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Potential contribution of exposed resin to ecosystem emissions of monoterpenes

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HIGHLIGHTS

- We measured emission of monoterpenes (MT) from Ponderosa pine resin.
- Freshly exuded resin can emit 10,000× more MT than the same area of needle tissue.
- If resin appeared over 10 days, it would be 10% of the ecosystem emission each day.
- Resin could explain gaps between tower and chamber estimates in pine forests.

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ABSTRACT

Conifers, especially pines, produce and store under pressure monoterpene-laden resin in canals located throughout the plant. When the plants are damaged and resin canals punctured, the resin is exuded and the monoterpenes are released into the atmosphere, a process that has been shown to influence ecosystem-level monoterpene emissions. Less attention has been paid to the small amounts of resin that are exuded from branches, expanding needles, developing pollen cones, and terminal buds in the absence of any damage. The goal of this study was to provide the first estimate of the potential of this naturally-exposed resin to influence emissions of monoterpenes from ponderosa pine (*Pinus ponderosa*) ecosystems. When resin is first exuded as small spherical beads from undamaged tissues it emits monoterpenes to the atmosphere at a rate that is four orders of magnitude greater than needle tissue with an equivalent exposed surface area and the emissions from exuded beads decline exponentially as the resin dries. We made measurements of resin beads on the branches of ponderosa pine trees in the middle of the growing season and found, on average, 0.15 cm^2 of exposed resin bead surface area and 1250 cm^2 of total needle surface area per branch tip. If the resin emerged over the course of 10 days, resin emissions would make up 10% of the ecosystem emissions each day. Since we only accounted for exposed resin at a single point in time, this is probably an underestimate of how much total resin is exuded from undamaged pine tissues over the course of a growing season. Our observations, however, reveal the importance of this previously unrecognized source of monoterpenes emitted from pine forests and its potential to influence regional atmospheric chemistry dynamics.

1. Introduction

Monoterpene emissions from forests exert a natural control over gas-phase oxidative chemistry in the atmosphere. In addition, the products of monoterpene oxidation have been implicated in the formation and early growth of atmospheric aerosol (*e.g.*, Laaksonen et al., 2008) and also partition onto existing particles (Kanakidou et al., 2005), thus affecting both heterogeneous chemistry and radiative dynamics in the atmosphere (Engelhart et al., 2008; Kulmala et al., 2004; Mentel et al., 2009; Peñuelas and Staudt, 2010; Spracklen et al., 2008). Most models and inventories of forest monoterpene emissions assume a source that is entirely from the leaves and use measures of leaf area or mass to scale emissions up to the ecosystem from observations using leaf or branch cuvettes (*e.g.*, Geron et al., 2006; Guenther et al., 1995; Otter et al., 2002).

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However, monoterpene-laden resin is often exuded naturally from undamaged branches and from damaged needles, which could provide a source of emissions from plants that would not be captured in most leaf-based measurements or upscaling exercises.

One of the most common anti-herbivory mechanisms in conifers is the production of resin (also called oleoresin or pitch), a mixture of volatile mono- and sesquiterpenes and non-volatile rosin (comprised of diterpenoid acids) (reviewed by Phillips and Croteau, 1999; Trapp and Croteau, 2001) with MT making up about 50% of the mixture (Trapp and Croteau, 2001). Pines in particular produce large quantities of resin, which is located throughout the plant in resin canals that run through the wood and extend the length of the needles (Lewinsohn et al., 1991). When a canal is ruptured (whether by herbivores or physical damage), resin will flow from the wound site and create a bead or drip, which then hardens as the mono- and sesquiterpenes volatilize, leaving behind a protective barrier (Michelozzi, 1999; Phillips and Croteau, 1999; Pasqua et al., 2002). Studies have shown that damage to pines caused by herbivores (Litvak et al., 1999), severe storms (Haase et al., 2011), industrial tapping of trees for resin collection (Pio and Valente, 1998), and tree felling (Schade and Goldstein, 2003; Räisänen et al., 2008) have the potential to increase the exposure of resin to the atmosphere. In all of these cases, some type of damage to the resin canal system underlies the increased volatilization of MT and this, in turn, influences local atmospheric chemistry, albeit episodically over a short time interval.

