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Environmental Sampling of Volatile Organic Compounds during the 2018 Camp Fire in Northern California

By

LESLIE ALLYN SIMMS  
THESIS

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## Abstract

Trace analysis of volatile organic compounds (VOCs) during wildfires is imperative for environmental and health risk assessment. Because air is a heterogeneous system composed of gases, liquids, and solid particles that are continuously evolving in time and space, sampling is essential for assessing combustion related chemicals in air. The use of gas sampling devices mounted on unmanned aerial vehicles (UAVs) to chemically sample air during wildfires is of great interest because these devices can move freely about their environment, allowing for more representative air samples and the ability to sample areas dangerous or unreachable by humans. This work presents chemical data from air samples obtained in Davis, CA during the deadliest and most destructive wildfire in California's history - the 2018 Camp Fire. The air sampling mechanism was an in-house manufactured micro-gas preconcentrator ( $\mu$ PC) embedded onto a compact battery-operated sampler that was returned to the laboratory for chemical analysis. Compounds commonly observed in wildfires were detected using gas chromatography mass spectrometry (GC-MS), including BTEX (benzene, toluene, ethylbenzene, m+p-xylene, and o-xylene), benzaldehyde, 1,4-dichlorobenzene, naphthalene, 1,2,3-trimethylbenzene and 1-ethyl-3-methylbenzene. Concentrations of BTEX were calculated and we observed that concentrations of benzene and toluene were highest with average concentrations of 4.7 and 15.1  $\mu\text{g}/\text{m}^3$ , respectively. Total BTEX values ranged from 4 to 48.5  $\mu\text{g}/\text{m}^3$  with an average value of 20.2  $\mu\text{g}/\text{m}^3$ . A moderate negative correlation between daily AQI and toluene, benzene and toluene/benzene ratios. were observed as well. The viability of deploying this sampling technology in future wildfires was evaluated by fixing the  $\mu$ PC sampler to a UAV and sampling air while flying in the presence of a controlled experimental fire. Fuel contents of the experimental fire included various woods, carpet, electronics, and biomass. Numerous fire-related compounds including BTEX and aldehydes such as octanal and nonanal were detected upon fire ignition, even at a much smaller sampling time compared to air samples taken during the 2018 Camp Fire. Analysis of the air samples taken both stationary during the 2018 Camp Fire and mobile during an experimental fire show the successful operation of our sampler in a fire environment. Mobile VOC sampling technology has the potential to monitor important VOCs in localized areas during wildfires and provide additional information on the effects that wildfires have on the ambient environment.

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## Author Contributions

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## Chapter 1. Introduction

Volatile organic compounds (VOCs) exist ubiquitously in the environment and some are strongly associated with health risks when directly inhaled for extended periods of time, even at low levels [1-3]. Common toxic VOCs include aromatic compounds such as benzene, toluene, xylene and carbonyl compounds such as formaldehyde, acetaldehyde, and acrolein. These VOCs have long been identified to originate from industrial and vehicular emission sources [4, 5]. They have also been documented to originate from solvents used in the home and from emulsifiable concentrate (EC) formulations of pesticides [6]. In addition, acute emissions of VOCs and accompanied pollutants from wildfires have been an ongoing environmental and health concern due to the massive complex mixture of gases they release into the atmosphere very rapidly during wildfire events.

Various low-cost gas sensors have been used in air pollution monitoring including metal oxide (MOx) sensors, photo-ionization detectors (PID), amperometric or potentiometric electrochemical cells, and micro preconcentrators ( $\mu$ PC) [7].  $\mu$ PCs are specifically useful for obtaining forensic samples of air which are then laboratory tested to determine chemicals that were present in the environment. Because these devices can sample air for prolonged periods of time, they can successfully enhance the presence of chemicals at very low ambient concentrations. This method is highly valuable because a representative sample can be taken in air which is a complex heterogeneous system composed of chemicals evolving in space and time.

There have been efforts to identify and monitor ambient VOCs via mobile sampling in a variety of environments such as classrooms [8, 9], homes [10, 11], offices [12], and outdoor settings including farms [13] and city streets [14]. However, there exists no widely accepted mobile sampling technique of VOCs during wildfires. Chemical identification during wildfires is imperative for environmental and exposure health risk assessment. Hydrocarbons and other organic chemicals produced in wildfires can remain in the air for many days and are insufficiently classified for toxicity, time-weighted averages, and short-term exposure limits which directly affect firefighters and populations that remain near areas affected by wildfires [15].

