Atmos. Chem. Phys. Discuss., 11, 26849–26865, 2011
www.atmos-chem-phys-discuss.net/11/26849/2011/
doi:10.5194/acpd-11-26849-2011

Atmospheric
Chemistry
and Physics
Discussions

The atmospheric potential of biogenic volatile organic compounds from needles of White Pine (*Pinus strobus*) in Northern Michigan

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Received: 22 July 2011 – Accepted: 25 August 2011 – Published: 28 September 2011

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

The key role biogenic volatile organic compounds (BVOC) play in atmospheric chemistry requires a detailed understanding of how BVOC concentrations will be affected by environmental change. Large-scale screening of ecosystems is difficult with enclosure methods. In this study, BVOC in needles of 71 white pine trees (*Pinus strobus*), which are becoming a large part of Midwest forests, are tracked for three summers at the University of Michigan Biological Station (UMBS). α-pinene, the dominant terpene in all samples, accounts for 30–50 % of all terpenes on a mole basis. The most abundant sesquiterpenoid was a C15 alcohol identified as germacrene-D-4-ol. The abundance of this material and its atmospheric relevance has not been considered previously. The relationship between limonene and α-pinene clearly shows two distinct trends in the population of these forests. About 15 % of the trees showed high levels of limonene (up to 36 % of the total BVOC) in the same trees every year. With this mixture, limonene contributes 11 % of the α-pinene contribution to total gas-phase OH loss at UMBS compared to less than 2 % considering the composition of the majority trees. Hence we show that chemotypic variation within forests can affect atmospheric chemistry and that large-scale screening of BVOC can be used effectively to study the importance of BVOC variation for predicting atmospheric chemistry in future forests.

1 Introduction

Biogenic volatile organic compounds (BVOC) lead to the formation of tropospheric ozone in the presence of NO_x (Atkinson, 2000) as well as to formation and growth of secondary organic aerosol (SOA) (Andreae, 2009; Laothawornkitkul et al., 2009). The total global estimated emission rate of BVOC is about 1.2×10^{15} g C per year, while the global anthropogenic VOC emission rate is about 1.0×10^{14} g C per year (Muller, 1992; Guenther et al., 1995). The BVOC emissions in North America are dominated by isoprene (51 %), terpenes (31 %), and oxygenated VOC (16 %), based on OH reactivity

(Guenther et al., 2000). The organic component of aerosols is the largest single fraction with an average of 45 % (Zhang et al., 2007). The large mass of emission and atmospheric reactivity makes estimation of BVOC emission rates important.

Several field studies have suggested that some atmospheric reactivity is not accounted for by current emission estimates in temperate forests of North America. Goldstein et al. (2004) showed that forest thinning dramatically enhanced MT emission and ozone uptake in a California ponderosa pine plantation. They suggested that ozone uptake was due to reactions with unmeasured BVOC, with ozone reaction rates fast enough to allow oxidation within the forest canopy. Di Carlo et al. (2004) directly measured total OH reactivity in a northern Michigan forest, which was significantly greater than calculations based on measurements of individual compounds.

Emission rates, especially of terpenes, are related to vapor pressure within plant tissues and are greatly influenced by temperature (Lerdau et al., 1997). BVOC emission rate estimates mostly have been derived from leaf or branch enclosure measurements (e.g., Ortega and Helmig, 2008; Ortega et al., 2008) with temperature and light correction (Guenther et al., 1995). Time requirements make enclosure measurements logistically difficult to evaluate a whole forest ecosystem. Lerdau et al. (1994, 1995) studied the relationship using MT in ponderosa pine and Douglas-fir and suggest that terpene concentrations in leaves could be used to predict emission rates in models. This would make it possible to measure a large number of samples from a wide area in a short time and to estimate with precision the BVOC content of an area of forest.

