{S_0}{S}\right) = k_s C_s \quad (7)$$

where γ_0 and γ are the solute activity coefficients (on a Henry's law convention) for the solute in water and saline solution, S_0 and S are the solute solubility in water and saline solution, respectively, k_s is the Setschenow constant, and C_s is the total salt concentration (expressed as molality) in solution. The value of γ_0 for pure water is 1.0 and for dilute solutions like apoplastic fluids Eq. (7) is rewritten as follows:

$$\log \gamma_{A2*} = k_s C_s \quad (8)$$

where C^* is the concentration (M) of electrolytes and non-electrolytes in the apoplastic fluid.

Copolovici and Niinemets (2007) evaluated salting-out and salting-in effects of apoplastic electrolytes and sugars, respectively, on limonene and linalool partitioning from water into air and octanol to derive values of k_s . Activities of nonelectrolytes like limonene and linalool are expected to be greater than solubilities in apoplastic fluids containing electrolytes due to the salting-out effect, and thus, values of γ_{A2^*} for nonelectrolytes like limonene and linalool in apoplastic fluids composed of electrolytes would be greater than 1. However, in apoplastic fluids containing nonelectrolytes like sugars, activities of limonene and linalool are expected to be less than the solubilities in apoplastic fluids due to the salting-in effect and values of γ_{A2^*} would be less than 1. Copolovici and Niinemets (2007) reported salting-out coefficients for limonene and linalool were 0.0231 and 0.167, respectively, in aqueous solutions of potassium chloride at 30°C and average salting-in coefficients for limonene and linalool in aqueous solutions of glucose and sucrose were -1.0159 and -0.0173, respectively. Lohaus et al. (2001) reported average levels of 32.3 and 4.3 mM of inorganic electrolytes and sugars, respectively, in apoplastic fluids of several agricultural crops. At these concentrations, values of γ_{A2^*} calculated for terpenes and terpenoids in apoplastic fluids using Eq. (8) are 1.0, and thus, activities of the terpenes and terpenoids in the apoplastic fluid are equivalent to aqueous solubilities [Eq. (6)]. If values of γ_{A2^*} (on a Henry's law convention) for the terpenes and terpenoids in apoplastic fluids are 1.0, then values of γ_{A2} (on a Raoult's law convention) do not require a correction for salting-in or -out effects.

The equilibrium condition for terpenes and terpenoids in the oleoresin with the apoplastic fluid is represented as follows:

$$f_{A4} = x_{A4}\gamma_{A4}f_{A4}^o = x_{A2^*}\gamma_{A2}f_{A2}^o = f_{A2^*} \quad (9)$$

where f_{A4} , x_{A4} , γ_{A4} , and f_{A4}° are the fugacity, mole fraction, activity coefficient, and reference fugacity, respectively, of the individual terpenes and terpenoids in the oleoresin and f_{A2}^* and x_{A2}^* are the fugacity and mole fraction of the individual terpenes and terpenoids in the apoplastic fluid. Reference fugacities, f_{A4}° and f_{A2}° , are defined as the vapor pressure of the pure liquid solute. Combining Eqs. (9) and (5) and replacing mole fraction by molar concentration results in the following:

$$c_{A2^*} = x_{A4} \gamma_{A4} c_{A2}^\circ \quad (10)$$

where c_{A2^*} is the concentration (mol m^{-3}) of a terpene or terpenoid in the apoplastic fluid and c_{A2}° is the aqueous solubility (mol m^{-3}). The molar concentration is proportional to the mole fraction in dilute solutions like the apoplastic fluid, and thus, mole fractions are replaced by molar concentrations in Eq. (10).

