Methyl Chavicol: Characterization of its Biogenic Emission Rate, Abundance, and Oxidation Products in the Atmosphere

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Bouvier-Brown, N. C, A. H Goldstein, D. R Worton, D. M Matross, J. B Gilman, W. C Kuster, D. Welsh-Bon, et al. 2009. “Methyl Chavicol: Characterization of Its Biogenic Emission Rate, Abundance, and Oxidation Products in the Atmosphere.”
Methyl chavicol: characterization of its biogenic emission rate, abundance, and oxidation products in the atmosphere

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Received: 26 September 2008 – Published in Atmos. Chem. Phys. Discuss.: 19 November 2008
Revised: 16 February 2009 – Accepted: 5 March 2009 – Published: 23 March 2009

Abstract. We report measurements of ambient atmospheric mixing ratios for methyl chavicol and determine its biogenic emission rate. Methyl chavicol, a biogenic oxygenated aromatic compound, is abundant within and above Blodgett Forest, a ponderosa pine forest in the Sierra Nevada Mountains of California. Methyl chavicol was detected simultaneously by three in-situ instruments – a gas chromatograph with mass spectrometer detector (GC-MS), a proton transfer reaction mass spectrometer (PTR-MS), and a thermal desorption aerosol GC-MS (TAG) – and found to be abundant within and above Blodgett Forest. Methyl chavicol atmospheric mixing ratios are strongly correlated with 2-methyl-3-buten-2-ol (MBO), a light- and temperature-dependent biogenic emission from the ponderosa pine trees at Blodgett Forest. Scaling from this correlation, methyl chavicol emissions account for 4–68% of the carbon mass emitted as MBO in the daytime, depending on the season. From this relationship, we estimate a daytime basal emission rate of 0.72–10.2 µgCg⁻¹h⁻¹, depending on needle age and seasonality. We also present the first observations of its oxidation products (4-methoxybenzaldehyde and 4-methoxy benzene acetaldehyde) in the ambient atmosphere. Methyl chavicol is major essential oil component of many plant species. This work suggests that methyl chavicol plays a significant role in the atmospheric chemistry of Blodgett Forest, and potentially other sites, and should be included explicitly in both biogenic volatile organic carbon emission and atmospheric chemistry models.

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1 Introduction

Plants contain thousands of different volatile and semi-volatile organic compounds (Adams, 2007), and the atmospheric chemistry community has historically focused on a small subset of these. With continuing improvements in analytical instrumentation, a wider suite of biogenic volatile organic compounds (BVOCs) have been measured in the atmosphere in recent years (e.g. Goldan et al., 1993; Schade and Goldstein, 2001; Helmig et al., 2007), and the list of specific BVOCs included in emission inventories and atmospheric chemistry models is growing (e.g. Sakulyanontvittaya et al., 2008; Steiner et al., 2008). Here we focus on methyl chavicol (IUPAC name: 1-methoxy-4(2-propenyl)-benzene; CAS# 140-67-0), a compound previously uncharacterized in the atmosphere. Known as estragole or 4-allylisoI, methyl chavicol (C₁₀H₁₂O) is an oxygenated aromatic BVOC, and although it has 10 carbon atoms, it is not a terpenoid compound. Plants synthesize this compound, which smells like licorice, from the amino acid phenylalanine via the shikimate pathway (Sangwan et al., 2001) (Fig. 1). Analysis of extracted plant oils show that methyl chavicol is produced by a variety of plants (Table 1). For example, methyl chavicol is a major essential oil component of many common herbs such as basil (up to 70%) (Simon et al., 1990; Leung and Foster, 1996; Sajjadi, 2006), tarragon (up to 86%) (Werker et al., 1994; Leung and Foster, 1996; De Vincenzi et al., 2000), and fennel (up to 65%) (Barazani et al., 2002; De Vincenzi et al., 2000). It is also a major component in the oils of culturally-significant plants found worldwide, including a Latin American herb (up to 97%) (Ciccio, 2004), an ubiquitous Korean herb (up to 49%) (Shin and Kang, 2003).
an Indian herb (up to 93%) (Hazarika and Nath, 1995), a Turkish herb (up to 90%) (Kaya et al., 2007), and a Mexican avocado (up to 95%) (Pino et al., 2006b; Leung and Foster, 1996). Methyl chavicol has been identified in the resin of pines (*Pinus* spp.) (Mirov, 1961; Salom and Hobson, 1995 and references therein), such as Caribbean (Snyder and Bower, 2005), black (Rezzi et al., 2001), Scots, slash (Chadwick and Palkin, 1941), longleaf (Mirov, 1948), lodgepole, loblolly (Strom et al., 2002; Werner, 1972), and ponderosa (e.g. Cobb et al., 1972; Adams and Edmunds Jr., 1989). In fact, studies of ponderosa pine oil show that methyl chavicol accounts for 3–40% of the total needle oil (Zavarin et al., 1971), an abundance comparable to (Krauze-Baranowka et al., 2002) or higher than the monoterpene 3-carene (Kurose et al., 2002) or higher than the monoterpene 3-carene (Kurose et al., 2002). Branch enclosure emissions and emission rates have been notably absent in the literature (Lerdau et al. 1997; Fuentes et al., 2000). Methyl chavicol is emitted from the ponderosa pine as the source plant for methyl chavicol emissions to the Blodgett forest ecosystem and provided estimates of emission rates and ecosystem flux (Bouvier-Brown et al., 2009). Emissions of methyl chavicol were 9–117% of the total measured terpene (sum of the total measured monoterpenes and sesquiterpenes) flux, but each branch had a different emission profile which varied over time (Bouvier-Brown et al., 2009). As a result of this variation, methyl chavicol basal emissions ranged from 0.159 to 1.09 µg Cg d−1 m−2 h−1 and an average daytime ecosystem flux was estimated to be 1.37 µmol m−2 h−1 (Bouvier-Brown et al., 2009).

