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High Hydroquinone Emissions from Burning Manzanita

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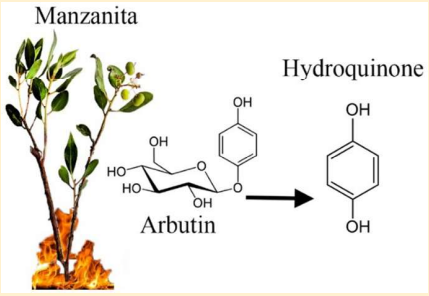
Supporting Information

ABSTRACT: California wildfires are becoming larger and more frequent because of climate change and historical fire suppression. The 2017 fire season was record-breaking in terms of monetary damage, area burned, and human casualties. In addition, roughly 20 million people were exposed to dense wildfire smoke for days. Understanding the health impacts of wildfire smoke requires detailed chemical speciation of smoke produced from different fuels. This study demonstrates the unique chemical fingerprint observed in smoke from burning manzanita, a common chaparral and forest understory shrub found in several ecosystems of California. Burning manzanita during the FIREX Fire Laboratory experiments emitted hydroquinone (1,4-dihydroxybenzene with an emission factor of 0.4 g/kg) and two sterol/triterpenoid tracer compounds at levels up to 100 times higher than those of the other common wildland fuels in California such as pine trees, other shrubs, grasses, and duff. Additionally, these compounds were detected in Berkeley, CA, from smoke produced during the October 2017 wildfires in northern California, a region where manzanita grows. In contrast, the identified fingerprint for manzanita burning emissions was not observed during prescribed fires of a mixed conifer forest in California's Sierra Nevada, indicating negligible amounts of manzanita were burned. As confirmed by shrub inventory data collected prior to the burns, small amounts of manzanita remain after prescribed burning, a low-severity forest management technique, but larger amounts can occur after recovery from high-severity events like wildfires. Results from this study show that chemical signatures in smoke can be traced back to specific fuels like manzanita and that forest management techniques can be used to limit certain types of wildfire emissions.



INTRODUCTION

California ecosystems, including coastal chaparral and montane forests, regularly experience wildfires during the dry season, with their size and frequency increasing over the past several decades.[1,2] Climate change, continued development, and fire suppression will likely further exacerbate California's fire season in the coming years.[3−5] Specifically, 2017 was a record-breaking fire season in California, with approximately 0.5 million ha burned,[6] billions of dollars in damaged property, dozens of human causalities, and ∼20 million people exposed to dense smoke for days. Impacts of prolonged smoke exposure on Californians in 2017 remain to be understood, but determining the chemical makeup of fuel-specific smoke is an important step in (1) tracing fuel consumption based upon chemical signatures in smoke and (2) linking possible fire mitigation techniques to reducing negative health impacts from smoke.

The health effects of smoke depend on the chemical composition of emitted gases and particles. One compound of interest, hydroquinone (1,4-dihydroxybenzene), is a phenolic compound that has previously been observed in biomass burning smoke but not specifically reported from chaparral and forest understory shrubs.[7−9] Hydroquinone exposure can cause eye irritation/damage and blurred vision, has been linked to oxidative damage in DNA[10] and leukemia[11,12] in humans, and is tumorigenic in rats.[13] Overall, the body of research suggests that hydroquinone exposure is dangerous to humans, though more work must be done to better understand the effects of acute or prolonged exposure.