Terpenes and terpenoids that dissolve in the apoplastic fluid will partition to the aqueous environment of the mesophyll, which is in contact with intercellular airspaces leading to the substomatal cavity. Assuming dissolution in octanol and the mesophyll are similar, the concentration of the chemical species in octanol is calculated as follows:

$$c_{AO} = c_{A2^*} K_{OW} \quad (11)$$

where c_{AO} is the concentration (mol m^{-3}) of the substance in octanol and K_{OW} is the dimensionless octanol/water partition coefficient ($\text{vol water vol}^{-1} \text{ octanol}$). If the substance were partitioning directly from the apoplastic fluids to the intercellular airspace, the concentration of the substance in the intercellular airspace would be calculated as follows:

$$c_{AIF} = c_{A2*} K_{AW} \quad (12)$$

where c_{AIF} is the concentration in the substomatal cavity of foliage (mol m^{-3}) and K_{AW} is the dimensionless Henry's law constant ($\text{vol water vol}^{-1} \text{ air}$). Dividing Eq. (12) by Eq. (11) is the definition of the dimensionless air/octanol partition coefficient (K_{AO} , $\text{vol octanol vol}^{-1} \text{ air}$), which is ratio of concentration of chemical species in air and octanol. Thus, at equilibrium in the 3-phase system (i.e., apoplastic fluid, the aqueous environment of the mesophyll, and airspace of the substomatal cavity) fugacities of the chemical species in the phases are equal, and c_{AIF} is essentially governed by Eq. (12). Making the substitution for c_{A2*} given by Eq. (10) into Eq. (12) and converting c_{AIF} to mole fraction results in the following expression that is used to calculate the mole fraction of the substance above the mesophyll in the substomatal cavity:

$$y_{AIF} = \frac{x_{A4} \gamma_{A4} c_{A2}^o K_{AW} RT}{P} \quad (13)$$

where y_{AIF} is the mole fraction of the terpene or terpenoid in the substomatal cavity, R is the ideal gas law constant ($8.314 \text{ Pa m}^3 \text{ K mol}^{-1}$) and T and P are the temperature and total pressure, respectively (assumed to be 298.15 K and $1.01325 \times 10^5 \text{ Pa}$ for the subject study). Mole fractions of the terpenes and terpenoids in the substomatal cavity are the same as partial pressures, which are equivalent to mixing ratios of the chemical species (vol vol^{-1}), when P is expressed in atm.

2.2. Fugacity of the Bole Emission Pathway

Terpenes and terpenoids evaporate from resin blisters and traumatic resin ducts on the bole of the tree directly into the atmosphere and are estimated from the composition of the oleoresin and species vapor pressure as follows:

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$$282 \quad y_{A1B} = \frac{x_{A4} \gamma_{A4} P_A^{\circ}}{P} \quad (14)$$

283

284 where y_{A1B} is the mole fraction of a terpene and terpenoid in air above resin blisters and traumatic resin
 285 ducts on the bole of the tree. Dividing the fugacity of terpenes or terpenoids above resin blisters and
 286 traumatic resin ducts by the fugacity of terpenes or terpenoids in the substomatal cavity of foliage, which
 287 is represented by Eq. (13), results in the following:

288

$$289 \quad \frac{y_{A1B}}{y_{A1F}} = \frac{P_A^{\circ}}{c_{A2}^{\circ} K_{AW} RT} \quad (15)$$

290

291 At infinite dilution, partitioning of the terpenes and terpenoids between air and the apoplastic fluids is
 292 governed by Henry's law, which is the ratio of p_A° to c_{A2}° when the aqueous solubility of the chemical
 293 species is $< 1 \times 10^4$ M (Mackay and Shiu, 1981). The ratio, $p_A^{\circ} / c_{A2}^{\circ}$ is the Henry's law constant (H ; Pa
 294 $\text{m}^3 \text{mol}^{-1}$) that is equivalent to $K_{AW} \times RT$, and thus, fugacities of terpenes and terpenoids for the foliar and
 295 bole pathways are identical. Thus, Eq. (14) can be used to calculate emission fugacities for terpenes and
 296 terpenoids when the foliar and cortical oleoresin compositions are the same and the rate of partitioning of
 297 the terpenes and terpenoids between phases in foliage and the bole of the tree is rapid relative to the time
 298 required to attain equilibrium.

