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Sesquiterpene emissions from loblolly pine and their potential contribution to biogenic aerosol formation in the Southeastern US

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Abstract

Sesquiterpene (SQT) and monoterpene (MT) emissions from loblolly pine (*Pinus taeda* L.) were studied by branch enclosure experiments at Duke Forest in Chapel Hill, NC. Four SQT (β -caryophyllene, α -bergamotene, α -humulene, β -farnesene), five MT (α -pinene, β -pinene, β -myrcene, β -phellandrene, limonene), and the oxygenated MT linalool were identified. Emission rates of both compound classes increased exponentially with temperature, albeit SQT temperature coefficients (0.12 – 0.18 K^{-1}) were higher than for MT (0.068 – 0.15 K^{-1}), resulting in an increased contribution of SQT to the overall biogenic volatile organic compound (BVOC) flux during warm temperature conditions. The highly correlated variables of light and temperature conditions preclude a rigorous characterization of their individual roles in driving these emissions. However, the observations indicate that there may be both temperature-only and temperature/light-dependent components contributing to SQT emission variations. When normalized to 30°C using the best-fit temperature algorithm, total SQT basal emission rate was $450\text{ ng g}^{-1}\text{ h}^{-1}$. The potential contribution of SQT from all pine trees (based on the loblolly pine emission factors) to secondary, biogenic organic aerosol in 12 southeastern US states was estimated to be $7 \times 10^6\text{ kg}$ for the month of September which constitutes an appreciable portion of the overall PM 2.5 emission budget. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Sesquiterpenes; Monoterpenes; Emission factors; Organic secondary aerosol

1. Introduction

Sesquiterpene (SQT) hydrocarbons have been identified in biogenic volatile organic compound (BVOC) emissions in numerous studies (e.g. Winer

et al., 1992; Helmig et al., 1999). Quantitative SQT emission rate and landscape flux estimates have been scarce and are highly uncertain. This deficiency stems largely from the high chemical reactivity and low volatility of these compounds which render quantitative landscape flux measurements an experimentally challenging task (Ciccioli et al., 1999). Unidentified reactive BVOC emissions, possibly including SQT, have been speculated to be responsible

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for the unaccounted for OH reactivity in forested environments (Di Carlo et al., 2004). Characterization and recent further developments of analytical techniques for SQT measurements (Helmig et al., 2003, 2004a, b; Pollmann et al., 2005) were applied in this study for a focused study of SQT emission rates from loblolly pine (*Pinus taeda* L.), which is a leading timber species in the United States, predominating on more than 13.4 million hectares of southern forest lands (Shultz, 1997).

2. Experimental

This experiment was conducted during a 1-week study period in September 2004 within a loblolly pine plantation (established in 1983) in the Blackwood division at the Duke Forest FACTS-1 site in North Carolina (35°97'N, 79°09'W). Emission rates were determined by the branch enclosure technique. Only a brief summary of the most pertinent parameters will be provided here; further details will be presented by Ortega et al. (2006). Four similar branch enclosure systems (E1–E4) were used. Branches were enclosed with 0.05 mm film FEP Teflon bags. Enclosure volumes were ~50–80 l. Branches were carefully enclosed with the bags, avoiding wall contact with needles, and branches were allowed to acclimate for ~1 day before sampling was started to avoid the sampling of artificially enhanced, stress-induced BVOC emissions. The enclosures were suspended externally to prevent them from touching the needles. Since SQTs rapidly react in ambient air and can be depleted during the sampling procedure in the presence of ozone (Pollmann et al., 2005), the enclosure purge (ambient) air was first passed through ozone scrubbers (charcoal) for all enclosures. In addition, enclosure E3 was equipped with a scrubber in series composed of 25 MnO₂-coated copper screens (OBE Corporation, Fredricksberg, TX) for ozone removal. The purge flow rates into the enclosures were 10–19 l min⁻¹, resulting in typical bag residence times of approximately 3–6 min. Ozone in the enclosure air was routinely measured with an ozone monitor and found to be <2–3 ppb at all times. In order to (a) minimize excessive heating of the air inside the enclosure and to (b) reduce condensation on the bag walls from transpired water vapor, an ice-bath cooled water trap was used in the inflowing air stream of enclosures E1, E2 and E4 to lower the dewpoint and air temperature. In one of the enclosures (E3) air circulation was increased with