Upper US Midwest forests are recovering from widespread logging and wildfires from the early 20th century (Frelich, 1995; Schmidt et al., 1996). Forest succession is allowing eastern white pine (*Pinus strobus*), once a dominant species in many parts of the Great Lakes region, to grow back to replace aspens (Bergen and Dronova, 2007; Ziegler, 2010). Succession from aspen forests to a higher representation of pines will cause “chemical succession”, whereby isoprene gives way to terpenes in the atmosphere. This can lead to a number of atmospheric implications and to issues of forest health. For instance, Lee et al. (2006b) report that terpenes, especially sesquiterpenes

(SQT), produce SOA in higher yields than isoprene from photooxidation. Analysis of white pine needles provides baseline information about the pools of BVOC available in the growing forest and helps predict future atmospheric BVOC composition in the Midwest. This work reports BVOC levels in white pine needles in northern Michigan measured over three growing seasons and the atmospheric influence of genetic diversity among populations.

2 Material and methods

Sampling was performed at the University of Michigan Biological Station, (UMBS), (45°30′ N, 84°42′ W) during summers of 2008, 2009, and 2010. Two forest sites were sampled. One forest was an intact, early successional forest (Ameriflux) and the other was a disturbed forest (FASET). A detailed map of the sampling area is in Fig. S1. In the FASET forest, early successional tree species (aspen and birch) were selectively girdled by collaborators in Spring 2008, which will accelerate the growth of late successional species, such as terpene-emitting pines. The two forests were within a kilometer of each other and exist in similar soil conditions and with similar forest composition. The present cover type of the UMBS forest is aspen (60.9 %), northern hardwoods such as maple and american beech (16.6 %), and white and red pines (13.3 %) (Bergen and Dronova, 2007).

Primarily understory white pine trees were sampled at Ameriflux ($n = 34$) and FASET ($n = 36$). Year-old needles were collected from the southern branches at 1.3 m and stored in a freezer at −80 °C until extraction, which was conducted within one month. In addition, needles were sampled from the top (6–17 m) and bottom (2–4 m) of the same large canopy trees ($n = 4$ trees, 2008; $n = 8$, 2009; $n = 10$, 2010). Frozen needles (0.2 g) were cut into small pieces (5 mm) and were soaked in 45 ml hexane (with 100 μmol l^{-1} tridecane added as internal standard) for 24 h at 23.0 °C. The dry weight (dwg) of needles was obtained by heating the residue at 55 °C for 24 h after extraction. The extracted solution was analyzed by gas chromatography-mass spectrometry (GCMS). The Instrument, parameters, and calibration methods are described in supporting material. SPSS 16 (SPSS Inc., USA) was used to calculate statistical significance.

3 Results and discussion

3.1 Understory trees

Table 1 lists average concentrations of the 12 major compounds that accounted for more than 90 % of the total area in the chromatograms of understory trees. The same BVOC compounds were observed in all three years and in both forests. Concentrations did not show statistically significant differences between the two forests. Despite girdling in the FASET site, the forest structure had not been dramatically affected as of 2010, and this was reflected in the analysis of needles. Therefore, the data from both forests were combined in Table 1. The dominant terpene in all samples was α-pinene, which accounts for 30–50 % of all terpenes on a mole basis. The most aboundant SQT was germacrene-D and a sesquiterpene alcohol (SQT-ol), as will be discussed in further detail.

The concentration of total BVOC did not change significantly over the three years, although partitioning between total MT and total SQT showed annual changes. MT and SQT concentrations in 2009 were significantly different from 2008 and 2010. In 2009, total MT showed larger concentration and a wider range of standard deviations than in 2008 and 2010. In contrast, total SQT species were smaller in concentration in 2009 than in 2008 and 2010.

In conifers, MT and SQT are produced by different biosynthetic pathways. MT are formed from geranyl diphosphate with monoterpene synthase in plastids, while SQT are formed from farnesyl diphosphate with sesquiterpene synthases in cytoplasm (Martin et al., 2002). Given that 2009 was a cooler summer (average temperature at UMBS in 2009 was 17.8 °C, about 2–3 °C cooler than in 2008 or 2010). The different responses of MT and SQT might be related to enzyme activity and environmental factors such as light and temperature.