299

300 *2.3. Activity Coefficients of Terpenes and Terpenoids in Oleoresin*

301

302 Values of activity coefficients for terpenes and terpenoids in oleoresin matrices [γ_{A4} in Eq. (13)] were
 303 derived using Hansen solubility parameters (Hansen, 2007). The parameters include contributions from
 304 dispersive, polar, and H-bonding interactions between the solute and polymer matrix and are designated

as δ_d , δ_p , δ_h , respectively. Structural contributions (Hansen, 2007) were used to estimate molar volumes and solubility parameters for terpenes, terpenoids, and 2 oleoresin matrices (Table 1). Activity coefficients for terpenes and terpenoids in oleoresin were estimated as follows (Hansen, 2007):

$$\ln \gamma_{or}^i = \frac{V_i}{RT} \left[(\delta_d^{or} - \delta_d^i)^2 + 0.25(\delta_p^{or} - \delta_p^i)^2 + 0.25(\delta_h^{or} - \delta_h^i)^2 \right] + \left[\ln \left(\frac{V_i}{V_{or}} \right) + 1 - \frac{V_i}{V_{or}} \right] \quad (16)$$

where γ_{or}^i is the activity coefficient for the terpene or terpenoid in the oleoresin, V_i and V_{or} are molar volumes of the terpene or terpenoid and oleoresin ($\text{cm}^3 \text{ mol}^{-1}$), respectively, and RT is 592 cal mol^{-1} at 298.15 K . Hypothetical oleoresin matrices were selected to demonstrate effects of oleoresin composition on emission fugacities. Analyses of several species of *Pinus* indicate mole fractions of monoterpenes and resin acids in oleoresin (x_{MT} and x_{RA} , respectively) are about 0.20 and 0.80 (Mirov, 1961). Molecular analyses of the cortical oleoresin of *Pinus contorta* (Lewinsohn et al., 1993) indicate α -pinene and levopimaric acid are the principal monoterpene and resin acid in the oleoresin. Hypothetical oleoresins with a high monoterpene content (OR_{MT} ; 80% α -pinene and 20% levopimaric acid) and resin acid content (OR_{RA} ; 20% α -pinene and 80% levopimaric acid) were selected as model cases and values of γ_{or}^i were estimated with Eq. (14) (Table 1). Values of γ_{or}^i estimated with the universal functional group activity coefficient (UNIFAC) model (Fredenslund et al., 1975; Hansen et al., 1991) were similar.

3. Results and discussion

3.1. Effects of Oleoresin Composition on Emission Fugacities

Mixing ratios of the non-functionalized terpenes, α -pinene and germacrene D, above oleoresin with an 80% resin acid content were 19% and 55% higher, respectively, than the mixing ratios above oleoresin with a 80% monoterpene content (Fig. 1). Averages of the activity coefficients of monoterpenes and sesquiterpenes in the nonpolar, monoterpene-rich oleoresin, with the exception of myrcene, were 1.03 and 1.05, respectively, and 1.26 and 2.11, respectively, in the polar, resin-acid-rich oleoresin (Table 1). The activity coefficient of myrcene, which lacks a cyclic moiety, was 1.31. The results indicate the non-polar, terpene solutes were more soluble in the monoterpene-rich oleoresin, which was similar in structure and functionality. Dispersive interactions contributed 74% of the total interactions (i.e., Σ dispersive, polar, and H-bonding) involved in solubility of terpenes in the monoterpene-rich oleoresin. Mixing ratios of germacrene D above the resin acid-rich oleoresin compared to the monoterpene-rich oleoresin were much greater than α -pinene, which demonstrates the effect of solute molecular size on solubility.

Mixing ratios of the terpenols, α -terpineol and germacrene D-4-ol, above oleoresin with an 80% monoterpene content were 58% and 10%, higher, respectively, than the mixing ratios above oleoresin with an 80% resin acid content (Fig. 1). α -Terpineol exhibited a greater disparity between activity coefficients for the monoterpene- and resin-acid-rich oleoresin than germacrene D-4-ol, which explains higher mixing ratios of α -terpineol than germacrene D-4-ol above the monoterpene-rich oleoresin relative to the resin-acid-rich oleoresin. Contributions of H-bonding interactions to the total interactions involved in the solubility of α -terpineol and germacrene D-4-ol were 33.4 and 31.2, respectively (Table 1), which explains the relatively lower mixing ratios above the resin-acid-rich oleoresin that contained a carboxylic acid moiety.