Methyl chavicol oxidation has been studied in the laboratory using a PTR-MS. Full photochemical oxidation of methyl chavicol in a smog chamber produced a 42% yield of an unknown compound detected at *m/z* 137 and a 23% yield of a compound, hypothesized to be a C9H10O2 aldehyde, detected at *m/z* 151 (Lee et al., 2006b). An unidentified product detected at *m/z* 151 was also generated from ozonolysis experiments at a 25% yield, which was the largest *m/z* 151 yield of any terpene tested (Lee et al., 2006a). These experiments also showed that methyl chavicol oxidation leads to the production of secondary organic aerosol (SOA) with yields of 40% from full photochemical oxidation (Lee et al., 2006b) and 6% from ozonolysis (Lee et al., 2006a).

Here we report a more detailed characterization of the environmental factors that drive methyl chavicol emissions in Blodgett Forest, a ponderosa pine forest. We also present the first observations of its oxidation products in the ambient atmosphere. To elucidate processes driving methyl chavicol emissions, we compare its mixing ratios and average diurnal profiles to that of 2-methyl-3-buten-2-ol (MBO) and the monoterpene α-pinene. MBO, a known prominent biogenic emission from this site, is emitted from the ponderosa pine trees as a function of light and temperature in a similar manner to that of isoprene (Baker et al., 1999; Lamanna and

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**Fig. 1.** Schematic of methyl chavicol synthesis modified from the glucose → phenylalanine and phenylalanine → methyl chavicol mechanisms presented by Yoshida (1969) and Sangwan et al. (2001), respectively.
Table 1. A variety of plants are known to produce methyl chavicol. Percentage of methyl chavicol present in the plant's essential oil is noted if available. The primary reference describes the measurement and analytical technique; the secondary reference provides numerical data without detailed analytical information.

