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Authors

Hatch, Lindsay E
Jen, Coty N
Kreisberg, Nathan M
[et al.](#)

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Highly Speciated Measurements of Terpenoids Emitted from Laboratory and Mixed-Conifer Forest Prescribed Fires

Lindsay E. Hatch,[†] Coty N. Jen,^{‡,§} Nathan M. Kreisberg,[§] Vanessa Selimovic,^{||} Robert J. Yokelson,^{||} Christos Stamatis,[†] Robert A. York,[‡] Daniel Foster,[‡] Scott L. Stephens,[‡] Allen H. Goldstein,^{‡,⊥} and Kelley C. Barsanti^{*,†}

[†]Department of Chemical and Environmental Engineering and College of Engineering—Center for Environmental Research and Technology (CE-CERT), University of California—Riverside, Riverside, California 92507, United States

[‡]Department of Environmental Science, Policy, and Management, University of California, Berkeley, Berkeley, California 94720, United States

[§]Aerosol Dynamics, Incorporated, Berkeley, California 94710, United States

^{||}Department of Chemistry, University of Montana, Missoula, Montana 59812, United States

[⊥]Department of Civil and Environmental Engineering, University of California—Berkeley, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: Wildland fires in the western United States are projected to increase in frequency, duration, and size. Characterized by widespread and diverse conifer forests, burning within this region may lead to significant terpenoid emissions. Terpenoids constitute a major class of highly reactive secondary organic aerosol (SOA) precursors, with significant structure-dependent variability in reactivity and SOA-formation potential. In this study, highly speciated measurements of terpenoids emitted from laboratory and prescribed fires were achieved using two-dimensional gas chromatography. Nearly 100 terpenoids were measured in smoke samples from 71 fires, with high variability in the dominant compounds. Terpenoid emissions were dependent on plant species and tissues. Canopy/needle-derived emissions dominated in the laboratory fires, whereas woody-tissue-derived emissions dominated in the prescribed fires. Such differences likely have implications for terpenoid emissions from high vs low intensity fires and suggest that canopy-dominant laboratory fires may not accurately represent terpenoid emissions from prescribed fires or wildland fires that burn with low intensity. Predicted SOA formation was sensitive to the diversity of emitted terpenoids when compared to assuming a single terpene surrogate. Given the demonstrated linkages between fuel type, fire terpenoid emissions, and the subsequent implications for plume chemistry, speciated measurements of terpenoids in smoke derived from diverse ecosystems and fire regimes may improve air quality predictions downwind of wildland fires.



INTRODUCTION

Wildland fires, including wildfires and prescribed fires, occur throughout the western United States (U.S.). This region is characterized by diverse landscapes, including widespread conifer forests and chaparral scrublands.^{1–3} The frequency of wildfires burning with high severity has increased in recent decades in some forest types^{4–7} and is projected to increase further due to a changing climate.^{8,9} Wildland fires emit high levels of trace gases (CO, CO₂, CH₄), nonmethane organic gases (NMOGs), and particulate matter (PM)^{10,11} that substantially influence air quality on local to regional scales.^{12,13} Emitted pollutants, PM in particular, can cause a number of negative health effects, including respiratory distress and premature mortality,^{14–16} and can additionally influence atmospheric chemistry and climate.⁹ The chemical evolution of

smoke plumes affects PM levels downwind of fires through a combination of dilution-driven evaporation of primary organic aerosol (POA) and condensation of oxidized NMOGs via secondary organic aerosol (SOA) formation.^{17–21} Thus, improved speciation of the fire-derived NMOGs that can act as SOA precursors can help to better predict air quality and health effects downwind of wildland fires.

Terpenoids represent one important class of SOA precursors. Many plants, particularly conifers, produce and store resins rich in monoterpenes, sesquiterpenes, and di- or

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Table 1. Fuels Burned and Number of Analyzed Samples from the FIREX Laboratory Fires

common name	scientific name	source location ^a	composite ^b	canopy ^c	litter ^d	duff ^e	rotten log	other
<i>Conifers</i>								
Ponderosa pine	<i>Pinus ponderosa</i>	MT	5	2	2		2	
Lodgepole pine	<i>Pinus contorta</i>	MT	5	2	2			
Engelmann spruce	<i>Picea engelmannii</i>	MT/UT	4	3		3		
Douglas-fir	<i>Pseudotsuga menziesii</i>	MT	4	3	2		1	
Subalpine fir	<i>Abies lasiocarpa</i>	UT	2	2	1	1		
Juniper	<i>Juniperus communis</i>	MT		2				
Loblolly pine	<i>Pinus taeda</i>	NC			1			
Jeffrey pine ^f	<i>Pinus jeffreyi</i>	CA-1				1		
<i>Shrubs</i>								
Chamise	<i>Adenostoma fasciculatum</i>	CA-2		6				
Manzanita	<i>Arctostaphylos</i>	CA-2		4				
Sagebrush	<i>Artemisia tridentata</i>	MT		2				
Snowbrush ceanothus	<i>Ceanothus velutinus</i>	MT		2				
<i>Miscellaneous</i>								
Excelsior								2
Yak dung		MT						1
Peat ^f		Indo.						1
Rice straw ^f	<i>Oryza sativa</i>	AR						1
Bear grass	<i>Xerophyllum tenax</i>	MT						1
Untreated lumber								1

^aMT = Clearwater Wildlife Management Area or Lubrecht Experimental Forest, Montana; UT = Fishlake National Forest, Utah; NC = Kinston, North Carolina; CA-1 = Sierra Nevada Range, California; CA-2 = San Dimas or North Mountain, California; Indo. = Kalimantan, Indonesia; AR = Arkansas. ^bComposite fires included all individual fuel components. ^cCanopy = intact branches with fresh, green needles. ^dLitter = dead, fallen needles. ^eDuff = partially decomposed plant matter. ^fThese fuels had been stored under refrigeration for several years prior to burning.