3.2. Emission Rate Algorithm

The correlation between emissions of terpenes and terpenoids from *Pinus strobus* and the mole fraction in foliar oleoresin was very good ($R = 0.92$), with the exception of myrcene, camphene, and germacrene D (Fig. 2). Emission rates are estimated by measuring the change in partial pressure (or mixing ratio) of the terpene or terpenoid within an enclosure containing the branch of a live tree. Thus, emission rates should be related to oleoresin composition and solute vapor pressure via Eq. (14) provided the rate of partitioning of terpenes and terpenoids between phases in foliage and the bole of the tree is rapid relative to the time required to attain equilibrium.

The Clausius-Clapyeron equation relates changes in the vapor pressure of a liquid solute with temperature to the molar enthalpy of vaporization and is written as follows:

$$p_i^o = A \exp\left(-\frac{\Delta H_{vi}}{RT}\right) \quad (17)$$

where p_i^o is the vapor pressure of the liquid solute, A_i is a constant related to the boiling point at atmospheric pressure (i.e., the normal boiling point), ΔH_{vi} (kJ mol^{-1}) is the molar enthalpy of vaporization of the liquid solute at temperature T (K), and R ($8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$) is the ideal gas law constant. Over relatively small temperature ranges, ΔH_{vi} can be assumed to be a constant and the integrated form of the Clausius-Clapyeron equation can be written as follows:

$$\ln p_{i2}^o = \frac{\Delta H_{vi}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + \ln p_{i1}^o \quad (18)$$

Values of ΔH_{vi} and p_i^o at 25°C for the terpenes and terpenoids, which were estimated by the SIMPOL.1 method (Pankow and Asher, 2008), are presented in Table 2.

Similarities exist between the monoterpene algorithm [Eq. (1)] and the integrated form of the Clausius-Clapyeron equation [Eq. (18)]. The monoterpene algorithm is empirically derived and relates monoterpene emission rate, which is a measure of the change in partial pressure (or mixing ratio) of the monoterpene emitted by vegetation over time, to temperature. However, the Clasius-Clapyeron equation expresses the relationship between vapor pressure of a liquid solute and temperature. Tingey et al. (1991) observed a correlation between monoterpene vapor pressure and emission rate when expressed as mm Hg and $\mu\text{g C gdw}^{-1} \text{ h}^{-1}$, respectively. The average value of β for α -pinene emitted from 7 species of *Pinus* reported by Guenther et al. (1993) was 0.099 ± 0.021 ($\pm 21\%$). Geron et al. (1994) report a value of $3.0 \mu\text{g C gdw}^{-1} \text{ h}^{-1}$ for E_s for *Pinus*. A graph of $\ln E$ and p° versus T^I for α -pinene using the average and range of β values and E_s (Fig. 3) demonstrates the relationship observed by Tingey et al. (1991). When values of E for α -pinene at 25°C and 20°C are estimated with Eq. (1) using the widest range of β values and a single value of E_s , the estimates vary by 22% and 43%, respectively.

The partial pressure of a terpene or terpenoid in equilibrium with oleoresin is given by the following:

$$p_i = x_{or}^i \gamma_{or} p_i^\circ \quad (19)$$

where p_i and p_i° are the partial and vapor pressure, respectively, and x_{or}^i is the mole fraction of the pure liquid solute in the oleoresin. The vapor pressure of the oleoresin is the sum of the partial pressures of the pure liquid solutes in the oleoresin as follows:

$$p_{OR}^\circ = \sum_{i=1}^n x_{or}^i \gamma_{or} p_i^\circ \quad (20)$$

where p°_{OR} is the vapor pressure of the oleoresin and n is the number of terpenes and terpenoids in the oleoresin. The value of E_S is essentially the partial pressure of the terpene or terpenoid at 30°C, which is a fraction of p°_i also at 30°C that is determined by x^i_{or} and interactions of the solute with oleoresin quantified by γ^i_{or} . Unlike A_i in the Clausius-Clapeyron equation [Eq. (17)], E_S for a terpene or terpenoid will vary by conifer species and oleoresin composition. Thus, estimates of E using Eq. (1) and a single value of E_S to represent all *Pinus* species are thermodynamically inaccurate.