an aluminum-blade mixing fan (driven by a shaft/fan motor outside of the enclosure). Needle temperatures were recorded with small thermocouple wires that were attached to needles inside the bag. Air temperature inside and outside the enclosures was measured with temperature probes and radiation shielded thermocouples. Photosynthetically active radiation (PAR) was recorded with PAR sensors (LI-190SA quantum sensor, LI-COR, Lincoln, NE) outside the enclosures and corrected for ~5% transmission loss through the Teflon film. Photosynthesis rates were measured in E1, E2 and E4 with a photosynthesis system (LI-6400, LI-COR). E1 and E4 were deployed on branches approximately 10 m above the ground using a walk up tower within the canopy and E2 and E3 sampled branches on smaller trees on the edge of the stand near ground level. Branches were harvested after the field portion of the study and needles were picked and dried for scaling emission rates to the dry needle mass in each enclosure. Air samples were drawn from the inside of the bag by pulling air through continuously purged 0.32 mm o.d. Teflon tubing onto solid adsorbent cartridges, either with an automated sampler (E1, E4) as described previously (Helmig et al., 2004a) or with small personal sampling pumps (E2, E3). Most samples were collected onto Tenax GR-filled (Alltech Assoc. Inc., Deerfield, IL) glass adsorbent tubes (a few additional samples were collected onto Tenax TA (Alltech) and Carbotrap C adsorbent (Supelco, Bellefonte, PA)). Adsorbent cartridges from E1 and E4 were temperature-controlled at 40 °C to minimize water retention on the adsorbent material during sampling. Adsorbent tubes from E2 and E3 were dry-purged (Karbiwnyk et al., 2002) to eliminate condensed water prior to analysis. Typical sampling rates and times were approximately 175–200 ml min⁻¹ (accurate flow measurements were taken for each sample) for 1 h resulting in approximately 9–12 l sample volumes. Sodium thiosulfate impregnated glass fiber filter ozone scrubbers (Helmig, 1997; Pollmann et al., 2005) were placed in the sampling flow upstream of the adsorbent cartridges to further reduce potential SQT sampling losses from ozone reactions during the sampling procedure. These filters were tested daily and found to reduce ozone to <2 ppbv at ~1 l min⁻¹ flow rate (which was ~6 times higher than the BVOC sampling flow rate) at ambient ozone levels ranging between ~15 and 60 ppbv. It has been demonstrated that SQTs are not lost to

these filters (Pollmann et al., 2005). Adsorbent and cartridge properties as well as further analytical conditions for sample analysis and calibration by thermal desorption (Perkin Elmer ATD-400), gas chromatography, and dual detection flame ionization and mass spectrometry (GC/MS/FID), and calibration procedures were similar to those described previously (Helmig et al., 2003, 2004a,b). A low flow ($7.2 \pm 0.2 \text{ ml min}^{-1}$) of a multi-component, ppm-level reference standard (toluene; 1,3,5-trimethylbenzene; 1,2,3,4-tetrahydronaphthalene; 1,3,5-tri-isopropylbenzene; *n*-nonylbenzene) was added to the enclosure purge air flow in E1 and E4 to provide an independent, second calibration approach. The recoveries of this series of increasing molecular weight aromatic compounds were also monitored to validate the recoveries of analytes over a wide range of vapor pressures. Samples were stored in a freezer (-10°C) between sample collection and analysis of adsorbent cartridges in the laboratory. Montoterpene (MT) and SQTs were identified by their MS and GC retention indices. Alpha-pinene, β -pinene, limonene, β -caryophyllene and α -humulene identifications were furthermore confirmed by analysis of respective standards. From extensive laboratory experiments as well as from the comparison of the reference standard measurements, SQT concentrations and calculated emission rates are estimated to have $\pm 15\%$ precision and uncertainty. Analysis of recoveries of the reference and MT standards demonstrated that MT were not completely retained on the adsorbent tubes under the selected sampling conditions. Therefore, corrections were applied for these partial sampling losses resulting in an accuracy and precision of $\pm 30\%$ for the MT data.