3.2 Canopy (overstory) trees

Table 2 show the variations related to height of average concentrations of BVOC in needles from the top and the bottom of large trees that occupy the forest overstory. In 2009 and 2010, the average concentrations of MT at the top of trees were 30–50 % higher than at the bottom, while SQT levels appeared to be largely unchanged. The average of total BVOC in needles at the top of the canopy trees is also larger than understory trees by about 50 %. This suggests that terpene concentration will increase as understory white pine trees grow into the canopy. Temperature has a stronger influence on terpenes emission into the atmosphere than light because terpenes are stored in structures within the leaf (Lerdau et al., 1994). Even though terpenes emission from needles is not very light-dependent, synthesis has been seen in expanding conifer needles with light dependency (Lerdau and Gray, 2003). Needles on large canopy trees exist in different light environments at the top and the bottom. Results in Table 2 suggest that light exposure may contribute differently to production of MT than to SQT. This agrees with Gleizes et al. (1980), who reported that synthesis of MT is more sensitive to photodependent activation than SQT. They showed that MT are not formed without light exposure; however, SQT are formed in both light and darkness. In addition, the tops of canopy trees will experience higher wind speeds, which could affect the temperature of needles in this environment. Plants produce some terpenes to protect themselves from insect larvae (Laothawornkitkul et al., 2009), and the number density of larvae might vary with tree height.

3.3 Needles vs. gas-phase

Hunt et al. (1990) reported seeing in Ontario and Wisconsin some of the same terpenes as in this study of white pine needles. They also reported germacrene D and a related alcohol. Identified BVOC species and their composition in needles are substantially different from the literature gas phase values. Ortega et al. (2008) reported basal emission rates from seven white pine trees over the 2004–2006 growing seasons at UMBS and other places. They reported total MT as 76.0–98.7 % and total SQT as 1.3–24.0 %, normalized to 100 % terpenes. α-Pinene was the dominant MT in the gas phase, similar to the needles from this work, but SQT in gas phase were present in lower amounts and showed different composition. In contrast to compounds found in needles, β-Caryophyllene was present in higher amounts in the gas-phase than germacrene D, and α-Farnesene, which was a dominant SQT in the gas phase, was not seen in needles collected from the UMBS. The difference between BVOC reported in the gas-phase and measured in needles might be due to the volatility of different terpenes.

To statistically evaluate the atmospheric effect of BVOC from white pine in northern Michigan forest by measuring BVOC concentration in needles, it is important to determine the relationship between needle concentrations of specific BVOC and their gas-phase emission rates. To do this, the emission rate and needle concentration from white pine tree must be measured at the same site and time, because BVOC composition varies on a yearly basis, as demonstrated by this work.

3.4 Sesquiterpene alcohol

Surprisingly, after α-pinene, one of the most abundant compounds consistently seen in field samples was a sesquiterpene alcohol (SQT-ol). Several experiments showed that this compound was not an artifact of sampling. It has been tentatively identified as germacrene-D-4-ol (CAS# 72120-50-4). A mass spectrum of the compound in a field sample and in the NIST 98 MS library are shown in Fig. 1. The presence of the hydroxyl group was confirmed by derivatization to the TMS ether (the MS spectrum in Fig. S2). Authentic standards of germacrene-D-4-ol are not available. Using the same response factor of standard for SQT without an hydroxyl group to quantify this alcohol, we estimate that its concentrations in white pine needles can be upwards of 50 % of

α-pinene on a mole basis. The concentrations vary in concert with other SQT and so may indicate that this compound is produced and stored via similar mechanisms as SQT.

Germacrene-D-4-ol (or its isomers) has been reported in the sap of several pine species and appears to protect trees from attack by various insects (Nevalainen and Koskinen, 2002; Smitt and Hogberg, 2002). No report of this compound in the atmosphere has been made and little is known about its gas-phase properties. It can be inferred that the hydroxyl group makes it more polar and thus less volatile than most SQT, while retaining much of the increased reactivity with ozone and so is likely to stick to surfaces and to have higher yield of SOA in the atmosphere (Lee et al., 2006a).

3.5 Variation within population (chemotype variation)

About 15 % of the trees sampled at UMBS showed anomalously high levels of limonene, comprising up to 36 % of the total BVOC. In the majority of samples, the relative composition of limonene was about 3 %. The relationship between limonene and α-pinene clearly shows two distinct trends, designated Mode I and Mode II in Fig. 2. This phenomenon was observed in specific trees and always the same trees every year, although they were not close to each other and were randomly distributed in the forest.