Data from measurements of emission rates of several monoterpenes as a function of *Pinus elliotii* needle temperature (Tingey et al., 1980) are plotted with monoterpene vapor pressures in Fig. 4. Structures of α -pinene and β -pinene are very similar, and thus, estimates of ΔH_{vi} and p°_i were the same (Table 2). Lines for vapor pressures and emission rates are nearly parallel, with the exception of α -pinene/ β -pinene that exhibits some deviation above 30°C. Slopes of the lines that relate vapor pressures of α -pinene/ β -pinene and myrcene to temperature are equal to $\Delta H_{vi} R^{-1}$ via Eq. (18). Values of ΔH_{vi} for α -pinene/ β -pinene and myrcene are 54.2 and 56.3 kJ mol⁻¹, respectively. Products of the slopes of the lines for emission rates of α -pinene, β -pinene, and myrcene and R are 50.3, 57.7, and 57.3 kJ mol⁻¹, respectively, which are within ± 7.6 , ± 6.2 , and $\pm 1.7\%$ of the estimated values of ΔH_{vi} for the monoterpenes (Table 2). The analysis indicates β in Eq. (1) is specific to the terpene or terpenoid and not to the species of vegetation. Lines for the monoterpene emissions rates have unique y-intercepts that are related to oleoresin composition through x_{i4} and γ_{i4} , which together with p°_i determine p_i . Thus, emission rates of terpenes and terpenoids from oleoresin should be related to the pure liquid solute vapor pressure as follows:

$$E_i = x^i_{or} \gamma^i_{or} p^{\circ}_i \quad (21)$$

where E_i and p°_i are the emission rate ($\mu\text{g C gdw}^{-1} \text{ h}^{-1}$) and vapor pressure (mm Hg) of the pure liquid solute, respectively.

Data for terpene and terpenoid composition of foliar oils from *Pinus strobus* (Toma and Bertman, 2012) and essential oil content of oleoresin (Mirov, 1961) were used to predict x_{or}^i . Values of γ_{or}^i and p_i° at 30°C were estimated using Eq. (16) and Eq. (18), respectively, and were used in Eq. (21) to predict emission rates at 30°C (Table 2). Ortega et al. (2008) report measurements of terpene and terpenoid emissions (normalized to 30°C) from *Pinus strobus* (Table 2). The correlation between measured and predicted emission ($R = 0.95$; Fig. 5) is slightly better than the correlation between mole fraction in the emissions and foliar oleoresin ($R = 0.92$; Fig. 2), which is likely due to the incorporation of γ_{or}^i in the emission prediction. The range and average of the standard error between the measured and predicted emission of the monoterpenes was $\pm 6 - \pm 86\%$ and $\pm 54\%$, respectively. Standard errors were about 200% for α -terpineol, β -caryophyllene, and germacrene D.

Reliable estimates of x_{or}^i depend on an accurate value of the volatile liquid content of oleoresin. Oleoresin is composed of essential oil, which contains terpenes and terpenoids, and rosin that is composed of diterpenoic resin acids. Mirov (1961) determined yields of essential oil from oleoresins via vacuum distillation and gravimetric analysis. However, the rosin fraction remaining after distillation might also contain nonvolatile resin acids, which would lead to an error in estimates of x_{or}^i . Toma and Bertman (2012) sampled 1-yr old *Pinus strobus* needles and analyzed the foliar oil content of about 90 trees at UMBS from 2008-2010, which was the basis for the average composition of foliar oils for the subject study. Emission rates predicted by assuming foliar oils represent the volatile liquid content of oleoresin (Table 2) grossly overestimated emission rates for several monoterpenes, which indicates the volatile liquid content of oleoresin is greater than the foliar oil content.