| Plant species containing methyl chavicol | Common name/description | Oil % methyl chavicol | Primary reference | Secondary reference |
|----------------------------------------|-------------------------|-----------------------|-------------------|---------------------|
| Ocimum minimum                         | basil                   | 36.3%                 | Tchoumbougouang et al. (2006) |                      |
| Ocimum basilicum L. cv. purple         | purple basil from Iran  | 52.4%                 | Sajjadi (2006)     |                     |
| Ocimum basilicum L. cv. green          | green basil from Iran   | 40.5%                 | Sajjadi (2006)     |                     |
| Ocimum basilicum L. (Lamiaceae)        | basil (sweet)           | 5-43%                 | De Vincenzi et al. (2000) | Salom and Hobson (1995); Simon et al. (1990); Duke (2001) |
| Ocimum basilicum L. (Labiatae)         | basil (sweet)           | 70%                   | Leung and Foster (1996); Duke (2001) |                      |
| Artemisia dracunculus L. (Asteraceae)  | French tarragon         | 77-86%                | Werker et al. (1994) | Salom and Hobson (1995) |
| Artemisia dracunculus L. (Asteraceae)  | Russian tarragon        | 0.1-0.3%              | Werker et al. (1994) |                     |
| Artemisia dracunculus L. (Asteraceae)  | tarragon                | 60-81%                | De Vincenzi et al. (2000) | Leung and Foster (1996); Duke (2001) |
| Foeniculum vulgare var. vulgare       | bitter fennel           | 3-65% cultivated/wild | Barazani et al. (2002) | Salom and Hobson (1995); Leung and Foster (1996); Duke (2001) |
| Foeniculum vulgare Mill. (Apiaceae)   | sweet fennel            | 5-20%                 | De Vincenzi et al. (2000) |                     |
| Pimpinella anisum L.                   | anise                   |                       | Leung and Foster (1996) |                     |
| Pimpinella anisum L. (Apiaceae)        | anise vert              | 1%                    | De Vincenzi et al. (2000) |                     |
| Illicium verum Hook f. (Magnoliaceae)(Illiciaceae) | star anise | 5-6%                  | De Vincenzi et al. (2000) | Salom and Hobson (1995); Duke (2001) |
| Pimpinella anisum L.                   | Mexican spice (grain)   | 1-2%                  | Ondarza and Sanchez (1990) |                     |
| Syzygium aromatitic L. Merril.          | clove                   |                       | Salom and Hobson (1995); Duke (2001) |                     |
| L.M. Perry                             |                         |                       |                   |                     |
| Pimenta racemosas F.W. Moore           | West Indian bay         |                       |                   |                     |
| Origanum majorana L. (Labiatae)        | marjoram                |                       |                   |                     |
| Anthisicus cerefolium Hoffm. (Apiaceae) | chervil                |                       |                   |                     |
| Backhousia ansa Asiatica (Myrtaceae)   | sub-tropical Australian tree | 4.4-77.5%           | Brophy and Boland (1991) |                     |
| Tagetes lucida (Asteraceae)             | aromatic herb (Latin America) | Costa Rican: 95-97% | Ciccio (2004) |                     |
| Agastache rugosa Kunze                 | Korean herb             | 42-49%                | Shin and Kang (2003) |                     |
| Agastache foeniculum                   | anise byssop/W.N. American shrub/herb | 96-97% | Maza and Kiehn (1992) | Adams (2007) |
| Amonum longiflora                     | rhizomatous herb (India) | 93.2%                 | Hazarika and Nath (1995) | Adams (2007) |
| Clausena dolensis                     | S. China shrub          | 93.1%                 |                    | Adams (2007) |
| Dictamus gymnostylis                  | “burning bush”/middle-east bush | 15%                 | Fleisher and Fleisher (2004) |                     |
| Dictamus hispanicus                   | endemic to Mediterranean area (Spain) | 79%            | Merle et al. (2006) |                     |
| Helinium amarum (Raf.) H. Rock         | yellowwicks – Cuba, also present in US | 84.4% | Pino et al. (2006a) |                     |
| Scandix iberica Bieb.                 | herb in Turkey          | 85.8-90.5%            | Kaya et al. (2007) |                     |
| Echinops graucus                      | endemic to Greece       | 42.5%                 | Papadopoulos et al. (2006) |                     |
| Ravensara aromatica Sonn.             | endemic to Madagascar   | 79.7%                 | Ramananelina et al. (2006) |                     |
| Pseuda artemiscana Mill. (Lauraceae)   | Mexican type of avocado | 53.9-95%              | Pino et al. (2006b) | Leung and Foster (1996) |
| Ocotea punctata (Myrtaceae)            | Straggly Baecke (Australia) | 81.6% | Southwell et al. (2003) |                     |
| Pinus caribaea Morlet                  | Caribbean pine           | 1.5-3%                | Snyder and Bower (2005) |                     |
| Pinus nigra Arnold                    | black pine              | 0-1.3%                | Rezzi et al. (2001) |                     |
| Pinus sylvestris L.                   | Scots pine              | 5-13%                 | Chadwick and Pallin (1941) |                     |
| Pinus elliott var elliott             | slash pine              |                       |                     |                     |
| Pinus elliott var densa               | (Florida)               | 3%                    | Mirov (1961) |                     |
| Pinus palustris Mill                  | longleaf pine, southern yellow pine | 1-5%        | Salom and Hobson (1995); Hayes et al. (1994) |                     |
| Pinus palustris Mill                  | longleaf pine (Southern US) | 0-0.7%         | Mirov (1948) |                     |
| Pinus taeda L.                        | lobolly pine (South Eastern US) | 1-1% | Sutherland and Welles (1956); Werner (1972) | Salom and Hobson (1995); Mirov (1961) |
| Pinus taeda L.                        | lobolly pine            | 0.22-2.5% oleoresin weight | Strom et al. (2002) |                     |
| Pinus contorta Dougl.                 | lodgepole pine          |                       | Nebeker et al. (1995) | Joseph et al. (2001) |
| Pinus hartwegii                       | (upper elevations Mexico) | 3%                   | Mirov (1961) |                     |
| Pinus lamboltzii                      | (western Mexico)         | 2-3%                  | Mirov (1961) |                     |
| Pinus michoacana                      | (Mexico)                | 2-3%                  | Mirov (1961) |                     |
| Pinus patula                         | (Mexico)                | 5%                    | Mirov (1961) |                     |
| Pinus jeffrii                         | Jeffrey pine (Western US) | 7.4-25.7%       | Cobb et al. (1972) |                     |
| Pinus ponderosa                       | ponderosa pine          | 8%                    | Krauze-Baranowska et al. (2002) |                     |
| Pinus ponderosa                       | ponderosa pine          | present               | Himejima et al. (1992) |                     |
| Pinus ponderosa                       | ponderosa pine          | 0.4-5.3%              | Adams and Edwards (1989) |                     |
| Pinus ponderosa                       | ponderosa pine          | 3-40%                 | Zavarin et al. (1971) |                     |
| Pinus ponderosa                       | ponderosa pine          | 10.50%                | Kurose et al. (2007) |                     |
| Pinus ponderosa                       | ponderosa pine          | 0-2% depend on location | Mirov (1961) |                     |
Goldstein, 1999; Schade et al., 2000; Schade and Goldstein, 2001; Gray et al., 2005). α-Pinene is a significant contributor to the monoterpene flux out of this forest, and like other monoterpenes at this site, it is emitted as a function of temperature (Shade et al., 1999; Schade and Goldstein, 2003; Lee et al., 2005; Holzinger et al., 2005, 2006).

2 Experimental

2.1 The site

Methyl chavicol was measured at the Blodgett Forest Ameriflux site, a ponderosa pine plantation owned by Sierra Pacific Industries, located on the western slope of the Sierra Nevada Mountains of California (38.90° N, 120.63° W, and 1315 m elevation) as a part of BEARPEX (Biosphere Effects on AeRosols and Photochemistry EXperiment) 2007. The site’s vegetation is dominated by an overstory of ponderosa pine (Pinus ponderosa L.) with an average height of 8 m and an understory of manzanita (Arctostaphylos spp.) and whitethorn ceanothus (Ceanothus cordulatus) shrubs. Mixing ratios and fluxes of carbon dioxide, water vapor, and ozone, along with meteorological parameters, have been measured at the site since 1997, and are reported in detail elsewhere (e.g. Goldstein et al., 2000; Bauer et al., 2000).