triterpenes.²² Basal emissions of volatile resin constituents have been extensively studied (refs 23–26 and references therein); hundreds of compounds have been identified,²⁶ and the compounds stored and emitted can vary considerably by plant species, in terms of both isomer speciation and the relative concentration of different compound classes (e.g., monoterpenes, oxygenated monoterpenoids, and sesquiterpenes).^{23,27–29}

Once emitted into the atmosphere, many terpenoids react rapidly with atmospheric oxidants (hydroxyl and nitrate radicals, ozone) governed by rate constants that can vary an order of magnitude or more with chemical structure.^{30–32} The propensity of terpenoids to form SOA is also structure dependent;^{33–37} sesquiterpenes exhibit significantly higher SOA yields than monoterpenes.^{34,36} This variability in atmospheric reactivity, as well as in plant composition, illustrates the need for speciated measurements of terpenoid emissions. For example, one recent study found that accounting for monoterpene complexity in Scots pine (*Pinus sylvestris*) emissions led to 1.5–2.3× higher predicted SOA formation than assuming α -pinene as a single, representative surrogate compound.³⁸

Heating of vegetation causes substantial release of resin constituents via distillation out of storage ducts/glands,^{39–44} demonstrating the potential for high emissions of terpenoids during vegetation fires of resinous fuels. Although a few studies have observed high total terpenoid emissions from wildland fires,^{45–47} there have been relatively few measurements of speciated terpenoid emissions. The most comprehensive speciation of terpenoids has been achieved for laboratory fires, with several studies reporting 10–20 terpenoids emitted from a very limited number of fuels/fires.^{48–51} During the fourth Fire Lab at Missoula Experiment (FLAME-4), Hatch et al.⁵² identified >40 terpenoids from two coniferous canopy

fuels and linked plant composition to fire emissions; however measurements of more fuel types are needed to better understand such relationships. Of the studies that reported speciated terpenoid emissions from wildland fires, only three included measurements of numerous terpenoids (<10 compounds, predominantly monoterpene isomers);^{45,53,54} others have focused only on isoprene and α - and β -pinene,^{47,55,56} which may not capture the terpenoid emissions from ecosystems where plant resins are dominated by or contain significant contributions from other compounds.²³ For example, oxygenated monoterpenoids can constitute a large fraction (>50%) of some plant essential oils,²³ although they are generally a small fraction of basal plant emissions.²³ Whether such compounds are substantially released intact during fires is largely unknown, however one recent study found significant contributions of eucalyptol-derived SOA in smoke from Australian bushfires.^{57,58} Thus, there remain significant knowledge gaps regarding terpenoid emissions from wildland fires and their subsequent effect on plume chemistry, including SOA formation.

Despite multiple suggestions in the literature that terpenoid emissions from biomass burning will depend on fuel type,^{42,50,52} there has been no published survey of speciated terpenoid emissions from a wide variety of fuels, including resinous conifers. Such comprehensive analyses, including the wide range of possible mono/sesquiterpene isomers and oxygenated monoterpenoids, require enhanced separation capability due to the large number of pyrogenic compounds emitted during biomass burning.^{59,60} In this work, two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC-TOFMS) was used to broadly characterize terpenoids emitted during laboratory and mixed-conifer forest prescribed fires.

MATERIALS AND METHODS

Laboratory Fires. Fires were conducted at the U.S. Forest Service Fire Sciences Laboratory (FSL); details of the facility⁶¹ and campaign (Fire Influence on Regional and Global Environments Experiment, FIREX)⁶² have been discussed previously. Briefly, fuel samples were ignited below an inverted funnel where smoke was carried up the stack to the measurement platform 17 m above the floor. NMOG samples were analyzed from 71 laboratory fires in which a range of biomass fuel types were burned, including chaparral, coniferous fuels from several ecosystems, and miscellaneous fuels; the specific fuels used and associated number of analyzed burns are listed in Table 1. “Composite” fires of coniferous fuels included representative amounts of individual forest components (i.e., canopy, dead/down sound woody debris, litter, duff, and shrubs) arranged naturally. Those fuel components, except dead/down sound woody debris, were also burned individually (Table 1).

NMOG samples were collected onto dual-bed sorbent tubes using the Direct Emission Fire CONcentrator (DEFCON), described previously.⁶³ Additional sampling details are provided in the Supporting Information (SI). Briefly, a 1.27 cm o.d. × 20.3 cm long stainless-steel tube passivated with Inertium (AMCX, PA) was passed through the stack wall into the well-mixed smoke. DEFCON included two sorbent-tube channels (mounted <15 cm from the subsampling point), each sampling at ~150 mL/min with the actual flows logged for each channel. Replicate samples were periodically collected to assess the reproducibility of the measurements and are discussed in the SI. Teflon filters (PTFE, 1.2 μm pore size) were used upstream of each sorbent tube to remove particles, while minimizing NMOG adsorption. Samples were collected for the duration of each fire (~7–50 min). Background samples were collected daily, with a median sample duration of 39 min. A background sample was collected either before the first fire of the day or during a mid-day break; there were no significant differences in the average background concentrations between the morning and mid-day background samples. Several breakthrough samples were also collected to assess the collection efficiency of the target compounds. Samples were stored in a freezer until analysis was completed, within approximately one month following the end of the study.