The bimodal behavior in the ratio of α-pinene/limonene can arise from either environmental or genetic factors. Environmental variations can be assessed by looking at annual changes and by looking at samples through a growing season. Separate samples from representative trees at Ameriflux of both modes were tracked from June to August in 2010. Even though absolute concentrations of α-pinene and limonene changed as the growing season progressed, the ratio for each tree stayed in the same mode (see Fig. S3). In some cases, trees of both modes were within 2 m of each other at UMBS (Fig. S1), so almost all environmental parameters were likely to be very similar. A more expansive seasonal study (April–October in 2010) was conducted with local samples, which is a different environment from UMBS. This study also showed that the ratio of limonene and α-pinene did not change as the seasons changed (see Fig. S4) and reflected one of the same modes seen at UMBS. Hence, these trends suggest that the bimodal behavior in the ratio of these two compounds is not related to environmental factors.

Changes in volatile compounds could be due to induction of enzyme activity. Martin et al. (2002) studied resin composition of Norway spruce (*Picea abies*) in bark and wood before and after the induction by methyl jasmonate. Limonene concentration was tremendously enhanced after the induction. However, our results are more likely due to genetic difference because the same trees show high concentration of limonene over three years (there is no degradation of limonene concentration). We hypothesize that genotypic variation within the population of trees in this forest leads to different pools of BVOC that could alter BVOC emission estimates and therefore atmospheric oxidant chemistry.

The impact of Mode II levels of limonene on atmospheric chemistry was assessed by looking at the loss of hydroxyl radical, assuming that this bimodal distribution of genotypes is reflective of the upper Midwest. Total loss of hydroxyl radical is expressed relative to α-pinene

$$\frac{d[\mathrm{OH}]}{dt} = \left(1 + \frac{k_{\mathrm{Limonene}}[\mathrm{Limonene}]}{k_{\alpha\text{-Pinene}}[\alpha\text{-Pinene}]}\right) k_{\alpha\text{-Pinene}}[\alpha\text{-Pinene}] \tag{1}$$

$$\frac{d[\mathrm{OH}]}{dt} = \gamma(k_{\alpha\text{-Pinene}}[\alpha\text{-Pinene}]) \tag{2}$$

where γ is “the relatives contribution to OH loss”. If BVOC emissions from white pine needles scales with needle concentration and temperature based on Raoult’s Law, γ can be derived from the measured ratio in pine needles.

$$\frac{[\mathrm{Limonene}]}{[\alpha\text{-Pinene}]} = \frac{P_{\mathrm{Lim.}}}{P_{\alpha\text{-Pin}}} = \frac{X_{\mathrm{Lim.}}\,P^{\circ}_{\mathrm{Lim.}}}{X_{\alpha\text{-Pin}}\,P^{\circ}_{\alpha\text{-Pin}}} \tag{3}$$

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where the partial vapor pressure of a component P, X is the mole fraction, and P° is the vapor pressure of the pure substance at a particular temperature. The relative contribution to OH loss, γ, were calculated at 298 K for Mode I ($\gamma_\mathrm{I} = 1.02$), Mode II ($\gamma_\mathrm{II} = 1.61$), and a mixture of Modes I and II ($\gamma_\mathrm{I\&II} = 1.11$) based on the distribution observed at UMBS. $X_\mathrm{Lim}/X_{\alpha\text{-Pin}}$ are obtained by the slope of regression lines in Fig. 2. Parameters for P° and k are shown in supplementary materials. That γ_I is close to 1 suggests that the effect of limonene is small in this mode. However, the higher concentration of limonene in Mode II shows that total loss of OH increases 61 %. The UMBS forest showed a mixture of trees, which suggests an 11 % increase in OH loss if the higher limonene concentration is considered compared to using a BVOC mixture of the single, most abundant phenotype. As these young forests continue to transition at UMBS and the upper Midwest, terpenes will begin to rival or replace isoprene as the dominant BVOC in the near-canopy atmosphere. Since limonene reacts faster with ozone as well as with OH and yields more SOA than α-pinene, individual tree variation within the forest population of white pine could be a significant factor in the BVOC impact on atmospheric chemistry and should be considered in canopy models.