BEARPEX included two distinctly different meteorological periods. The first period from 20 August to 12 September (day of year 232–255) was characterized by warm and dry conditions (average daytime meteorological parameters: temperature 27°C, relative humidity 26%, and maximum photosynthetically active radiation (PAR) 1410 µmol m−2 s−1). The second period from 13 September to 10 October (day of year 256–283) was characterized by cool and wet conditions (average daytime meteorological parameters: temperature 15°C, relative humidity 49%, and PAR 1010 µmol m−2 s−1). Figure 2 shows the temperature and rainfall time series during BEARPEX and highlights the measurement periods for the gas chromatography techniques described below.

2.2 Analytical techniques

2.2.1 Berkeley GC-MS

The gas chromatograph with quadrupole mass spectrometer (GC-MS) instrument described by Millet et al. (2005) was optimized to quantify C_{10}-C_{15} biogenic compounds with the redesign of the inlet system described here. Methyl chavicol was never reliably observed at Blodgett Forest during the 10 years of sampling until these modifications were made. To reduce sample loss due to condensation, all tubing and fittings prior to the GC oven were heated to ~50°C (Omega Engineering Stamford, CT) and the sub-zero water trap was eliminated. With ambient water vapor in the sample, the hydrocarbon preconcentration trap packed with Tenax TA remained at ambient temperature during sample collection. All tubing and fittings were changed from PTFE (Oakland Valve and Fitting, Inc., Fremont, CA) to Silcosteel (Restek Corporation, Bellefonte, PA) because the metal tubing allows for even heat dispersal and the internally passivated surface minimizes wall reactions and subsequent losses. To reduce the chance of sample adsorption, the chemically-active ozone trapping material was changed from impregnated glass wool to a 1 µm pore size Pall A/E glass fiber filter (VWR, Ann Arbor, MI). This filter was coated with sodium thiosulfate (Sigma-Aldrich, St. Louis, MO), following Pollmann et al. (2005), and housed in a heated stainless steel filter holder (Cole-Parmer, Vernon Hills, IL). The filter was also used to remove particulate matter from the sample. To ensure its effectiveness, the ozone filter was changed at least once per day.

Ambient air was pulled through 6.35 mm outer diameter Silcosteel tubing at ~4 L min−1, scrubbed of ozone, and subsampled through 3.18 mm outer diameter Silcosteel tubing at ~20 mL min−1. Once per hour, a 600 mL sample was collected over a 30 min period. The pre-concentrated sample was heated from ambient temperature to 220°C within 10 s to desorb the trapped compounds into ultra high purity helium carrier gas and transferred to the head of the chromatographic column (30 m×0.25 mm×0.25 µm phase thickness, Rtx-5; Restek Corporation). The GC oven temperature was held at 43°C for 4.25 min, increasing to 160°C at 5°C min−1, then to 220°C at 10°C min−1 and held at this temperature for 11.75 min. The mass spectrometer (HP 5971) was operated in single ion mode, and methyl chavicol was quantified with m/z 148.

Since methyl chavicol is a semi-volatile compound, it is not readily available as a gas phase standard. Bouvier-Brown et al. (2007) produced a gas phase methyl chavicol standard by volatilizing diluted pure liquid standards in a Tedlar
were cryofocused and then separated using a metal MXT-washed Alumina column and analyzed first. Iso- 

solute of 12 m of 6.35 mm outer diameter PFA tubing through (24–27 September, day of year 267–270) (Fig. 2) and con-
to the analysis system will be briefly described here. The in-

fractions of volatile C$_2$–C$_{10}$ were separated and monoterpenes were 27% and 18%, respectively.

berkeley GC-MS measurements were made at two differ-

ent inlet heights during two distinct sampling periods. One 
inlet was located 1.5 m above the forest floor, below the main 
trees of the canopy but near the juvenile saplings, from 19 
August through the morning of 12 September (day of year 
231–255). The other inlet was located 9.3 m above the for-
est floor, which corresponds to ~2 m above the mean forest 

canopy height, from the afternoon of 12 September through 8 October (day of year 255–281). The sampling timeline is 

outlined in Fig. 2.

2.2.2 NOAA GC-MS

Volatile C$_2$–C$_{10}$ organic compounds, in particular 2-methyl-

3-buten-2-ol (MBO) and isoprene, were quantified using a 
gas chromatograph with mass spectrometer detector (NOAA 
GC-MS). The sample acquisition procedure is described in 

detail by Goldan et al. (2004), but more recent modifications 
to the analysis system will be briefly described here. The in-

let was located at 9.3 m above the canopy floor for three days 
(24–27 September, day of year 267–270) (Fig. 2) and con-

sisted of 12 m of 6.35 mm outer diameter PFA tubing through 
which approximately 8 L min$^{-1}$ of air was drawn. Care 
was taken to prevent permeation of VOCs into the sample stream 
from the mobile laboratory housing the GC-MS. Once the 
sample inlet tubing entered the laboratory, it was contained 
inside a 12.7 mm outer diameter PFA line. The bulk sample 
flow (~95%) was then exhausted through the larger diameter 
coaxial line so that the sample flow itself acted as a counter-
flowing sheath gas.