Prescribed Fires. Prescribed fires were conducted at the UC Berkeley Blodgett Forest Research Station (BFRS; Georgetown, CA, 38.901256, -120.662719, elevation 1200–1500 m) from 30 October –01 November 2017. Three approximately 15-ha forest stands (BFRS #s 340, 60, and 400) were burned (one per day). These stands were previously burned in 2002, which represented the first fire activity in approximately 100 years,⁶⁴ and in 2009. The overstory vegetation at BFRS (Figures S2–S4) includes white fir (*Abies concolor*), ponderosa pine (*Pinus ponderosa*), Douglas-fir (*Pseudotsuga menziesii*), sugar pine (*Pinus lambertiana*), incense-cedar (*Calocedrus decurrens*), tanoak (*Notholithocarpus densiflorus*), and California black oak (*Quercus kelloggii*), with shrub understory.

Sampling equipment was mounted onto a utility task vehicle that was parked at different locations directly adjacent to the three stands (Figures S2–S4). The mobile station included measurements of CO (Horiba PG250) and CO₂ (LI-COR 840A), as well as an automated sampler equipped with six

parallel sorbent-tube and quartz-fiber-filter samples. Whereas PTFE prefilters were used in the FIREX laboratory study, glass-fiber filters (GFFs) coated with sodium thiosulfate were used in the BFRS field study to scrub particles as well as ozone⁶⁵ prior to sampling onto the sorbent tubes. The effects of greater NMOG adsorption on GFFs relative to PTFE filters are discussed in the SI. Background samples were collected prior to the first fire. Additional experimental details are described in the SI.

Sample Analysis. All sorbent tubes were analyzed using automated thermal desorption coupled to GC×GC-TOFMS (see SI for details). Raw GC×GC-TOFMS data were processed using Chromatof (Leco Corp., St. Joseph, MI). Peaks with $S/N > 200$ were selected for analysis, except in the sesquiterpene region where $S/N > 100$ was used. The identification and calibration of terpenoids are discussed in the SI. For each study, the maximum observed background signal for a given peak was used for background subtraction; Figure S6 shows the terpene concentrations in the background and smoke samples. In the FIREX breakthrough samples, the maximum detected breakthrough of isoprene was <1% of the front sample and no evidence of breakthrough was detected for any other compounds reported here; thus no breakthrough corrections have been applied. Data were converted to emission factors (EFs, g/kg fuel burned) following the calculations outlined in the SI for the FIREX and BFRS samples.

RESULTS AND DISCUSSION

Laboratory Fires. The total terpene EF is defined here with and without isoprene as $EF_{\text{TERP+ISOP}}$ and EF_{TERP} , respectively. Average $EF_{\text{TERP+ISOP}}$ values as a function of fuel type are given in Figure 1a, where each bar is segmented by the average fractional contribution from each major compound class. For context, Figure 1b shows the percentage contribution of terpenoids to the estimated total NMOG EF (EF_{NMOG}). EF_{NMOG} was calculated for each fire by combining an estimated NMOG EF measured by GC×GC-TOFMS with that measured by open-path Fourier-transform infrared spectroscopy (OP-FTIR).⁶² Previous comparisons between GC×GC-TOFMS and OP-FTIR data sets have demonstrated that these two techniques measure complementary and substantial fractions of the total NMOG emissions from biomass burning.⁶⁰ The GC×GC-TOFMS-derived total NMOG emissions were estimated by scaling the background-corrected total peak area within each chromatogram by an average response factor based on several representative standard compounds (ethylbenzene, naphthalene, nonane, furfural, and phenol).

Across all FIREX samples, 93 terpenoids were detected, including isoprene, 36 monoterpenoids (monoterpenes + santene and *p*-cymene), 26 oxygenated monoterpenoids, and 31 sesquiterpenes; Table S3 lists all detected terpenoids and their EFs for each fire. Isoprene was the only terpene detected in all 71 samples. Furthermore, it was the dominant terpene observed from most shrubs (68–98% of $EF_{\text{TERP+ISOP}}$, except sagebrush) and from most miscellaneous fuels (60–100% of $EF_{\text{TERP+ISOP}}$, except dung) (Figure 1). Because isoprene is not stored by plants following its synthesis²⁴ and was universally detected, these results are consistent with isoprene being emitted partly as a combustion product.^{45,66} Thus, isoprene was omitted from further analysis to better isolate fuel-dependent terpene emissions.