Large disparities between measured and predicted emission rates for *Pinus strobus* were expected. Foliar oil composition of the same species of conifer can vary widely with phenology and age and biotic and

abiotic stresses (see, e.g., Flores, 2013). Toma and Bertman (2012) sampled branches of understory trees of *Pinus strobus* at a height of 1.3 m and branches of large canopy trees were sampled at heights of 6-17 m and 2-4 m. The range and average of the standard deviations of the monoterpene concentrations in foliar oils (n = 210) were $\pm 38 - \pm 51\%$ and $\pm 67\%$, respectively. Terpene and terpenoid emission rates were measured at the UMBS during the 2004-2006 growing seasons (Ortega et al., 2008). Uncertainties in foliar oil composition are similar in magnitude to values of standard errors that were observed between the correlation of measured and predicted monoterpene emission rates. Emissions of α -terpineol were predicted using the foliar oil composition of *Pinus strobus* in Tsukuba, Japan (Yatagai and Sato, 1986), and thus, the significant disagreement between measured and predicted emissions was expected.

Biogenic emission models use values of E_{Si} for broad classes of plant functional types to estimate BVOC emissions at regional and global scales (see, e.g., Guenther et al., 2012). Values of β are used together with E_{Si} to estimate E_i at environmentally relevant temperatures using the monoterpene exponential temperature response function of Eq. (1). According to Eq. (21), a measurement of E_i normalized by p^{ϕ_i} is essentially a measure of $x_{or}^i \gamma_{or}^i$. Based upon the analysis here, compilations of E_{Si} for various species of conifers can be used to estimate terpene and terpenoid emissions as follows:

$$E_i = E_{Si} \exp \left[\left(\frac{\Delta H_{vi}}{R} \right) \left(\frac{1}{T_s} - \frac{1}{T_i} \right) \right] \quad (22)$$

However, values of E_{Si} vary in concert with oleoresin composition, which fluctuates considerably with conifer species (see, e.g., von Rudloff, 1975). Thus, to improve BVOC estimates requires development of conifer-specific emission inventories. Furthermore, application of the algorithm assumes terpenes and terpenoids are released from specific storage sites and partitioning between phases in foliage is rapid relative to the time required to attain equilibrium. Release of some terpenes and terpenoids from the

stoma can be delayed through nonspecific storage in hydrophobic and hydrophilic plant tissues within the leaf (Niinemets and Reichstein, 2002; Niinemets et al., 2004). Thus, the time scale over which emission measurements and predictions are compared is critical. Eav (2011) observed emissions of myrcene from *Pinus nigra* foliage during light and dark periods; however, myrcene was not found in foliar oils. Biosynthesis of myrcene might be light induced and temporarily stored in non-specific storage sites of conifer foliage.

4. Conclusions

A new algorithm for estimating emission rates of terpenes and terpenoids from specific storage sites, which is based on thermodynamics of nonelectrolyte partitioning with a polymer matrix, was developed to estimate emissions from conifer oleoresin composition. Emissions through leaf stomata and from resin blisters and traumatic resin ducts induced by herbivore and pathogen infestations are calculated by the same algorithm and depend on the mole fraction of terpene or terpenoid in the oleoresin, activity coefficient (on a Raoult's law convention), and vapor pressure of the pure liquid solute. The SIMPOL.1 method (Pankow and Asher, 2008) was used to estimate vapor pressures of terpenes and terpenoids at 25°C and molar enthalpies of vaporization (ΔH_{vi}), which can be used to estimate vapor pressures at environmentally relevant temperatures using the integrated form of the Clausius-Clayperon equation. Hansen solubility parameters (Hansen, 2007), which include contributions from dispersive, polar, and H-bonding interactions between solute and oleoresin, were used to derive values of the activity coefficients. Solubilities of α -pinene and germacrene D were largely the result of dispersive interactions with monoterpene-rich oleoresin, which was more similar in structure and functionality to the solutes than resin-acid-rich oleoresin. Thus, mixing ratios of non-functionalized terpenes above the monoterpene-rich oleoresin were lower compared to mixing ratios above the resin-acid-rich oleoresin. α -Terpineol and germacrene D-4-ol, can form H-bonds with resin-acid-rich oleoresin that included a carboxylic acid

moiety, and thus, mixing ratios of the terpenols above monoterpene-rich oleoresin were higher compared to mixing ratios above resin-acid-rich oleoresin.