The 2-channel custom built system consisted of parallel 
systems for sample acquisition and separation for subse-
quent analysis by a single mass spectrometer (formally a GC-
FID/MS system). Two 5 min samples were acquired concurren-
tly every 30 min at a rate of 70 mL min$^{-1}$ then analyzed 
serially. Light alkanes and alkenes (C$_2$–C$_5$) were separated 
on a KCl washed Alumina column and analyzed first. Iso- 

prene and MBO, along with the heavier species (C$_2$–C$_{10}$), 
were cryofocused and then separated using a metal MXT-

624 column (Restek) with a temperature program ramping 
from 38°C to 127°C at 8.1°C min$^{-1}$ and a helium carrier 
flow of 2 mL min$^{-1}$. The two columns were plumbed into a 4-port valve (Valco) which was then connected to the linear quadrupole mass spectrometer (Agilent 5973).

2.2.3 PTR-MS

Volatile organic compounds were also quantified by proton 
transfer reaction mass spectrometry (PTR-MS), which has 
been described elsewhere in detail (Lindiniger et al., 1998; de 
Gouw and Warneke, 2007). Five inlets were used to sample 
vertical gradients within (1.5 m, 6.0 m above the forest floor) 
and above (9.3 m, 14.3 m, 17.7 m above the ground) the for-
est canopy where ambient air from each height was sampled 
using 6.35 mm outer diameter PFA tubing. The set-up was 
similar to that described by Holzinger et al. (2005). Ambient 
air was drawn down from the tower at 20 L min$^{-1}$ continu-
ously from all levels simultaneously and sub-sampled di-
rectly into the instrument at 400 mL min$^{-1}$. Each hour-long 
sample cycle consisted of a 6-minute sampling period at each 
level. Twelve individual ions, including the primary m/z signal for methyl chavicol, were measured with a variable dwell 
time that increased at higher m/z ratios to obtain reasonable 
signal to noise ratios across the set. Methyl chavicol was de-
tected at m/z 149, and although the PTR-MS likely detected 
other compounds at m/z 149, methyl chavicol is assumed to 
dominate the signal. The PTR-MS instrument described be-
low was used during branch enclosure measurements to ver-
ify this assumption.

Methyl chavicol was quantified by correlating the PTR-
MS response detected at m/z 149 to the Berkeley GC-MS 
quantification of methyl chavicol using an authentic standard 
when the two measurements were co-located at 9.3 m. The 
slope of correlation had a 19% relative standard error. MBO 
was quantified by correlating the sum of m/z 87 and m/z 69 
to the NOAA GC-MS quantification of MBO using an au-

thentic standard when the two instruments were co-located 
at 9.3 m. The slope of correlation had an 8% relative stan-
dard error. Since isoprene is also detected at m/z 69, MBO 
was isolated from the isoprene interference after determining 
the ratio of MBO to isoprene present using the NOAA GC-
MS measurements. MBO can be separated this way because 
the isoprene mixing ratio diurnal pattern is very predictable. 
The only significant isoprene influence at Blodgett Forest is 
regularly transported to the site in the afternoon from down-
wind sources (e.g. Dreyfus et al., 2002).

2.2.4 PIT-MS

Proton transfer ion trap mass spectrometry (PIT-MS) uses 
the same proton transfer reactions employed in PTR-MS to ion-
ize VOCs, but subsequent ion analysis occurs with an ion trap 
mass spectrometer (Warneke et al., 2005a, b). In addition 
to measuring VOCs with high time resolution, the PIT-MS
Organic constituents in particulate matter were separated and measured using a Thermal Desorption Aerosol GC-MS (TAG) instrument (custom built from Agilent GC6890/MS5973), which has been described in detail elsewhere (Williams et al., 2006; Kreisberg et al., 2009). Briefly, ambient aerosol samples (PM$_2.5$) are collected by humidification and inertial impaction. Following collection, the contents were thermally desorbed into helium carrier gas and transferred onto the head of a gas chromatographic column prior to separation (30 m, 0.25 mm, 0.25 μm film Rxi-5ms column; Restek Corporation) and detection by mass spectrometry. Samples (0.75 m$^3$ volume) were collected for 1.5 of every 2 h at a sampling rate of 9 L min$^{-1}$ through 9.52 mm outer diameter insulated stainless steel tubing from an inlet located 9.3 m above the ground. The TAG methyl chavicol data are normalized to the maximum response observed during the study.

2.2.6 SPME fibers

Solid Phase MicroExtraction (SPME) fibers were periodically used for qualitative analysis of ambient air during BEARPEX. Field portable 65 μm polydimethylsiloxane-divinylbenzene (PDMS/DVB) Stableflex fibers (Supelco, Bellefonte, PA) collected analytes in air samples pulled over their surfaces at ∼4 L min$^{-1}$ for 4–24 h and were analyzed using a gas chromatograph with ion trap mass spectrometer as described by Bouvier-Brown et al. (2007). SPME fibers were co-located with both Berkeley GC-MS inlets at 1.5 and 9.3 m above the forest floor.