The purpose of this study is to report the surprisingly high abundance of hydroquinone in smoke emitted from burning manzanita (*Arctostaphylos*) and demonstrate that, along with several other specific tracers, it provides a clear indicator that manzanita burned in a wildfire. Manzanita is a fire-adapted

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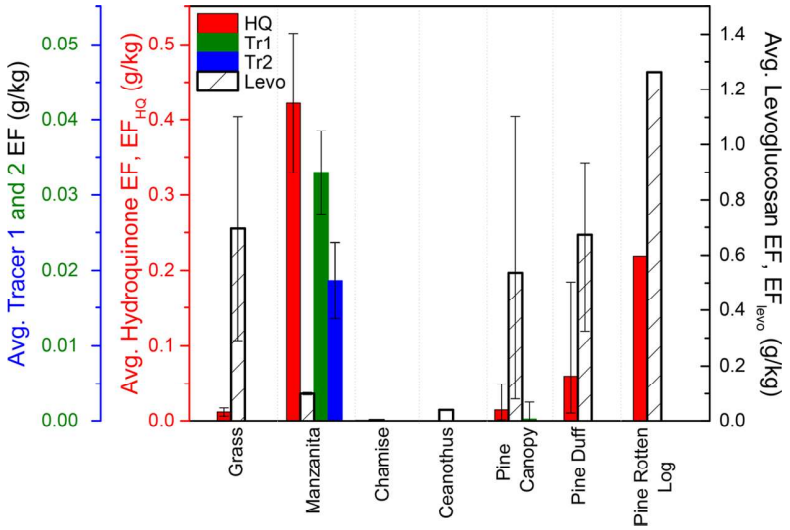

Figure 1. EF of hydroquinone (red) for a variety of fuels and EF for two sterol/triterpenoid tracer compounds (tracer 1 in green and tracer 2 in blue) only observed in emissions from manzanita. The levoglucosan EF is presented as hashed bars. Bars are grouped showing averages by fuel type such as pine canopy (abbreviated as pine) and pine duff. Error bars represent the range of measured EFs.

genus of shrubs with >100 species and subspecies.[14] They are widely distributed in California and form part of the canopy in typical chaparral communities along the coast. In the oak woodlands and conifer forests of the Sierra Nevada, manzanita is a major component of the understory.[15] Given the extent of its distribution and abundance in California's fire prone landscape, manzanita represents an important and frequently burned source of fuel.

Smoke produced from burning common western U.S. fuels such as manzanita, chamise (*Adenostoma fasciculatum*), and ceanothus (*Ceanothus*), three abundant chaparral shrubs in California, was intensively studied at the U.S. Forest Service Fire Science Laboratory in Missoula, MT, during the 2016 NOAA Fire Influence on Regional and Global Environments Experiment (FIREX). The chemical signature of manzanita smoke was then related to observations of California wildfire smoke: prescribed burns in a managed, mixed conifer forest located in the Sierra Nevada during fall 2017 and large wildfire burns centered in Sonoma County and Napa County in northern California during fall 2017.

MATERIALS AND METHODS

Twenty-two types of fuels commonly found in the western United States, including multiple species of pine trees, pine duff, pine rotten logs, and chaparral shrubs, were burned during the FIREX campaign at the U.S. Forest Service Fire Science Laboratory in Missoula, MT. Each fuel was burned multiple times inside a multistory room, the setup of which has been described previously.[16] Fresh smoke emissions were passed through a 1 μm cutoff cyclone at 10 L/min prior to being sampled onto a prebaked quartz fiber filter (see the Supporting Information for more details). One filter was collected for each burn and represents a fire-integrated observation. Emission factors (EFs, mass of compound produced per kilogram of dry fuel burned) were calculated from EF_{CO_2} values reported by Selimovic et al.[17]