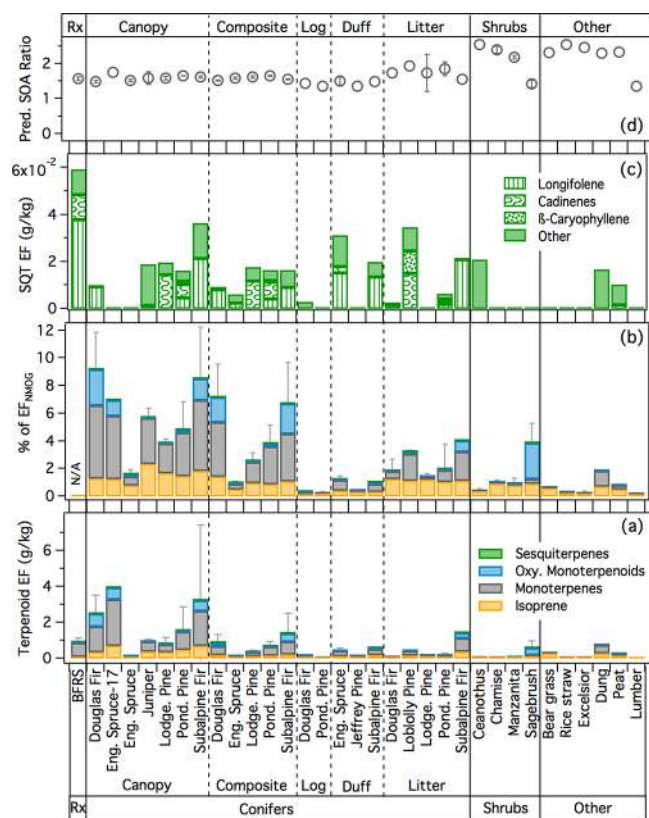


Figure 1. For the Blodgett Forest Research Station (BFRS) prescribed (Rx) fires and each fuel type studied during FIREX: (a) average total terpenoid emission factors ($EF_{\text{TERP}+\text{ISOP}}$), (b) percentage contribution of $EF_{\text{TERP}+\text{ISOP}}$ to the estimated total nonmethane organic gas EF (EF_{NMOG}), (c) sesquiterpene (SQT) EF, and (d) the ratio of predicted monoterpene-derived SOA based on isomer-specific SOA yields relative to applying an α -pinene SOA yield to all isomers (see SI for details). In (b), the percentage contribution to EF_{NMOG} could not be assessed for the BFRS fires. Engelmann spruce fire #17 is shown separately from the other Engelmann spruce fires (see SI).

The number of terpenoids above detection limit in any given smoke sample ranged widely (0–45, median = 14). The highest terpenoid emissions by all metrics (EF_{TERP} , % of EF_{NMOG} , and number of compounds) were found for coniferous fuels, sagebrush, and dung (Figure 1). Excluding dung and sagebrush, smoke from the nonconiferous fuels contained five or fewer detectable terpenoids, which were generally a negligible fraction of EF_{NMOG} (Figure 1b). For those nonconiferous fuels, limonene and *p*-cymene were generally the dominant terpenoids in smoke and were the most commonly detected compounds; they were found in 62 and 64 of the fires, respectively (Table S3). Similarly, Palozzi et al.⁵¹ reported that limonene was the only monoterpene detected across all fires they studied, in which needles, branches, and litter from both a pine and a deciduous tree species were burned. Yak dung smoke contained a surprisingly high fraction of monoterpenoids (Figure 1b), which was also dominated by limonene (~77% of EF_{TERP}). Because limonene and *p*-cymene were predominant in emissions from fuels such as rice straw that do not store/emit monoterpenes,²⁴ these compounds may be emitted as a result of combustion/pyrolysis processes, in addition to distillation from resin stores where present.

Among the coniferous fuels, the canopy and composite fires generally displayed the highest EF_{TERP} , accounting for up to ~11% of EF_{NMOG} (Figure 1a,b). These observations are consistent with basal terpenoid emissions from forest vegetation that arise predominantly from foliage (canopy), with minor contributions from woody tissues and soil.^{26,67} Additionally, we found no clear, consistent relationships between EF_{TERP} and modified combustion efficiency based on the suite of conifer fires sampled here (see SI). Terpenoid emissions from litter-only fires were generally lower than the canopy/composite fires of the same species (Figure 1). For example, average EF_{TERP} of the two ponderosa pine litter fires was 7 \times and 14 \times lower than that of the corresponding composite and canopy fires, respectively. Subalpine fir and loblolly pine litter displayed higher EF_{TERP} than other litter types; however, only one fire sample was available for each of those fuels and therefore their emissions variability is unknown. Rotten-log fires also emitted low levels of terpenoids for both Douglas-fir and ponderosa pine (Figure 1). Low terpenoid emissions from aged/decomposed plant matter can be explained by volatile losses during senescence.

The terpenoid speciation profiles were further compared among the high terpenoid emitting fuels (conifers and sagebrush), including only composite and canopy fires. For each fuel type, the top 10 compounds based on their median EFs are shown in Figure 2 by their fractional contribution to EF_{TERP} (Engelmann spruce fires displayed greater variability in EF_{TERP} and isomer speciation, shown and discussed in the SI). The top 10 compounds accounted for >85% of EF_{TERP} in all fires included in the analysis. The dominant compounds varied considerably between plant types (Figure 2). For example, lodgepole pine fires emitted predominantly β -phellandrene and β -pinene, whereas subalpine fir and Douglas-fir fires emitted predominantly bornyl acetate and camphene. One or both of the top two most abundant terpenoids from all fuels except juniper are not commonly reported in wildland fire emissions.¹⁰

The differences in terpenoid speciation arise from the fuel resin stores, as demonstrated by the plant essential oils (EOs; extracts of the volatile resin constituents²²). Overlaid on each plot in Figure 2 is the reported EO composition within needles and twigs/wood (where available) based on literature data of tree samples collected as close as possible to the geographic source region of the corresponding FIREX fuel. For example, we used the EO composition from the Rocky Mountain variety of Douglas-fir, which is predominant throughout Montana and has a markedly different EO composition than the coastal variety.⁶⁸ Figure 2 illustrates a clear relationship between the dominant terpenoids detected in smoke with those present in the corresponding EOs, particularly needle extracts. Moreover, the monoterpene speciation of ponderosa pine smoke during FIREX is comparable to our previous analysis of ponderosa pine smoke during FLAME-4.⁵² The new, expanded data set provided by the FIREX study unequivocally confirms that fire emissions of terpenoids are highly fuel dependent and that the sorbent-tube GC \times GC analysis method accurately captures the terpenoid speciation in smoke.