3. Results

Four SQT (β -caryophyllene, α -bergamotene, α -humulene, β -farnesene) and five MT (α -pinene, β -pinene, myrcene, β -phellandrene, limonene) and the oxygenated MT linalool were identified in the loblolly pine emission samples. SQT and MT emission rates for the four most predominant SQT and MT in E1 over a 2-day period as well as concurrent temperature and PAR measurements are illustrated in Fig. 1. The temperature shown in this figure is the air temperature inside the enclosure. Temperatures inside the enclosures were typically within 1°C of ambient air temperatures during morning, evening and nighttime hours, and within

$2\text{--}4$ and $6\text{--}7^\circ\text{C}$ during most of the day and times of maximum solar radiation (noontime clear skies conditions), respectively. These temperatures were always within normal September conditions for this site. Needle temperatures typically were $\sim 1\text{--}3^\circ$ below the air temperatures inside the enclosure. The gas exchange measurements indicated that mid-day photosynthetic rates ranged from 4 to $5 \mu\text{mol m}^{-2} \text{ s}^{-2}$ which is consistent with other light-saturated measurements at the site (Myers et al., 1999). Results shown in Fig. 1 are representative and consistent with the three other (E2–E4) experiments.

These data clearly show the strong diurnal variability of SQT emissions from loblolly pine. Emission rates of all identified SQTs increased significantly during the day, reaching maximum values in the early afternoon and dropping to less than 5% of their daytime maxima at night. Beta-caryophyllene constituted the largest contribution to the overall SQT emission flux, followed by smaller contributions from α -humulene, β -farnesene and α -bergamotene. Similar to the SQT results, MT emission rates show a strong diurnal variability. The temperature dependencies of SQT and MT emission rates are shown in Fig. 2 along with regression fits to the data. These graphs include data from all four enclosure experiments. The SQT and MT that are emitted at the highest rates are plotted in the upper graphs. The ones with the lowest emission rates are shown at the bottom. Both SQT and MT emission rates showed large increases with temperature. MT emission rates from pines have extensively been studied before and were found to be well described by exponential temperature algorithms (Guenther et al., 1993). Exponential temperature algorithms were approximated for both SQT and MT and are included in these figures.

The temperature response curves reveal a somewhat stronger temperature dependency for SQT than for MT. The four MT temperature coefficients ($\beta [\text{K}^{-1}]$) ranged from 0.068 to 0.15, while the SQT coefficients ranged from 0.12 to 0.18. The empirical MT temperature coefficients compare well with previous reports. Guenther et al. (1993), for example, recommended 0.09 K^{-1} for MT. Similarly, the range of SQT temperature coefficients falls within the range of previous reports for β -caryophyllene. Tarvainen et al. (2005) reported values of $0.124\text{--}0.186 \text{ K}^{-1}$ for β -caryophyllene emissions from *Pinus sylvestris* and Hansen and Seufert (2003) reported a coefficient of 0.173 K^{-1} from

Fig. 1. Two days of SQT (first graph) and MT (second graph) emission rate measurements on a single loblolly pine branch (E1). The third graph shows the 5-min averages of the photosynthetic photon flux density (PPFD) and the temperature inside and outside of the enclosure.

Citrus sinensis. The individual temperature response curves were used to calculate the normalized (30°C) emission rate of individual as well as the total SQT emission rate from loblolly pine (Fig. 3). Under these conditions, β -caryophyllene is the dominant individual SQT, constituting $\sim 66\%$ of the total SQT emission rate. The three other SQTs contribute ~ 10 – 13% each.