Low-severity, prescribed burning took place in a mixed conifer forest at the University of California Blodgett Forest Research Station (BFRS) in November 2017. BFRS is located in Sierra Nevada (Georgetown, CA) ~1300 m above sea level and consists mostly of conifer trees [ponderosa pine (*Pinus ponderosa*), sugar pine (*Pinus lambertiana*), white fir (*Abies concolor*), incense cedar (*Calocedrus decurrens*), and Douglas fir (*Pseudotsuga menziesii*)] with small stands of understory shrubs and California black oak (*Quercus kelloggii*) and tanoak (*Notholithocarpus densiflorus*) trees. More details can be found in ref 18. Three plots of ~20 ha each were burned, with previous prescribed burns in 2002 and 2009 as part of the Fire and Fire Surrogate study.[18] Fire behavior was characteristic of a maintenance-style prescribed burn, with flame lengths typically <2 m high. Samples were collected via drones flying above the tree line and a ground station positioned on the fire line perimeter. In addition, time-resolved samples (3–4 h/sample) were collected of aged smoke in Berkeley, CA (University of California, Berkeley, campus), during the Sonoma County and Napa County high-severity wildfires in October 2017 (Nuns, Tubbs, and Atlas Fires). The landscape burned in these fires contained vegetation types where manzanita is a common component in addition to oak trees and human-made materials (e.g., houses and cars). In both campaigns, smoke was passed through a 2.5 μm cutoff cyclone prior to collection on a quartz fiber filter. Further sampling details for each campaign are provide in the Supporting Information.

Punched samples with areas between 0.21 and 1.64 cm^2 from each filter were thermally desorbed at 320 °C in helium. The desorbed sample was then analyzed using two-dimensional gas chromatography separation coupled to electron impact/vacuum ultraviolet ionization sources with detection using a high-resolution time-of-flight mass spectrometer (GC×GC-EI/VUV-HRToFMS) with online derivatization (MSTFA, *n*-methyl-*n*-trimethylsilyltrifluoroacetamide).[19,20] GC×GC separation was performed with a 60 m × 0.25 mm × 0.25 μm semi-nonpolar capillary primary column (Rxi-5Sil MS, Restek) and then a medium-polarity secondary column (1 m × 0.25 mm × 0.25 μm, Rtx-200MS, Restek). VUV light was provided by the Advanced Light Source, beamline 9.0.2, at Lawrence Berkeley National Laboratories and was used to obtain each separated compound's parent mass. Hydroquinone (HQ) was detected at

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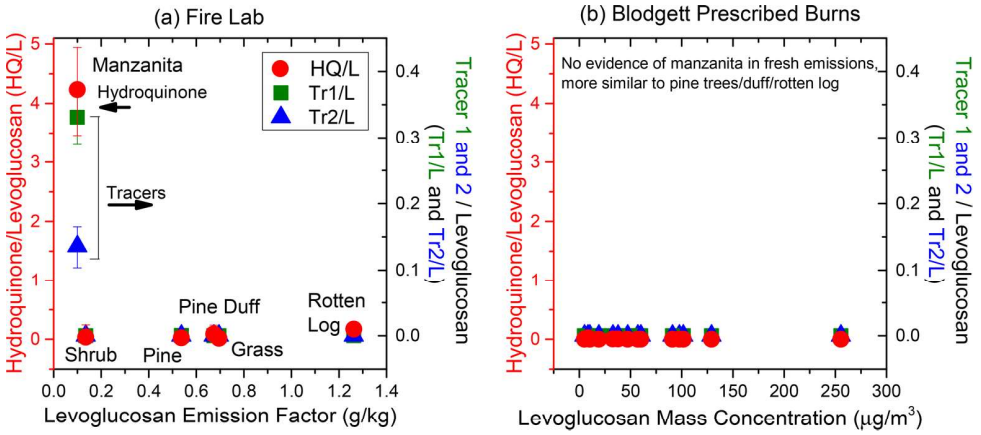

Figure 2. (a) Hydroquoinone EF normalized to levoglucosan EF (HQ/L, red points, left axis) for the various fuel groups from the Fire Lab. Note that shrubs includes chamise and ceanothus. Ratios of the two tracer compounds' EF to levoglucosan EF (Tr1/L and Tr2/L) as a function of levoglucosan EF are given as green squares and blue triangles, respectively (right axis). (b) Measured hydroquinone/levoglucosan mass concentrations (HQ/L) vs measured levoglucosan mass concentrations during the Blodgett Forest prescribed burns.