The emission rate algorithm is based on the Clausius-Clapyeron equation, which relates changes in the vapor pressure of a liquid solute with temperature to ΔH_{vi} . Values of ΔH_{vi} for α -pinene, β -pinene, and myrcene derived from plots of the variation of monoterpene emission rate for *Pinus elliotii* with needle temperature (Tingey et al., 1980) were in good agreement with values estimated by the SIMPOL.1 method (Pankow and Asher, 2008). The correlation between measurements of terpene and terpenoid emission rates from *Pinus strobus* (Ortega et al., 2008) and predictions based on the emission rate algorithm was very good. The average standard error for the monoterpenes was quite large ($\pm 54\%$). However, standard errors between measured and predicted emission rates were similar in magnitude to uncertainties in molar composition of foliar oils reported by Toma and Bertman (2012).

Developing conifer-specific emission inventories from oleoresin composition is a promising approach for reducing uncertainties in predictions of BVOC emissions. Collection and analysis of foliage to determine oleoresin composition (see, e.g., Lewinsohn et al., 1993) is much less complicated than sampling and analytic techniques for measuring emissions (see, e.g., Ortega et al., 2008). However, oleoresin composition is related to several factors including taxonomy, phenology and age, and abiotic and biotic stresses (see, e.g., Flores, 2013), which need to be addressed when developing emission inventories from oleoresin composition or from direct measurements of emissions. Thus, rigorous evaluation of the new algorithm will require measurement of emissions using the branch enclosure technique, harvesting of foliage and collection of oleoresin from the bole of the tree, and comprehensive, molecular characterization of the essential oil and rosin fractions of foliar and bole oleoresin.

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Table 1. Molar volumes (V), Hansen solubility parameters for dispersive (δ_d), polar (δ_p), and H-bonding (δ_h) interactions, and activity coefficients (γ).

Chemical Species	V (cm ³ mol ⁻¹)	δ_d (cal ^{1/2} cm ^{-3/2})	δ_p (cal ^{1/2} cm ^{-3/2})	δ_h (cal ^{1/2} cm ^{-3/2})	γ_{MT}	γ_{RA}
α -Pinene	151.5	8.08	0.72	1.54	1.01	1.22
Camphene	149.1	7.90	0.76	1.55	1.03	1.30
β -Pinene	149.1	8.16	0.76	1.55	1.00	1.17
Myrcene	172.2	7.49	1.09	2.50	1.21	1.67
α -Phellandrene	165.6	7.72	0.83	2.09	1.08	1.32
Limonene	161.3	7.95	1.01	2.11	1.03	1.14
β -Phellandrene	163.2	7.79	0.86	2.10	1.06	1.25
δ -Terpinene	161.8	8.03	1.11	2.11	1.02	1.16
α -Terpineol	162.6	8.37	2.69	5.55	3.10	1.70
β -Caryophyllene	273.0	7.67	0.77	1.62	1.07	2.42
Germacrene D	252.9	7.78	0.89	2.07	1.03	1.78
Germacrene D-4-ol	273.2	7.79	2.07	4.43	2.03	2.33
Levopimaric Acid	279.9	9.00	1.28	3.52	1.58	1.03
OR _{MT} ^a	177.2	8.26	0.83	1.94		
OR _{RA} ^b	254.2	8.82	1.17	3.12		

^aOleoresin composition: 80% α -pinene and 20% levopimaric acid.

^bOleoresin composition: 80% levopimaric acid and 20% α -pinene.

Table 2. Molar enthalpies of vaporization (ΔH_v), vapor pressures (p) at 25°C and measured and predicted emission rates of terpenes and terpenoids.