Nevertheless, there are some differences between the smoke samples and corresponding EOs. For all cases except subalpine fir, limonene is overrepresented relative to the EO (Figure 2). This could be due to thermal rearrangement, as both α - and β -pinene have been reported to thermally rearrange to limonene⁶⁹ and is consistent with the comparative under-

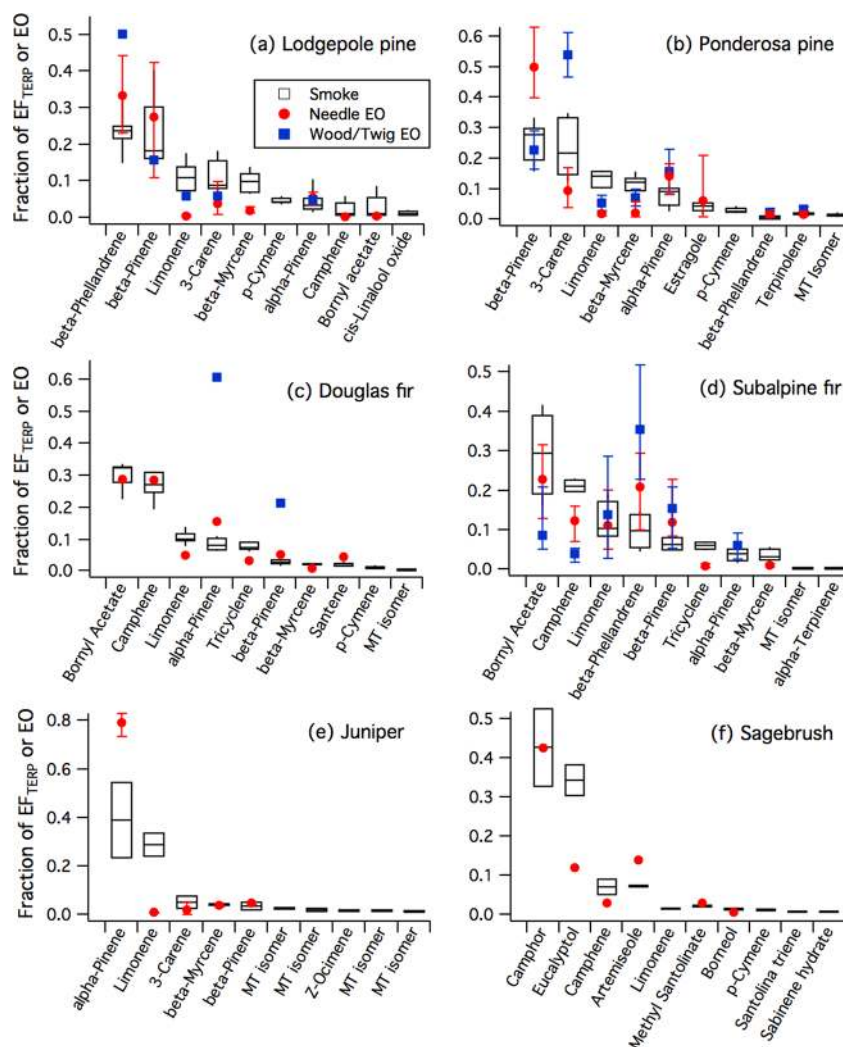


Figure 2. Box plots illustrate the fraction of the total terpenoid EF (EF_{TERP}) accounted for by the top 10 observed terpenoids within each of the six fuel types indicated; only FIREX canopy and composite fires were included in the analysis. “MT isomer” indicates an unidentified monoterpene isomer. The markers represent the fraction of each compound in the reported essential oil (EO) based on the following references: (a) needles: Pauly et al.,⁷² wood: Pureswaran et al.;⁸⁴ (b) needles: von Rudloff et al.,⁷³ wood: Latta et al.;⁸⁵ (c) needles: von Rudloff et al.,⁶⁸ wood: Pureswaran et al.;⁸⁴ (d) needles and wood: Hunt et al.;⁸⁶ (e) needles: von Rudloff et al.;⁷⁵ and (f) needles: Buttkeus et al.⁷¹

representation of α - and/or β -pinene in Figure 2b–e. Limonene was not detected during thermal desorption analysis of α - and β -pinene standards and therefore any monoterpene isomerization likely occurred during combustion/pyrolysis. Higher than expected limonene emissions may also provide further evidence that limonene could be a combustion product, as suggested above, or a thermal degradation product of higher terpenes (e.g., sesqui-, di-, or triterpenes). Similarly, *p*-cymene was present among the top 10 terpenoids for four of the six fuels (Figure 2a–c,f) despite its absence in the reported EOs.

Oxygenated monoterpenoids were present among the top 10 most abundant terpenoids in all of the six fuels except juniper (Figure 2). Bornyl acetate was the most commonly detected oxygenated monoterpene (present in 34 smoke samples) and was highly abundant in both Douglas-fir and subalpine fir smoke, as expected based on their EO content (Figure 2c,d). Hatch et al.^{52,60} suggested that bornyl acetate emissions could be significant in black-spruce smoke based on its EO composition; however a significant fraction of the bornyl acetate emissions was lost to the glass fiber prefilter used for sorbent-tube collection during FLAME-4,⁵² as supported by

tests conducted during FIREX (see SI). The results in Figure 2c,d demonstrate that bornyl acetate can be a highly abundant component of smoke in certain ecosystems, and may impact proton-transfer-reaction mass spectrometry measurements of monoterpenes, as fragments of protonated bornyl acetate interfere with monoterpene ions (m/z 81 and 137) even with high mass-spectral resolution.^{60,70}

Sagebrush was the only fuel for which oxygenated monoterpenoids dominated the emissions. The major oxygenated compounds emitted include camphor, eucalyptol, artemiseole, and methyl santolinate and are consistent with the EO from sagebrush collected from interior British Columbia⁷¹ (Figure 2f). Artemiseole and methyl santolinate were only observed in sagebrush smoke (Table S3). Although the relative fraction of eucalyptol in smoke is considerably higher than the EO, no evidence was found of eucalyptol-formation artifacts during analysis of standard compounds that are abundant in sagebrush smoke (e.g., camphor). The higher than expected eucalyptol fraction could be due to an unknown chemical conversion process during the fire or real differences in the

plant EO compositions between the FIREX fuels and those sampled by Buttkus et al.⁷¹