3 Results and discussion

To characterize methyl chavicol abundance, emission, and oxidation products, this section is broken into four parts: methyl chavicol mixing ratios, methyl chavicol emissions, atmospheric implications, and oxidation products. In 3.1, ambient mixing ratios are used to evaluate the measurement agreement among the three analytical instruments that detected methyl chavicol and show methyl chavicol’s variability relative to total terpene mass. In 3.2, methyl chavicol’s emission dependence on light and temperature is revealed through comparison to MBO and the monoterpene α-pinene. The correlation between methyl chavicol and MBO is then used to estimate methyl chavicol basal emission rates. An estimation of methyl chavicol reaction rates and its atmospheric lifetime as well as observations of the proposed oxidation products are discussed in Sects. 3.3 and 3.4, respectively.

3.1 Methyl chavicol mixing ratios

Methyl chavicol was simultaneously measured by the Berkeley GC-MS and PTR-MS, and at the same time it was also detected in the aerosol phase by the TAG instrument. Ambient measurements from the three instruments consistently show a methyl chavicol diurnal profile with mixing ratio maxima in the morning and late evening (Fig. 4). The slight differences in each instrument’s profile reflect the different sampling times and inlet types (see Sect. 2.2). The maxima occur at times when the light and temperature are high enough to induce emissions from the trees into a shallow boundary.
layer with low oxidant mixing ratios leading to an accumulation of emissions. The mid-afternoon minima are characteristic of vertical mixing into a deeper boundary layer and chemical destruction with both effects overwhelming the increased daytime emissions at higher temperature and solar radiation. Without the influence of vertical mixing and oxidation in the canopy, methyl chavicol mixing ratios would peak in mid-afternoon as observed during branch enclosure experiments (Bouvier-Brown et al., 2009).

The ratio of methyl chavicol to total terpene (sum of the total monoterpenes, sesquiterpenes and oxygenated terpenes) mass is highly variable. During the warm period (20 August–12 September, day of year 232–255), methyl chavicol mixing ratios averaged 15% of the total terpene mass measured at 1.5 m above the forest floor. During the cooler period (12 September–8 October, day of year 255–281), methyl chavicol mixing ratios averaged 36% of the total terpene mass just above the canopy at 9.3 m above the ground. These relative mixing ratios are both within the 9–117% range measured in ponderosa pine branch enclosures (Bouvier-Brown et al., 2009).

3.2 Methyl chavicol emissions

Although monoterpenes and methyl chavicol are all 10-carbon BVOCs emitted from this ecosystem, our results show different physical and environmental factors drive their emissions. For example, in this drought-stressed ecosystem, enhanced monoterpene emissions occur immediately following wetting by rain. Methyl chavicol emissions, following more closely the emissions of 2-methyl-3-buten-2-ol (MBO), do not increase until a few days after the rain when the temperature begins to increase and full light is available (Fig. 5). The correlation between ambient methyl chavicol and \( \alpha \)-pinene, an abundant monoterpene, mixing ratios is poor \((R^2=0.1, n=186)\) during this cool period.

During BEARPEX, ambient MBO and monoterpene mixing ratios were largest in the lower canopy and MBO showed the same diurnal pattern throughout the canopy, as seen by Holzinger et al. (2005). During the cool period (12 September–8 October, day of year 255–281), an average diurnal profile of methyl chavicol mixing ratios at each of the five gradient levels measured by the PTR-MS also show the largest mixing ratios low in the canopy (Fig. 6). This clearly indicates that methyl chavicol emissions are local and biogenic in origin, similar to MBO.

At 9.3 m above the ground during three cool days (24–27 September, day of year 267–270) following a large rain event, the average ambient diurnal profiles of methyl chavicol and MBO are strikingly similar, but differ from that of \( \alpha \)-pinene (Fig. 7). Characteristic of temperature and light-driven emissions, methyl chavicol and MBO mixing ratios are relatively constant during the hours of full sunlight and significantly larger during the day than at night. On the other hand, for monoterpenes, such as \( \alpha \)-pinene, mixing ratios are largest at night when vertical mixing is weak and there are continuous temperature-driven emissions from storage pools in plant resins.

During the warm measurement period (20 August–12 September, day of year 232–255) at 1.5 m above the forest floor, the average diurnal profiles of methyl chavicol and MBO measured by PTR-MS were similar, particularly with respect to the morning and evening peaks (Fig. 8). One important distinction between the profiles is the presence of methyl chavicol at night (Fig. 8). The evidence of nighttime emission is corroborated by the PTR-MS gradient data from the cool period (Fig. 6). Conversely, MBO mixing ratios are very low at night and do not show a vertical gradient (Holzinger et al., 2005). The presence of nighttime methyl chavicol mixing ratios and a vertical gradient indicates a likely temperature-dependent emission mechanism from storage pools similar to the monoterpene emission mechanism at this site. Contrary to monoterpenes, this temperature-dependent emission mechanism is less significant to methyl chavicol’s overall emission. Methyl chavicol mixing ratios are 1.8 times larger at night than during the day, whereas monoterpene mixing ratios average 3.5 times more at night at 1.5 m above the ground during the warm period. Methyl chavicol may have a hybrid emission mechanism where emission occurs both from storage pools and directly after production. However, the daytime emission dominantly occurs directly after production by a temperature and light-driven emission mechanism, similar to that of MBO.
Fig. 5. An example timeline of methyl chavicol (green ×) and α-pinene (red ⋆) mixing ratios measured by the Berkeley GC-MS, and 2-methyl-3-buten-2-ol (MBO •) mixing ratios measured by the NOAA GC-MS along with temperature (orange –), light (PAR, blue –), relative humidity (RH, brown – –) and rainfall (solid grey bars).