an *n*-alkane retention index of 1393, and its identity was confirmed with a combination of NIST mass spectral matching, a VUV parent mass ion of 254.12 amu (deriv.), and an authentic standard. The mass of sampled HQ was calculated by a mass loading calibration curve and is detailed in the Supporting Information. HQ mass loadings from the Fire Lab samples were converted to emission factors (EF_{HQ}) by first normalizing to background-corrected CO_2 mass and then multiplied by the CO_2 emission factor (EF_{CO_2}).[17] Emission factors for levoglucosan (EF_{levo}) and two additional specific manzanita tracer compounds were identified and quantified following a similar procedure.

Semivolatile thermal desorption aerosol gas chromatography (SV-TAG) with online derivatization (MSTFA) was also used to measure the gas-to-particle partitioning of HQ in Berkeley during the northern California events. Further instrument details are provided in ref 21 with sampling description given in the Supporting Information.

RESULTS AND DISCUSSION

Levoglucosan is commonly used as a tracer for biomass burning emissions,[22] but it is not a tracer for specific wildland fuels. Identifying unique tracers or combinations of tracers that can specifically indicate a particular type of fuel burned provides a powerful tool for understanding what materials burned and thus the origin of burning emissions. Among the thousands of chemicals separated and quantified in smoke from different materials burned during the Fire Lab experiments, HQ emission was observed in varying amounts from all fuels except for ceanothus. Figure 1 shows EF_{HQ} (red bars) for manzanita and other western U.S. wildland fuels, including chaparral shrubs (chamise and cenanothus). However, burning manzanita produced by far the highest EF_{HQ} (0.4 g/kg) compared to the values of all other studied fuels (<0.2 g/kg).

In addition to high HQ, EFs for two tracer compounds that were found to be unique to manzanita burning smoke are reported in Figure 1. These tracers are likely sterols/triterpenoids based upon their mass spectra and retention indices (see the Supporting Information), but they could not be specifically identified on the basis of NIST library matches or known standards. Emission factors for levoglucosan (EF_{levo}) are also provided in Figure 1 and were observed in emissions from all the fuels burned at the Fire Lab. EF_{levo} varies widely across the different fuels (from 10^{-5} to 1 g/kg) with rotten log at the high end and chamise at the low end.

EFs for all compounds depend strongly on fire conditions, increasing during inefficient smoldering as opposed to efficient flaming combustion.[23−26] For example, rotten log burns primarily through smoldering combustion and thus exhibits high EFs for most compounds, including levoglucosan and HQ. To separate the dependence of EF (and mass concentration) on fire conditions from fuel source, EFs of each compound were normalized to EF_{levo}. Ratios of HQ and the tracer compounds to levoglucosan (HQ/L, Tr1/L, and Tr2/L) measured at the Fire Lab are shown in Figure 2a as a function of EF_{levo}. HQ/L, Tr1/L, and Tr2/L are clearly higher for manzanita (4.2, 0.3, and 0.1, respectively) than for any of the other fuels (0.1, 0, and 0, respectively). These ratios unambiguously illustrate the unique chemical signature of freshly emitted manzanita smoke that includes large amounts of HQ, Tr1, and Tr2.

High HQ emissions in burning manzanita smoke strongly suggest that the compound must originate from a specific precursor compound that does not exist in the other fuels. This compound is most likely arbutin ($C_{12}H_{16}O_7$), which was also observed uniquely in burning manzanita smoke at 2% of the EF_{HQ}. Furthermore, arbutin has been identified at high concentrations in litter and leaf extracts of many manzanita species, including those burned at the Fire Lab (sp. *glandulosa*) and those endemic to northern California and Sierra Nevada (e.g., sp. *patula* and *viscida*).[27−30] During pyrolysis, the HQ branch of arbutin likely separates from the sugar backbone. To confirm, an arbutin standard solution was heated to 320 °C, cooler than flame temperatures, and the resulting products were analyzed via GC×GC-EI-HRToFMS. HQ and small amounts of arbutin (4% of HQ) were observed. In addition, filters extracted into methanol from the same manzanita burns at the Fire Lab were analyzed without thermal desorption via GC×GC-EI-HRToFMS and also showed large amounts of HQ instead of arbutin. Therefore, the observed high HQ from burning manzanita emissions from pyrolysis of arbutin likely occurs in high concentrations in all manzanita species.