Additional oxygenated monoterpenoids were commonly detected, including camphor (27 fires), borneol (22 fires), and α -terpineol (18 fires) (Table S3), and others were uniquely observed in some fuel types. Estragole is relatively abundant only in ponderosa pine smoke and is a significant fraction of the needle EO (Figure 2b). Estragole has also been reported as a minor constituent of lodgepole pine EO⁷² and was detected in one lodgepole pine fire (Table S3). Similarly, terpinyl acetate and myrtenyl acetate were only detected in ponderosa pine and juniper smoke samples, respectively (Table S3), consistent with their presence in the corresponding EOs.^{73–75}

A large number of sesquiterpene isomers (31) were detected although they constituted a small fraction of EF_{TERP} (<12%) from all fuel types except *Ceanothus*. Because the sesquiterpene abundances were closer to the detection limit than other terpenoids, the number of isomers detected per fire was highly variable. Therefore, the fuel-dependent sesquiterpene emissions are illustrated in Figure 1c by taking the maximum EF of each isomer within each fuel category (Table S3 lists the actual speciation for each fire). Longifolene was the most commonly detected sesquiterpene isomer (25 fires); however, it only dominated the sesquiterpene emissions from Engelmann spruce duff, subalpine fir, and Douglas-fir fuels (Figure 1c). Cadinenes include four isomers detected with a cadalane skeleton and were prominent in lodgepole and ponderosa pine emissions (Figure 1c), consistent with their previous detection in needle EOs of those species.^{72,73} β -Caryophyllene, previously reported as the dominant sesquiterpene in loblolly pine needle EO,⁷⁶ was a significant isomer only for loblolly pine litter (Figure 1c). Surprisingly, the sesquiterpene EFs from *Ceanothus*, dung, and peat were of similar magnitude as those of the coniferous fuels (Figure 1c) and largely consisted of miscellaneous isomers (Table S3). Sesquiterpenes can dominate the volatile fraction of resins in flowering plants,²² and they constituted the majority (89–100%, $N = 2$) of EF_{TERP} in *Ceanothus* fires, with two $C_{15}H_{24}$ isomers tentatively identified as α -selinene and α -bulnesene (Table S3). The source of the sesquiterpenes observed in dung and peat smoke is currently unknown; no evidence was found of artifacts or carryover from preceding fires in these samples. The diversity of observed sesquiterpene isomers suggests that limited characterization of few, selected sesquiterpene isomers in future studies may not sufficiently describe the emissions from a wide range of fires.

Prescribed Fires. Average $EF_{\text{TERP+ISOP}}$ measured during the BFRS fires was similar to that of the FIREX coniferous composite fires (Figure 1). Several samples intercepted little smoke based on the mixing ratios of CO and furfural (a smoke tracer^{49,77}); those samples have been omitted from the analysis due to high uncertainty. Across all included samples collected during the BFRS fires, 56 terpenoids were detected, including isoprene, 35 monoterpenoids, 8 oxygenated monoterpenoids, and 12 sesquiterpenes (Table S4). The average terpenoid speciation (Figure 3 pie chart) was determined by considering only compounds that were present in at least eight of the 23 analyzed samples. The top six monoterpenes accounted for $60 \pm 20\%$ of $EF_{\text{TERP+ISOP}}$, of which α -pinene was the most abundant followed by limonene, 3-carene, β -pinene, β -myrcene, and camphene (Figure 3); these dominant compounds are consistent with the six major monoterpenes

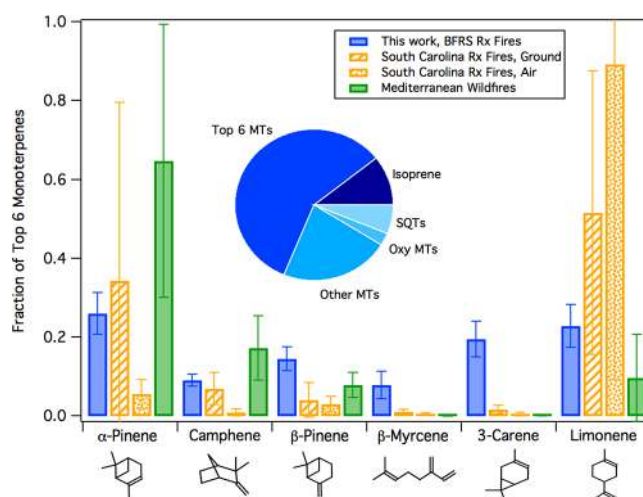


Figure 3. Bar chart shows the speciation among the top six monoterpenes observed during the BFRS prescribed fires. Measurements of prescribed fires in South Carolina⁴⁵ and Mediterranean mixed-pine forest wildfires⁵³ are included for comparison. Although Akagi et al.⁴⁵ report 4-carene, it is likely to be 3-carene (Don Blake, personal communication). The inset pie chart shows the average relative contributions of the different terpenoid classes to $EF_{\text{TERP+ISOP}}$ detected in the BFRS fire samples; MT = monoterpenes; SQT = sesquiterpenes.

in biogenic emissions identified by Geron et al.²³ Other monoterpenes contributed a further $22 \pm 6\%$ to $EF_{\text{TERP+ISOP}}$. Isoprene contributed $10 \pm 5\%$, only slightly more than sesquiterpenes at $6 \pm 2\%$. The observed sesquiterpene speciation is given in Figure 1c and represents the first such measurements reported for wildland fires. Longifolene was the dominant isomer, followed by cadinenes. The *Ceanothus* sesquiterpene signature observed during FIREX was not observed during the BFRS fires, indicating that either the different *Ceanothus* species present at BFRS (predominantly deer brush, *Ceanothus intergerrimus*) emit different sesquiterpene isomers or that the *Ceanothus*-derived sesquiterpene emissions were below detection limit.