3.2.1 Estimating methyl chavicol emission rates

Since methyl chavicol’s diurnal profile and atmospheric lifetime (discussed in Sect. 3.3.) are very similar to that of MBO, we can estimate the ecosystem emission of methyl chavicol by scaling the known emission rate for MBO to the slope of their correlation. When the NOAA GC-MS and the Berkeley GC-MS measurements were co-located (Fig. 2), a linear regression of methyl chavicol vs. MBO daytime mixing ratios yields a slope of 0.34±0.03 (mean ± standard deviation) and a correlation coefficient of 0.82 (Fig. 9). Assuming that these compounds have similar sources and sinks, their correlation during this cool period indicates that methyl chavicol emissions are, on average, 34% of MBO emissions. In terms of the amount of photosynthetic carbon lost to the atmosphere during the three days, methyl chavicol emissions account for 68% of the carbon mass of MBO emissions because methyl chavicol has twice the amount of carbon per molecule. Given a MBO basal emission range of ∼5–15 µgCg⁻¹h⁻¹, depending on needle age, from ponderosa pine trees at Bledgett Forest during a similar cool fall period (day of year 256–287) (Schade et al., 2000; Gray et al., 2005), an estimated basal emission rate for methyl chavicol is 3–10 µgCg⁻¹h⁻¹.

Additional analysis of the branch enclosure measurements from summer 2005 conducted in a warm and dry environment described by Bouvier-Brown et al. (2009) reveals that
this relative emission rate varies with season because MBO emissions have a stronger temperature dependence. A similar linear regression of methyl chavicol vs. MBO yields a slope within the range of 0.02–0.12, depending on the branch (R²=0.81–0.96, n=164–814). As a result, methyl chavicol emissions account for 4–24% of the carbon mass emitted by MBO in warm and dry conditions. Using the maximum average MBO basal emission rate from ponderosa pine trees at Blodgett Forest of 18 µgCg⁻¹ h⁻¹ (Schade et al., 2000), an estimated methyl chavicol basal emission rate ranges from 0.7–4.3 µgCg⁻¹ h⁻¹ in warm and dry conditions. The estimated ecosystem flux of 0.491 µgCg⁻¹ h⁻¹ (which is equivalent to 1.37 µmol m⁻² h⁻¹) reported by Bouvier-Brown et al. (2009) under similar warm and dry conditions is likely underestimated because controlled experiments were not conducted to assess the light dependence parameters of the emissions.

3.3 Atmospheric implications

No reaction rates for methyl chavicol have been reported in the literature, so we used data collected during ozonolysis and photooxidation chamber studies described by Lee et al. (2006a, b) to estimate reaction rate coefficients. We correlated the loss rate of methyl chavicol with the loss rate of other compounds tested that have reaction rate coefficients in the literature. These estimates (kOH = 5.7 × 10⁻¹¹ cm³ molec⁻¹ s⁻¹ and kO₃ = 1.4 × 10⁻¹⁷ cm³ molec⁻¹ s⁻¹) agree with rate coefficients calculated using the Environmental Protection Agency’s Estimation Program Interface Suite (kOH = 5.4 × 10⁻¹¹ cm³ molec⁻¹ s⁻¹, kO₃ = 1.2 × 10⁻¹⁷ cm³ molec⁻¹ s⁻¹) based solely on chemical structure (US EPA AOPWIN, 2000).

These estimated rate coefficients are very similar to that of MBO (kOH = 5.8 × 10⁻¹¹ cm³ molec⁻¹ s⁻¹, kO₃ = 9.7 × 10⁻¹⁷ cm³ molec⁻¹ s⁻¹; Atkinson and Arey, 2003), thus supporting our method of estimating methyl chavicol’s emission rate from that of MBO.

Significant amounts of methyl chavicol escape from the Blodgett Forest canopy and are transported downwind. Using an average OH mixing ratio of 5.4×10⁶ molec cm⁻³

Fig. 7. Average diurnal profiles of methyl chavicol (green ×), MBO (black ●), and α-pinene (red ●) (mean ± standard error). Measurements were made at 9.3 m from 24–27 September (day of year 267–270), and MBO was measured by NOAA GC-MS.

Fig. 8. Average diurnal profiles of methyl chavicol (green ×), MBO (black ●), and α-pinene (red ●) (mean ± standard error). Measurements were made at 1.5 m above the ground from 20 August–12 September (day of year 232–255), and MBO was measured by PTR-MS.