Assuming emissions from burning manzanita are similar between species, the identified signature compounds were then

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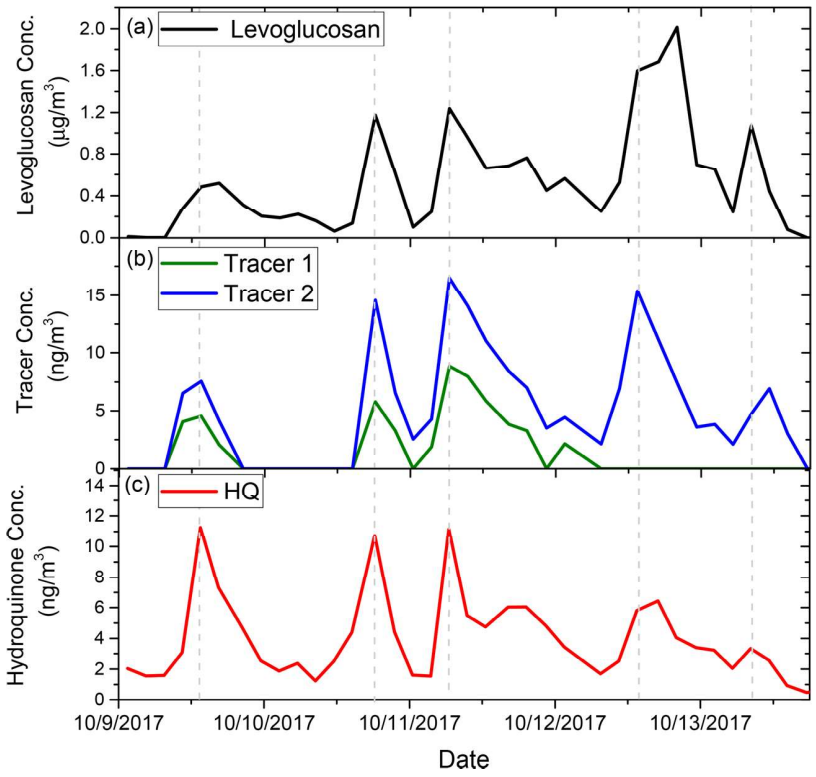

Figure 3. Timelines of observed mass concentrations of levoglucosan (a, black), tracers 1 and 2 (b, green and blue, respectively), and HQ (c, red) at the University of California, Berkeley, during the northern California burns in October 2017. Vertical dashed lines indicate times of peak concentrations during a plume.

used to investigate the consumption of manzanita fuels during wildland fires. Burns were conducted on previously fire-treated forest plots at Blodgett Forest. Averaged over 55 samples collected from fresh smoke, HQ was observed to be ~0.3 $\mu g/m^3$ and levoglucosan ~50 $\mu g/m^3$. Calculated HQ/L values as a function of levoglucosan concentration for the Blodgett samples are shown in Figure 2b and range from 0.001 to 0.02. These ratios match that of fresh emissions from burning pine/pine duff/pine rotten log measured at the Fire Lab and are far below the ratios that would indicate burning of manzanita. Moreover, no manzanita tracer compounds were seen in the filter samples; thus, Tr1/L and Tr2/L = 0. Combined, these observations clearly demonstrate that little to no manzanita was burned during these prescribed fires. Measured shrub abundance prior to the burns confirms this result: ceanothus accounted for 93% of shrub cover while manzanita was absent.