Whereas terpenoid emissions from the laboratory fires arose predominantly from canopy-only and canopy-rich composite fuel mixtures (Figure 1), the significantly higher live crown height at BFRS (e.g., 10 ± 4 m in compartment 60 compared to ≤ 1 m above the fuel bed during FIREX) and the minimization of canopy consumption during prescribed fires support that the influence of canopy fuels was significantly lower during these relatively low-intensity prescribed fires than during the laboratory fires. It therefore seems unlikely that terpenoid emissions predominantly originated from consumption or heating of fresh needles. However, a strong correlation ($R^2 \approx 0.89$) was observed between total terpenoid mixing ratio and particulate resin-acid mass concentrations determined from parallel filter measurements⁶³ (Figure 4a; BFRS data are compared to FIREX data in Figure S9). Because terpenoids and resin acids are both stored within plant resin ducts,²² their coemission is not surprising and suggests that the terpenoids observed during these prescribed fires were indeed distilled out of plant reservoirs.

To probe potential differences in the dominant tissues consumed during FIREX and BFRS fires, we used previous observations of differences in the nitrogen content of different plant tissues. Coggon et al.⁷⁷ demonstrated that significant

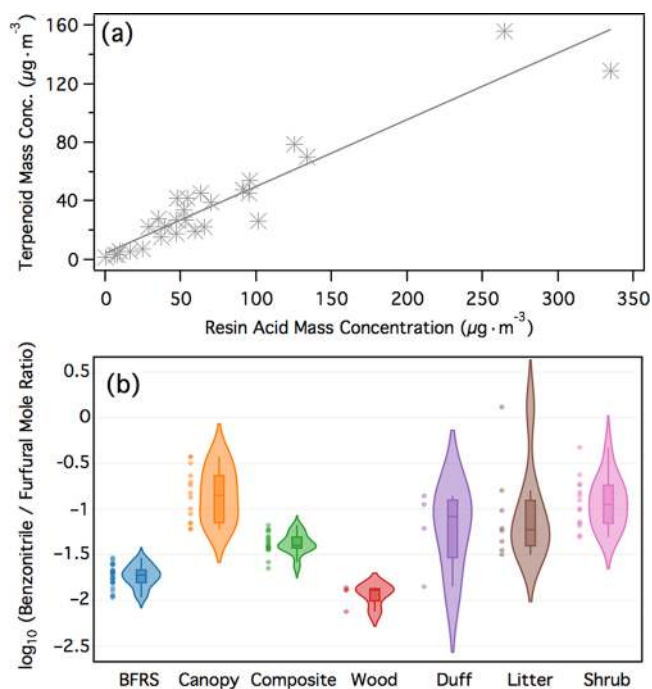


Figure 4. (a) Comparison of the terpenoid (gas phase) and resin acid (particle phase) emissions during the BFRS fires. The line is a linear regression fit of the data. (b) Comparison of the log-transformed ratio of biomass-burning tracers benzonitrile and furfural for the FIREX laboratory and BFRS prescribed fires. Data are presented as box plots with overlaid violin plots; the violin illustrates the probability density function of each fuel type. For reference, individual data points are shown to the left of each violin.

differences in nitrogen weight percent among plant tissues (N % of needles/leaves > bark > heartwood/sapwood) strongly influence the emissions of N-containing NMOGs, especially nitriles (e.g., the commonly used tracer acetonitrile), with little N-containing NMOG emissions from wood combustion. Because acetonitrile is known to breakthrough the sorbent tubes used in these studies,^{52,60} benzonitrile was used as the N-containing tracer, normalized to furfural. Both compounds were directly calibrated and neither exhibited losses to glass-fiber prefilters (used during the BFRS fires only); thus they represent the best metrics for comparison between the two studies.

A comparison of the log-transformed benzonitrile/furfural ratios are given in Figure 4b for each major fuel class; FIREX fuels were only included if relevant for comparison to the BFRS fires (i.e., bear grass, rice straw, peat, dung, and excelsior were omitted; lumber was included in the “wood” category). Among the FIREX coniferous fires, a clear trend emerges with the median benzonitrile/furfural ratio of canopy (0.14, $\log_{10} -0.85$) > composite (0.04, $\log_{10} -1.4$) > log/lumber (0.013, $\log_{10} -1.9$) fires (Figure 4b), illustrating the lower relative proportion of benzonitrile in fires with a greater fraction of woody tissues. Similar analysis of the BFRS fire samples illustrates that the median benzonitrile/furfural ratio (0.019, $\log_{10} -1.7$) falls between the wood-only and composite fires measured during FIREX (Figure 4b), suggesting that prescribed fire emissions were significantly influenced by combustion of woody tissues. The higher benzonitrile/furfural ratios observed for shrubs (0.11, $\log_{10} -0.95$), duff (0.06, $\log_{10} -1.1$), and litter (0.06, $\log_{10} -1.22$) compared to wood fires during FIREX (Figure 4b) indicate that mixing of smoke from