Schuh et al. (1997) used an environmental control chamber to investigate β -caryophyllene emissions from sunflowers and observed a strong light dependence when light levels were varied while temperature was held constant. In contrast to the light-dependent emissions of isoprene, the β -caryophyllene emissions were not negligible in the dark but were about 20% of the rate observed at a PAR of $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$. Tarvainen et al. (2005) and Hansen and Seufert (2003) both investigated β -caryophyllene emissions from tree branch enclosures exposed to ambient conditions of covarying light and temperature. While Tarvainen et al. (2004)

could not discern any light dependence, Hansen and Seufert (2003) observed a somewhat better agreement between observed and predicted β -caryophyllene emissions when using a light- and temperature-dependent algorithm rather than a temperature-only algorithm. This was also the case for the loblolly pine SQT emission rate variability observed during this study. Similar to the results reported by Schuh et al. (1997), model performance was maximized when it was assumed that 20% of the total SQT emission from loblolly pine is dependent only on temperature while 80% was light- and temperature-dependent. However, a Monte Carlo probabilistic approach assessment indicated that the performance of the light- and temperature-dependent algorithm for predicting SQT emissions was not significantly better than the simpler temperature-only algorithm that was used for the regional extrapolation described below. Although additional experiments are needed to develop a more robust SQT emission algorithm, the exponential temperature relationship

Fig. 2. Emission rates and exponential fit curves of four SQT and four MT as a function of enclosure air temperature. These graphs include data from all four (E1–E4) enclosure experiments.

Fig. 3. Contribution of four quantified SQT to the overall SQT emission rate from loblolly pine. This graph shows the normalized distribution at 30 °C. The total, normalized 30 °C SQT emission rate is 450 ngC g⁻¹ h⁻¹.

based on these observations is suitable for an initial assessment of regional SQT emissions from pines.

The observations described above indicate that SQT emission rates will increase proportionally more with increasing temperature than for MT. The sum of all SQT and MT emissions as a function of temperature is illustrated in Fig. 4. These data show that below 30 °C, MT make up the largest fraction of BVOC emissions from loblolly pine. With increasing temperature, the relative SQT contribution increases and above ~30 °C SQT become the dominating BVOC emission from loblolly pine. The normalized, 30 °C total SQT emission rate is 450 ngC g⁻¹ h⁻¹. At 40 °C the extrapolated total SQT emissions are twice the MT emission rates. This graph re-emphasizes that SQTs have an increasing significance to the BVOC flux and air

Fig. 4. Total SQT and MT emission rate from loblolly pine as a function of temperature.

chemistry during high temperature and solar radiation conditions. While these data consider only temperature, it is possible that emission rates could be further enhanced under light-saturated conditions. More rigorous light and temperature relationships need to be developed for a more accurate description of these dependencies.

These emission rates were used to develop estimates of landscape fluxes and aerosol yield from SQT oxidation. It is uncertain if the emission rates and temperature algorithms determined during these September experiments are applicable year-round. Other research has shown that MT basal emission rates from coniferous trees undergo significant seasonal changes (e.g. Peñuelas and Llusia, 2001; Komenda and Koppmann, 2002; Pressley et al., 2004; Kim et al., 2005), with maximum emission rates typically observed during the summer. The only seasonal SQT emission rate studies (Scots pine in Finland) reported so far (Tarvainen et al., 2005; Hakola et al., 2005, 2006) similarly suggest higher SQT basal emission rates during the middle of the growing season; early fall (September) emission rates were significantly lower than mid-summer values. These results imply that the emission rates determined in our September experiments may not be valid for other times during the year.

Because of these uncertainties in seasonal emission rate changes, the data from our experiments were used to develop a flux estimate for September conditions only. Typical pine stand needle biomass densities are 400–900 g m⁻² (dry weight) for fully stocked stands with leaf area indices of 2.5–4.0 (Geron et al., 1994). We used a typical biomass

density of 375 g m⁻² (the lower value is due to the abundance of plantation pines in the US, which on average are maintained at ~50% stocking), the Duke FACTS-1 forest annual 1/2-h temperature record for 1998–1999, and a vertical canopy temperature distribution according to the model by Guenther et al. (2000) to scale the branch enclosure emission rate data to an estimated SQT landscape flux for loblolly pine plantations. Results from these calculations show that during September, daily integrated SQT fluxes frequently reach the ~2–3 mg m⁻² d⁻¹ range. Applying the same basal emission rate to mid-summer temperature conditions will yield typical daily fluxes of approximately 2–5 mg m⁻² d⁻¹. If seasonal SQT emission rates from loblolly pine behave similarly to emissions from Scots pine in the boreal forests (see above), emission rates would be expected to peak during mid-summer, resulting in significantly larger SQT surface fluxes during the June–August period.