4 Summary

White pine will recover and affect the chemical composition of US Midwest forests in the future. The most abundant 12 BVOC were identified from white pine needles. MT and SQT showed annual change and different behavior. BVOC composition is significantly affected by environmental factors and has potentially significant variability in annual production. Variation of light levels appears to be the most important factor determining BVOC concentration in needles. More detailed measurements of light exposure at the top and the bottom of the canopy are needed to test this hypothesis.

A SQT-ol represents a large fraction of VOC mass in needles, but the compound is not reported in the gas phase literature. It is important to study its kinetic behavior in the gas phase to determine its role in canopy chemistry and SOA formation.

The large sample size of trees studied allows examination of the variation of individuals within the population. Fifteen percent of the trees at UMBS contain relatively high levels of limonene. The ratio between limonene and *α*-pinene concentrations in needles did not change seasonally or from year-to-year. Genotypic differences among individuals appears to affect the distribution of BVOC in these forests. If high levels of limonene are considered in the calculation of total OH loss in the gas-phase, limonene contributes 11 % of the *α*-pinene reactivity at UMBS, which suggests that chemotypic differences within forest populations should be considered when estimating BVOC calculate emissions.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/26849/2011/ acpd-11-26849-2011-supplement.pdf.

Acknowledgements. This research is supported by the NSF through grant ATM-0904147. We thank the staff of UMBS. We thank John Seeley, Oakland University, for discussions about analytical approaches, Hideo Naoki and Shiono Koryo Kaisha, Ltd. for providing essential oils. We also thank Jesse Thompson, Todd Barkman, and David Karowe, Western Michigan University for their technical support.

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Table 1. The average concentration (µmol dwg^{-1}) with standard deviation in needles of understory white pine trees in both forests at UMBS. "dwg" means dry mass in grams.

Year (No.)	2008 ($n = 71$)	2009 ($n = 70$)	2010 ($n = 69$)
MT			
α-Pinene	14.5 (±5.1)	23.6 (±11.3)	18.7 (±8.8)
Camphene	2.2 (±1.1)	2.8 (±1.9)	2.5 (±1.6)
β-Pinene	4.4 (±1.7)	5.5 (±2.9)	4.4 (±2.1)
Myrcene	2.4 (±1.5)	4.1 (±3.2)	2.1 (±1.6)
α-Phellandrene	1.0 (±0.4)	0.9 (±0.8)	0.9 (±0.4)
Limonene	*2.2 (±1.6)	1.3 (±2.7)	1.5 (±2.5)
β-Phellandrene		1.5 (±1.0)	1.2 (±0.7)
Terpinolene	0.2 (±0.1)	N.D.	0.4 (±0.1)
SQT			
β-Caryophyllene	1.0 (±0.3)	0.1 (±0.2)	1.2 (±0.3)
Germacrene D	4.7 (±1.9)	3.2 (±1.6)	4.7 (±2.4)
Germacrene B	1.2 (±0.4)	0.4 (±0.4)	1.6 (±0.6)
γ,δ-Cadinene	2.0 (±1.0)	0.1 (±0.2)	1.9 (±1.1)
SQT-ol	8.6 (±5.5)	2.3 (±2.0)	8.0 (±5.6)
Total MT	28.6 (±8.7)	39.7 (±17.5)	31.5 (13.4)
Total SQT	17.8 (±8.1)	6.1 (±3.5)	17.4 (±8.6)
Total BVOC	46.5 (±15.0)	45.8 (±19.7)	48.9 (±20.5)

* denotes limonene was not separated from β-phellandrene.

Table 2. Average concentration (µmol dwg^{-1}) of terpenes at the top (6–17 m) and bottom (2–4 m) of overstory trees.

Year (No.)		Total MT	Total SQT	Total BVOC
2008 ($n = 4$)	Top	*33.7	12.3	46.0
	Bottom	25.1	*21.0	46.1
2009 ($n = 8$)	Top	*57.1	5.5	*62.6
	Bottom	29.2	5.2	34.4
2010 ($n = 10$)	Top	*46.3	12.8	*59.1
	Bottom	24.9	12.3	37.3

* denotes statistical significance between top and bottom of needles. The Wilcoxon signed ranks test was used ($P = 0.05$).