Chemical Species	ΔH_v^a (kJ mol ⁻¹)	p^b (mm Hg)	Measured Emission Rate ^c (μg C gdw ⁻¹ h ⁻¹)	Predicted Emission Rate ^e (μg C gdw ⁻¹ h ⁻¹)	Predicted Emission Rate ^f (μg C gdw ⁻¹ h ⁻¹)
α-Pinene	54.2	2.22	0.20	0.38	1.3
Camphene	54.2	2.22	0.072	0.053	0.17
β-Pinene	54.2	2.22	0.14	0.28	0.97
Myrcene	56.3	1.42	0.090	0.049	0.17
α-Phellandrene	53.0	1.73	0.018	0.017	0.055
Limonene	53.0	1.73	0.044	0.026	0.090
β-Phellandrene	53.0	1.73	0.049	0.023	0.075
δ-Terpinene	53.0	1.73	0.011	0.0044	0.016
α-Terpineol	71.3	1.46E-02	0.0071	0.00017	0.00080
β-Caryophyllene	69.5	1.24E-02	0.018	0.00098	0.00034
Germacrene D	72.8	1.02E-02	0.0099	0.00016	0.0015
Germacrene D-4-ol	91.1	2.99E-04	^d	0.000039	0.00018

^aEstimated using SIMPOL.1 (Pankow and Asher, 2008).

^bEstimated at 25°C using SIMPOL.1 (Pankow and Asher, 2008).

^c(Ortega et al., 2008).

^dNot measured.

^ePredicted using the mole fractions in oleoresin estimated from the data of Toma and Bertman (2012) and Mirov (1961) and an oleoresin containing 75% levopimaric acid and 25% α-pinene.

^fPredicted using the average mole fraction in foliar oils (Toma and Bertman, 2012) and an oleoresin composition containing 25% levopimaric acid and 75% α-pinene.

Figure Captions

Figure 1. Mixing ratios (ppb_v) of terpenes and terpenoids in equilibrium with a monoterpene-rich and resin-acid-rich oleoresin (i.e., 80% α -pinene, 20% pimaric acid and 20 % α -pinene and 80% pimaric acid, respectively).

Figure 2. Correlation between the mole fraction of terpenes and terpenoids in foliar oleoresin of *Pinus strobus* and the mole fraction in emissions. Mole fractions were estimated from foliar oleoresin composition (Toma and Bertman, 2012) and emission rates (Ortega et al., 2008). (Camphene, Germacrene D, and Myrcene are the principal outliers.)

Figure 3. Variation in the α -pinene emission rate ($\mu\text{g C gdw}^{-1} \text{ h}^{-1}$) for *Pinus* species and the vapor pressure (mm Hg) of α -pinene with temperature. Emission rates were estimated using Eqn. (1) and the range and average value of β for α -pinene emitted from 7 species of *Pinus* (Guenther et al., 1993) and a value of $3.0 \mu\text{g C gdw}^{-1} \text{ h}^{-1}$ for E_s of *Pinus* (Geron et al., 1994). Values of ΔH_{vi} and p°_i at 25°C for α -pinene were estimated by the SIMPOL.1 method (Table 2; Pankow and Asher, 2008) and used in Eqn. (18) to estimate vapor pressures.

Figure 4. Variation in monoterpene emission rates ($\mu\text{g C gdw}^{-1} \text{ h}^{-1}$) for *Pinus elliotii* (Tingey et al., 1980) and monoterpene vapor pressures (mm Hg) with needle temperature. Values of ΔH_{vi} and p°_i at 25°C for the monoterpenes were estimated by the SIMPOL.1 method (Table 2; Pankow and Asher, 2008) and used in Eqn. (18) to estimate monoterpene vapor pressures.

Figure 5. Correlation between emission rates ($\mu\text{g C gdw}^{-1} \text{ h}^{-1}$) predicted from foliar oil composition reported by Toma and Bertman (2012) and measured emissions rates (Ortega et al., 2008) of

733 terpenes and terpenoids from *Pinus strobus*. (Camphene, Germacrene D, and Myrcene are the
734 principal outliers.)
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Fig. 3.

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