This work provides a chemical evaluation of air in Davis, California during California's deadliest, costliest, and most destructive wildfire – the 2018 Camp Fire [16]. The 2018 Camp Fire originated on Camp Creek Road near Pulga, California and occurred between 11/08/2019-11/25/2018. The fire burned over 150,000 acres of land, destroyed over 18,500 structures, and resulted in a total of 85 confirmed deaths [17]. In addition, an estimated 52,000 civilians underwent forced evacuated in eight nearby cities including: Berry Creek, Butte Creek Canyon, Centerville, Concow, Magalia, Paradise, Pulga, and Yankee Hill. Smoke from the fire extended hundreds of miles to the west and south of Pulga, into the greater San Francisco and Sacramento regions. Environmental circumstances leading to the start of the fire included hot persistent easterly winds (sustained 25-30 mph with 40-50 mph gusts), heavy grassland growth due to a rainy spring, a particularly dry fall, and abnormally low humidity [18].

Davis, a city 154.5 km away from the fire ignition site in Pulga, experienced extremely unhealthy air qualities during several days of the Camp Fire. In this work, we performed chemical analysis of the ambient air in a residential area of Davis during the worst days of reported air quality index (AQI) for the surrounding area. The gas sampling module is an in-house manufactured micro-gas preconcentrator ( $\mu$ PC) [19] embedded onto a compact sampler [20] previously developed by our group. This work also assesses the feasibility of using this sampling technology in future wildfires by implementing the  $\mu$ PC sampler onto a UAV, and sampling air in the presence of a controlled experimental fire. A mobile platform for chemical sampling during wildfires is of high interest as it would have the ability to enter hazardous areas or areas physically impossible to reach. Monitoring the chemical composition of the environment during wildfires is critical for understanding how detectable ambient chemicals are evolving in concentration and location as wildfires develop and persist.

## Chapter 2. Methodology

### VOC Sampling and GC-MS Analysis.

VOC sampling was accomplished using in-house microfabricated gas preconcentrator ( $\mu$ PC) chips manufactured for thermal desorption and chemical evaluation, which has been previously described by our group [19]. The  $\mu$ PC chips are made of borosilicate glass containing an integrated heater and RTD elements. The  $\mu$ PC chips are 2.54 cm on each side and 0.14 mm thickness. The sorbent bed located at the center of the chips holds  $6.994 \pm 0.821$  mg of Tenax TA sorbent, which is a sorbent designed specifically for trapping volatiles and semi-volatiles from air. The chips have the capability of quantifying analytes as low as 22 ppb with a sampling time as low as 2 minutes.

Each chip was thermally desorbed and verified as having blank background levels of chemicals before each sample collection. The blanked  $\mu$ PC chip was then inserted into an environmental sampler, also previously described by our group [20]. The environmental sampler contains a  $\mu$ PC chip housing as well as a pump and tubing system to transfer air through the channels of the chip. The sampler pump was set to operate at 50% power at all times during testing, producing a flow rate of 31 sccm. During testing, the  $\mu$ PC chip was placed inside the sampler and exposed to air under the conditions specified in the experimental design. Once sampling was complete, the  $\mu$ PC chip was removed from the sampler, sealed in a plastic container, and taken back to the laboratory for GC-MS analysis. Analysis was performed within 6 hours of experiment completion. The mobile  $\mu$ PC chip and environmental sampler components fit compactly within a sturdy housing for deployment (**Figure 1, top panel**).

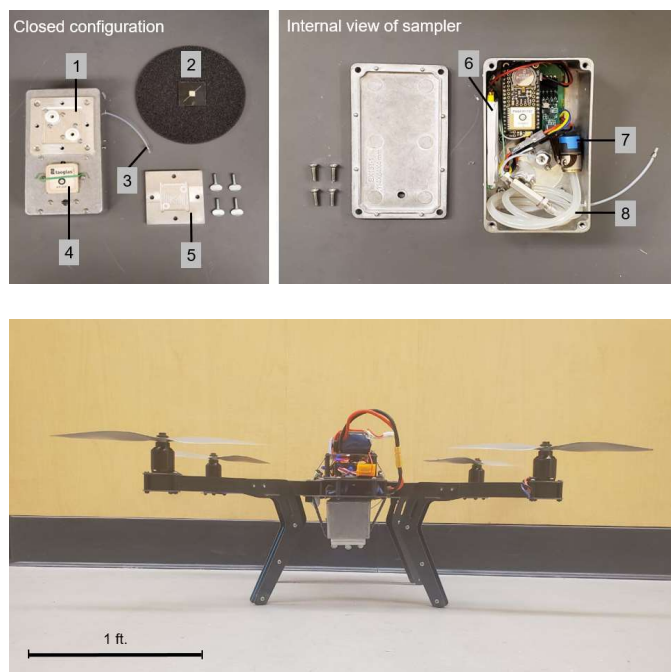


Figure 1: (Top panel) The  $\mu$ PC chip and environmental sampler are shown, including component parts: 1.  $\mu$ PC chip housing; 2. In-house manufactured  $\mu$ PC chip; 3. Environmental sampler inlet; 4. GPS module; 5.  $\mu$ PC housing lid; 6. Battery; 7. Air pump; 8. Soft tubing which connects to  $\mu$ PC inlet. (Bottom panel) Air sampler attachment to the underside of the UAV.