such fuels during the prescribed fires likely increased the benzonitrile/furfural ratios compared to wood-only fires, with variable impacts depending on the relative fuel consumption associated with each smoke sample. However, the low EF_{TERP} values from shrubs (sagebrush was not present at BFRS), duff, and litter (Figure 1a) suggest that those fuels likely did not contribute significantly to prescribed-fire terpenoid emissions. Furthermore, the higher EF_{TERP} measured in BFRS-fire smoke compared to the FIREX decomposed wood smoke (Figure 1a) suggests that terpenoid emissions at BFRS arose predominantly from live wood (e.g., tree stems) or dead wood that still contained significant resin stores (e.g., stumps and recently fallen logs).^{46,78} Smoldering stumps and live tree stems were observed throughout the compartments (e.g., Figure S10); analogous fuels were not burned during FIREX. The bark on tree stems may have also contributed to the elevated benzonitrile/furfural ratio in the BFRS fires compared to the FIREX wood fires, as bark has higher nitrogen content than heartwood.⁷⁷ Given the significant differences in the EO composition of needles vs woody tissues (e.g., Figure 2), these results illustrate that terpenoid emissions measured during canopy-dominant laboratory fires may not accurately represent such emissions from prescribed fires or wildland fires that burn with low intensity.

Measurements of fires in other ecosystems provide additional evidence for fuel-dependent terpenoid emissions in mixed forests. Here, BFRS results are compared with two studies that reported several monoterpene isomers: prescribed fires in South Carolina longleaf (*Pinus palustris*) and loblolly pine (*Pinus taeda*) forests⁴⁵ and wildfires in Mediterranean mixed-pine forests.⁵³ The speciation of the major monoterpenes is considerably different among the three studies, with the contribution of α -pinene observed in the Mediterranean wildfires nearly twice that observed during the BFRS and South Carolina prescribed fires (Figure 3; EF_{TERP} for each study is presented in Figure S11). Smoke from the South Carolina fires overwhelmingly contained limonene and α -pinene, with significantly different ratios measured in ground and aircraft samples (Figure 3). Akagi et al.⁴⁵ used ground-based mobile platforms to target point sources of residual smoldering combustion (RSC); they suggested based on the higher ratio of α -pinene in the ground samples that RSC primarily emits α -pinene. However, the EOs of the fuels targeted in that study, specifically loblolly and longleaf pine, are dominated by α -pinene;^{76,78–80} monoterpenes emitted by RSC of other fuels likely depend on the composition of the species-specific constitutive (stored) resin.

■ IMPLICATIONS

Highly speciated measurements of terpenoid emissions from vegetation fires illustrate that for resinous plants, the presence and distribution of terpenoids in smoke will strongly depend on the biomass resin composition. Given the significant contribution of terpenoids to fire emissions from resinous plants (e.g., conifers) and their high reactivity with atmospheric oxidants, terpenoids may significantly impact smoke plume chemistry during both daytime and nighttime oxidation. The range of terpenoid chemical structures leads to wide variability in oxidation kinetics and SOA production;^{30,35} therefore speciating terpenoid emissions may help to improve predictions of smoke processing and aging. Potential SOA formation from the measured terpenoids was estimated using published SOA yields from laboratory photooxidation experi-

ments (see SI). Among fuels with significant SOA formation potential, monoterpenes accounted for ~64–86% of the estimated SOA mass (Figure S12). Additionally, using monoterpene-specific SOA yields where available resulted in SOA predictions ~1.5–2.5× higher than applying the α -pinene SOA yield to all measured monoterpenes (as is conventional in many model representations of SOA formation from monoterpenes; Figure 1d), in general agreement with similar analysis of monoterpenes emitted from stressed Scots pine.³⁸ Although the contribution of terpenoids to SOA production in smoke from wildland fires remains largely unquantified, these results illustrate that chemically speciating such emissions will be essential for fully and accurately elucidating their chemistry.

Despite the potential importance of terpenoids in smoke plume chemistry, compound-specific terpenoid emission factors from laboratory measurements are difficult to generalize to wildland fires given the high interspecies variability in EO composition, intraspecies geographical variations,^{68,81,82} and different EO composition within different plant tissues of the same tree (e.g., Figure 2 and associated references). Emissions from different plant tissues may have varying contributions to smoke depending on fire intensity (e.g., woody tissues in low intensity fires vs canopy/needles in higher intensity crown fires). Further, different conifer ecosystems are prone to burn under different fire regimes, with high elevation subalpine forests containing Engelmann spruce, subalpine fir, and lodgepole pine most likely to experience high-intensity crown fires compared to lower elevation ponderosa pine, Jeffrey pine, and mixed conifer forests that have historically burned with low-moderate intensity.⁸³ Several of the abundant terpenoids present in the needle EOs and canopy emissions from the high-intensity fire prone conifers are not routinely speciated (e.g., β -phellandrene, camphene, bornyl acetate; Figure 2). Thus, more comprehensive speciated measurements of terpenoid emissions are needed from wildland fires occurring in a variety of ecosystems and with varying fire intensity to determine the level of routine analytical speciation needed to adequately characterize fuel-dependent terpenoid emissions, to generate more accurate terpenoid emissions inventories for mixed forests, and to elucidate the impacts of terpenoids on smoke plume chemistry and air quality.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b02612.

Experimental details; results of replicate comparisons, background concentrations, Engelmann spruce emissions, effect of prefilter material, terpenoid-resin acid comparisons, terpenoid-modified combustion efficiency relationships, and estimated SOA potential (PDF)

Tables of measured terpenoid emission factors (XLSX)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kbarsanti@engr.ucr.edu.

ORCID

Lindsay E. Hatch: 0000-0001-9037-9760

Coty N. Jen: 0000-0002-3633-4614

Kelley C. Barsanti: 0000-0002-6065-8643

Present Address

#Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, U.S.A.

Notes

The authors declare no competing financial interest.

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