Fig. 9. Methyl chavicol measured by the Berkeley GC-MS and MBO measured by the NOAA GC-MS were tightly correlated when daytime measurements were co-located at 9.3 m above the forest floor (24–27 September, day of year 267–270). A slope of 0.34±0.03 (R² of 0.82, intercept of −0.04, n=24) indicates that the methyl chavicol emissions average 34% of MBO emissions by molecule (or 68% by mass carbon) during this period, assuming their atmospheric loss rates are similar.
(0.25 ppt) observed at 9.4 m between 09:00–16:00 PST at BEARPEX (W. Brune and J. Mao, personal communication, 2008), an ozone mixing ratio of $1.18 \times 10^{12}$ molec cm$^{-3}$ (55 ppb), and the estimated reaction rates of methyl chavicol, the lifetimes are $\sim$55 min and $\sim$1100 min with OH and ozone, respectively. These lifetimes are significantly longer than the estimated 1–10 min canopy sweep time (Kuruppi and Goldstein, 2003; Holzinger et al., 2005; Farmer and Cohen, 2008), indicating that essentially all of the emitted methyl chavicol escapes from the forest canopy and contributes to regional photochemistry through reaction with OH. Looking at all the VOCs at Blodgett Forest, methyl chavicol contributes 1–3% to the overall OH reactivity just above the forest canopy (J. Mao, personal communication, 2008).

3.4 Oxidation products

Based on products reported from laboratory oxidation experiments presented by Lee et al. (2006a, b), we propose a schematic of methyl chavicol oxidation (Fig. 10) and identify the major products detected at PTR-MS $m/z$ 137 and 151. The photooxidation product observed at $m/z$ 137, 4-methoxybenzaldehyde (CAS# 123-11-5) was detected at Blodgett Forest during BEARPEX by TAG and SPME fiber analysis of ambient air. TAG detected 4-methoxybenzaldehyde in the aerosol phase, but the phase of compounds collected by SPME fibers in ambient air is unclear. SPME fibers, while usually employed for gas phase analysis are able to detect particulate matter (Kozel et al., 2001). Spada et al. (2008) quantified 4-methoxybenzaldehyde in Roseville, CA, a site that receives air from the Sierra Nevada Mountains during nighttime downslope flow, and highlighted its biogenic origin with increased summer concentrations.

Lee et al. (2006a, b) observed a product at $m/z$ 151 via both photooxidation and ozonolysis of methyl chavicol. The proposed oxidation product at PTR-MS $m/z$ 151 is identified as 4-methoxy benzene acetaldehyde (CAS# 5703-26-4) (Fig. 10). Previous observations of $m/z$ 151 have been made at Blodgett Forest, but this fragment was attributed entirely to pinonaldehyde (Holzinger et al., 2005). The observed gaseous $m/z$ 151 fragment at Blodgett Forest is most likely the combination of at least these two aldehydes. 4-Methoxy benzene acetaldehyde has also been tentatively detected in a reanalysis of particulate samples collected by Cahill et al. (2006) (Fig. 11). These results show that 4-methoxy benzene acetaldehyde was 1.3–5.5 times higher at night compared to the day, for a 5 day sampling period. This nighttime abundance is within the range of monoterpene oxidation product increases (2–8 times) at night reported by Cahill et al. (2006).

Due to methyl chavicol’s atmospheric lifetime, its oxidation products will be produced regionally and affect areas downwind from the emission sources. The observation of 4-methoxybenzaldehyde in Roseville demonstrates that methyl chavicol and its oxidation products contribute to regional secondary organic aerosol (SOA) loading.

4 Conclusions

Methyl chavicol is abundantly emitted by a ponderosa pine forest and was simultaneously quantified by three independent in-situ analytical methods (Berkeley GC-MS, PTR-MS, and TAG). In ambient air, its abundance equaled 15–36% of the total gas phase terpene mass within and just above the canopy. Methyl chavicol mixing ratios were highly correlated with MBO suggesting that methyl chavicol daytime
emissions can be modeled using a light- and temperature-dependent algorithm. Scaling from its correlation with MBO, methyl chavicol’s carbon mass accounts for 68% of the carbon mass emitted as MBO during cool and wet conditions and 4–24% of the MBO carbon mass emitted during warm and dry conditions. From these relationships, we estimate methyl chavicol basal emission rate from ponderosa pine trees to be $3–10 \mu \text{g C g}^{-1} \text{h}^{-1}$ during cool and wet conditions and $0.7–4.3 \mu \text{g C g}^{-1} \text{h}^{-1}$ during warm and dry conditions, depending on needle age and seasonality. These emission parameters should be incorporated in BVOC emission models.

Both methyl chavicol as a primary emission and its oxidation products (4-methoxybenzaldehyde and 4-methoxy benzene acetaldehyde) contribute to the aerosol loading at Blodgett Forest and throughout the region. Similar to MBO or monoterpenes, such as $\alpha$-pinene, methyl chavicol effectively escapes the forest canopy because its lifetime ($\sim 1\text{ h}$) is significantly longer than the estimated canopy sweep time (1–10 min). Therefore, methyl chavicol will have an impact on atmospheric chemistry at the regional scale, perhaps similar in scope to that demonstrated for MBO by Steiner et al. (2007), and therefore should be incorporated in atmospheric chemistry models.

A wide variety of plants around the world are known to contain methyl chavicol (Table 1), and therefore it is likely that biogenic emissions of methyl chavicol are common. With the deployment of improved analytical instrumentation targeting less volatile compounds, we predict that methyl chavicol will be found in the ambient air near many other ecosystems, where it will play a role in regional atmospheric chemistry and production of SOA.

Acknowledgements. This material is supported by the National Science Foundation Atmospheric Chemistry Program under grant 0443448. The authors would also like to thank Sierra Pacific Industries for the use of their land, the Blodgett Forest crew for their support, and S. Seybold (USDA Forest Service, Davis, CA) for background information regarding methyl chavicol’s use in entomology.

Edited by: J. Williams

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