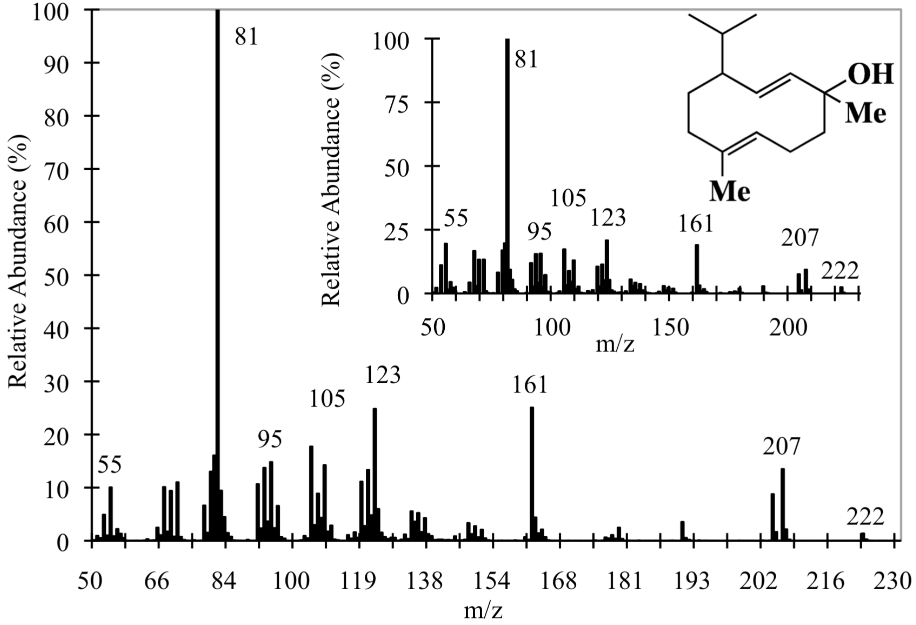

Fig. 1. Mass spectrum of germacrene D-4-ol from a field sample, and from the NIST mass spectral library (embedded) with proposed structure.

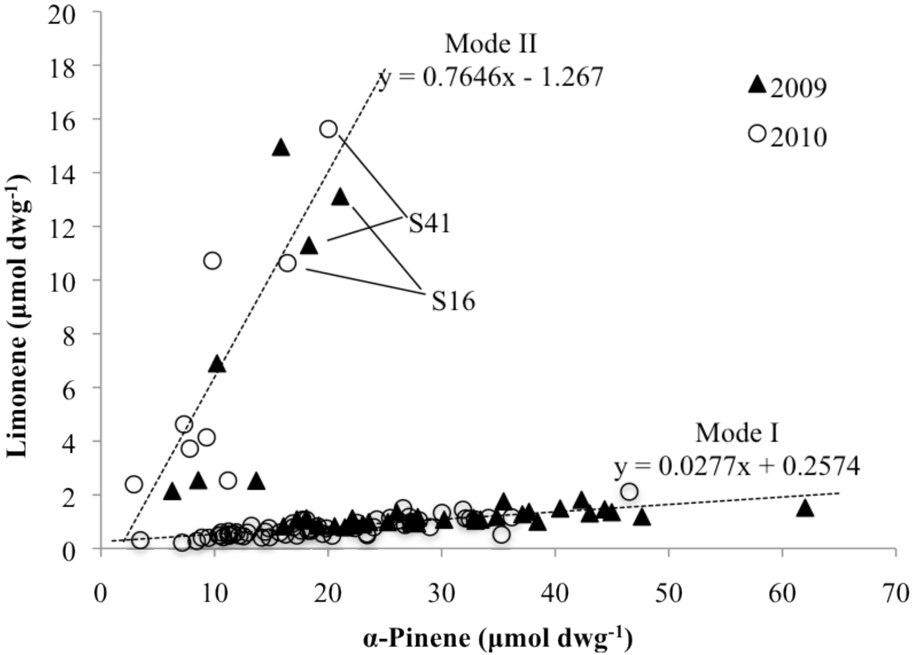

Fig. 2. The correlation between limonene and α-pinene concentration at UMBS in 2009 and 2010.