For developing a theoretical estimate of potential SQT fluxes in the southeastern US, these loblolly pine SQT fluxes were applied to all of the Southern pine coverage (but omitting all other conifer and deciduous tree land cover types) for 12 states (AR, AL, FL, GA, MS, NC, SC, OK, TN, TX, VA, LA) in the Southeastern US. Pine coverage in these 12 southeastern states is dominated by loblolly pine and exceeds 30 × 10⁶ ha (USDA, 1988). The resulting estimate for the total SQT flux for the southeastern US accounts to ~9 × 10⁶ kg for the month of September. Since other vegetation types not included in this model analysis are expected to have additional contributions to the overall SQT emissions, actual SQT landscape fluxes are expected to be higher than this estimate.

SQTs undergo rapid depletion in the atmosphere from reactions with atmospheric oxidants, in particular from reactions with OH and ozone. Atmospheric lifetimes are estimated to be only a few minutes (Grosjean et al., 1993; Shu and Atkinson, 1994, 1995; Hoffmann et al., 1997). Aerosol yields from SQT gas-phase oxidation are significant and vary depending on reaction conditions. Aerosol yield from 12% to close to 100% have been observed for β-caryophyllene (Grosjean et al., 1993; Hoffmann et al., 1997; Griffin et al., 1999a,b; Jaoui et al., 2003), the primary SQT identified from loblolly pine. Similar aerosol yields have been found in the oxidation of other SQT (Jaoui and Kamens, 2003; Jaoui et al., 2004). These yields generally reflect the percentage of reacted

carbon that was found in the aerosol phase. Since SQT oxidation will result in an increase in molecular weight (Turpin and Lim, 2001), the overall aerosol mass yield is expected to be higher than these estimates. We applied an estimated average total aerosol mass yield of 75% (which includes possible mass gain from oxidation) to the aforementioned SQT flux estimate, which, in respect of available literature, is likely a conservative estimate. This calculation results in an estimated aerosol production from SQT oxidation of $\sim 7 \times 10^6$ kg for the month of September. This mass is 3.5–7% of the estimated September anthropogenic primary PM_{2.5} emission burden of $1\text{--}2 \times 10^8$ kg in the southeastern US (EPA, 1999). This is a simplified estimate and it should be noted that the SQT flux estimates are based solely on the branch enclosure emission data. Above canopy fluxes and aerosol production could possibly be smaller due to deposition losses to non-aerosol surfaces within and below the canopy; however, the significance of such potential SQT losses cannot be quantitatively described with the current understanding of these processes. Aerosol growth and yields will also depend on the levels of primary aerosol and the temperature-dependent gas-particle partitioning of SQT and their oxidation products. The aerosol yields provided here are intended as a first estimate of the magnitude of the possible contribution of SQT to aerosol production.

4. Conclusion

SQTs constitute a significant portion of BVOC emissions from loblolly pine. Loblolly pine is an important tree species in the Southeastern US, used abundantly in forestry as well as in urban landscapes. The results presented here are from a single site during a narrow window of conditions. Further extrapolations will require studies on possible seasonal changes in the SQT basal emission rates. Furthermore, the derived estimates for an SQT landscape scale flux and aerosol yields rely on a number of assumptions that have large uncertainties and will require further investigations. More research is in progress to further evaluate the representativeness of the Duke forest results.

Nonetheless, these findings demonstrate the potentially significant contribution of SQT to the overall BVOC emission rate from selected tree species and to BVOC landscape fluxes. Until recently, SQT emissions have been considered

negligible or highly uncertain and have not been included in regulatory air quality model simulations. Our findings re-emphasize that SQT likely do have an important contribution to local atmospheric chemistry involving oxidants and are suspected to play an appreciable role in secondary organic aerosol formation in selected ecosystems and regions with warm climates and high densities of loblolly pine and other SQT emitting tree species.

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