One aspect of resin-flow physiology that has been overlooked is the potential for resin drips and beads to form at anatomical junctions between the follicle sheaths of needles and branches (i.e., where needle bundles meet the branch), on developing pollen and seed cones, and from apical buds, especially in spring when sap pressures are high and resin is apparently pushed to a point of exudation. In studies of needle MT emissions from Ponderosa pine trees (*Pinus ponderosa* var. *scopulorum* Engel.) in 2011, we frequently observed these 'beads' of resin at needle and bract junctures and hypothesized that this natural flow of resin to exit points, and its exposure to the atmosphere, would be of significance to the local MT emission inventory. The goal of this study was to generate the first estimate of the possible contribution of naturally-exposed resin to ecosystem MT emission.

2. Methods

This study was conducted at the Manitou Experimental Forest (Lat 36°6′0″ N, Long 105°5′30″ W), a United States Forest Service (USFS) site near Woodland Park, CO, USA. The forest on this site is dominated by Ponderosa pine (*P. ponderosa* var. *scopulorum* Engel.) in an open woodland landscape with little understory, except for sparse grass and forb coverage. During the study period the mean daytime temperature was 18 °C, with mean daytime high and nighttime low temperatures of 22, and 3 °C, respectively. The mean relative humidity was 44%. These conditions were typical for the season. Our aim was to determine how naturally-formed resin beads would influence MT emissions, but it was not possible for us to catch the exact moment of exudation and thus quantify MT emissions beginning at the point of bead origin. We developed an alternative method by which we could induce the formation of a resin bead of similar nature and size to those emitted naturally. We could then carefully characterize the age and progression of MT emission as a function of time since exudation.

In order to collect newly emerged resin, on August 28th 2011 four mature trees that were at least 5 m in height were selected and one sunlit branch ~2 m above the ground on each tree was nicked with a sharp knife. On those same trees, a terminal bud was pierced with a pin. The resin was allowed to flow for 2–3 h so that a bead of resin appeared on each branch and terminal bud. The tip of a pin was used to transfer resin from a single bead in order to make nine resin dots on a piece of aluminum foil (Fig. 1) creating one "tab" with a total resin surface area of 0.1–0.2 cm^2. This method was used to create 8 tabs, one from a branch and one from a bud on each of the four trees. One week later, branches on two more trees were nicked and two more tabs made in order to collect samples for identifying individual compounds in the MT emissions. Bud samples were not collected from those trees. In adopting this method we have assumed that the composition and volatility of monoterpenes in the collected resin does not change in response to artificial wounding during the 2–3 h exudation period. In between measurement times the tabs were stored in open glass containers in a tent at the Manitou Experimental Forest. They experienced ambient temperature and humidity, but were protected from precipitation and wildlife and were not exposed to direct sunlight.

The tabs were created to fit into the broadleaf chamber (internal area = 6 cm^2) of an LI-6400 portable gas exchange system (Li-Cor Biosciences, Lincoln, NE, USA) so that the temperature and light environment of each tab could be controlled. Each tab was first measured within 2 h of creation, i.e., 4–5 h after wounding (labeled "day 1") and then measured after 22–26 h (labeled "day 2"), 94–96 h (labeled "day 5"), 214–218 h (labeled "day 10"), 334–338 h (labeled "day 15"), and 668–670 h (labeled "day 30"). For every measurement, each tab was sampled for 20–30 min at 30 °C and 1000 μmol m^{-2} s^{-1} of photosynthetically-active radiation (400–700 nm) (PAR). The two samples collected for identifying individual MT were measured on day 25 instead of day 30.

Instantaneous MT emissions were measured using proton-transfer reaction mass spectrometry (PTR-MS) (for a detailed description of PTR-MS, see de Gouw and Warneke, 2007). A platinum catalyst heated to 350 °C was placed in-line between the console of the LI-6400 and the leaf chamber to remove VOCs from the air before it entered the cuvette. A Teflon T connector was used to replace the normal LI-6400 match tube, allowing us to route the sample air from the cuvette to the inlet of the PTR-MS. Because of emissions from components of the cuvette, the background readings of m/z 137 and 81 (which are used to determine monoterpene concentrations) in the empty cuvette were not zero, but were stable. GC data showed that the actual level of monoterpenes in the empty cuvette was zero and these background values are from some other compound or fragment with the same mass that is

Fig. 1. Example of a "tab" made of aluminum foil with 9 dots of recently collected resin. Each tab contains resin from one tree and is considered one sample. The scale bar is equal to 1.55 cm.