For comparison, the presence of manzanita's chemical fingerprint was also investigated in aged smoke collected in Berkeley during the northern California wildfires in October 2017. Timelines of measured HQ, Tr1, Tr2, and levoglucosan mass concentrations from filters are given in Figure 3. Note that SV-TAG measured HQ mostly in the gas phase, with only 10–30% in the particle phase. This is lower than the previously measured ~50% particle phase in fresh emissions because evaporation occurs while the plume is diluted during transport to Berkeley.[9] As a result, reported HQ concentrations in Figure 3 represent a lower limit, with >70% of its mass in the gas phase that is not efficiently captured by quartz fiber filters. At least five distinct smoke plumes were observed during the October 9–14 time period and are indicated by the vertical dashed lines in Figure 3. During these plumes, HQ and tracer concentrations peak at the same time as the levoglucosan concentration, consistent with the fact that all these compounds are from biomass burning. During the first three plumes, the HQ concentration was the highest (11 ng/m^3), corresponding to high tracer concentrations (7.6–17 ng/m^3) but varying amounts of levoglucosan (0.5–1.2 $\mu g/m^3$). This is in contrast to the last two plumes where HQ and tracer concentrations were lower (6 and 0–15 ng/m^3, respectively) but the levoglucosan concentration was relatively high (1.1–2.0 $\mu g/m^3$). This trend suggests that manzanita burning significantly contributed to the HQ concentrations during the first three plumes but contributed much less, if at all, during the last two plumes.

Combined Fire Lab and wildland fire observations suggest two key conclusions. First, fuels produce different chemical signatures that can be used to identify fuel sources from molecular speciation of wildfire smoke particles. Burning manzanita at the Fire Lab emitted large amounts of HQ (EF_{HQ} = 0.4 g/kg) and two unique sterol/triterpenoid tracer compounds. The atmospheric lifetime of HQ reacting with hydroxyl radicals is unknown but has been measured at 10–100 min for catechol (1,2-benzenediol; $k_{OH} = 1 \times 10^{-10}$ cm^3 s^{-1}),[31−33] HQ isomer, suggesting that HQ may have similar lifetimes. Thus, this fingerprint may apply in only relatively fresh emissions, though work should be done to determine reaction rates of HQ and tracer compounds with atmospheric reactants. Nevertheless, these compounds were used to conclusively determine the presence of manzanita burning in the large-scale northern California wildfires where concentrations of HQ and tracer compounds reached 11 and 17 ng/

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m^3, respectively. No tracer compounds were detected in smoke from prescribed burning in a mixed conifer forest in Sierra Nevada in California where manzanita was absent.

Second, results from this study also suggest that low-severity forest management techniques, such as prescribed burning, could be used to modify the chemical composition of fire emissions. Previous observations have shown that high-severity disturbances, including wildfires, tend to promote chaparral shrub dominance over forest regrowth in California for centuries after the incident.[34,35] In the Sierra Nevada where the prescribed burns took place, manzanita abundance is a function of a complex interplay among plant demography, disturbance regime, and forest management. Specifically at Blodgett Forest, manzanita develops into dense canopies following high-severity events that remove (e.g., clear-cut logging) or kill (e.g., wildfire) the overstory trees. Herbicides are then commonly used to control shrub abundance in managed forests after high-severity disturbances. Alternatively, a strategy that includes regular, low-severity treatments can be used to minimize shrub cover, with the three prescribed burn plots studied here exhibiting low shrub cover (6%) and almost no manzanita. This study suggests that silvicultural treatments can be used not only to reduce the likelihood of wildfires but also to help mitigate potentially negative human health impacts from toxic chemical exposure originating from burning particular types of fuels.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.8b00222.

Sampling setup during the Fire Lab, Blodgett, and northern California fires, mass loading calibration of hydroquinone, levoglucosan, and two manzanita tracer compounds, and mass spectra of two manzanita tracer compounds (PDF)

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Notes

The authors declare no competing financial interest.

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