VOCs sampled and absorbed onto each  $\mu$ PC chip were analyzed by gas chromatography mass spectrometry (GC-MS, Varian 3800 GC with 4000 ion trap MS) through a custom-built test fixture that heated the chip at 260 °C for 15 min. A helium flow (25 mL/min) allowed the desorption of VOCs that enter to a splitless mode inlet at 235 °C. A column (VF-5 ms 30 m x 0.25 mm x 0.25  $\mu$ m, Agilent Technologies Inc., Santa Clara, CA) was used with a temperature gradient to separate the desorbed compounds. Oven started at 40 °C and was heated to 170 °C at 10 °C/min, then raised to 250 °C at 30 °C/min and held for 6 min, with a helium flow at 1 mL/min. The compounds were finally detected by the MS from 35 to 249 m/z. Obtained data files were first deconvoluted using AMDIS (version 2.71, NIST.gov) and aligned using the Agilent Genespring (version B.14.9) with a time window set at 0.3 min. This allowed the identification of most of the sample compounds. These identifications were confirmed by comparing standard retention times, Kovats index (KI) values, as well as extracted mass spectra comparison to a database (NIST 14).

## **Generation of Calibration Curves.**

Calibration curves were created for specific compounds commonly used in pollution, industrial health, and safety applications: benzene, toluene, ethylbenzene, o-xylene, and m-xylene (BTEX). Calibration curves were also created for dichlorobenzene and naphthalene for chemical analysis during verification of the mobile sampling platform (see section 2.4). Each standard (Sigma-Aldrich, ACS Reagent grade) was dissolved in methanol and injected (0.6  $\mu\text{L}$ ) directly to the GC-MS using the same method previously described, except for a split mode injection (40:1) that avoided overloading of the detector. Curves contained duplicates at six concentration levels. The resulting mass values obtained by calibrations were distributed over the sampling volume to result in a concentration value of the ambient environment during sampling.

## **2018 Camp Fire VOC sampling.**

Air samples were taken in a residential area of east Davis, California during the 2018 Camp Fire, from 11/14/2018-11/19/2018. A sampler was loaded with a  $\mu\text{PC}$  chip and placed on a table resting on the balcony of a second story apartment building. A total of ten two-hour samples were taken at various times throughout the five days of sampling. Samples were taken as frequently as possible while ensuring the safety of the researchers during exposure to outdoor air when setting up the sampler and transporting  $\mu\text{PC}$  chips to the lab for analysis. The sampling dates, times and daily AQI [21] are shown (**Table 1**).

Sample Date	Sample Number	Sample Time	AQI	Ozone	PM <sub>2.5</sub>	NO <sub>2</sub>	PM <sub>10</sub>
11/14/18	1	2:00 pm	253	45	253	41	114
	2	6:00 pm					
11/15/18	3	10:40 am	314	41	314	56	169
	4	8:30 pm					
11/16/18	5	1:15 pm	275	45	275	61	149
	6	6:30 pm					
11/18/18	7	8:35 am	189	48	189	48	90
	8	6:30 pm					
	9	11:00 pm					
11/19/18	10	11:50 am	176	42	176	58	88

Table 1: Sampling frequency and daily AQI [21]

### Mobile VOC sampling verification.

For mobile sampling, the sampler was attached to a drone and manually operated by a designated pilot. The UAV was built on the 3DR ArduCopter Quad-C platform (3D Robotics; San Diego, CA). It contains a basic suite of sensors, a flight controller, motors, and a frame. The propulsion setup consisted of four 850 kV motors powered by a single 4 cell 5200 mAh lithium polymer battery. Each motor was equipped with a 10-inch (25.4 cm) diameter propeller at a pitch of 4.7. The drone sampler platform weighed 1807 g. Turbulent flow produced by the drone is directed downward from the propellers. To facilitate chemical ingestion into the sampler during flight, the sampler was attached underneath the vehicle using Velcro and a bungee cord that extend to either side. The input tube for air sampling was angled and fixed in the upwards position. This configuration was used during all mobile sampling (**Figure 1, bottom panel**).

The open source flight controller ArduPilot version 3.9.4 was used for all flights. General altitude control was performed using a built-in barometer. Calibration and tuning of these controls were completed using the companion open source software MissionPlanner version 1.3. Flights were initiated by taking off and flying into a starting position. Once at the starting position, an altitude hold setting was engaged where the flight controller would attempt to maintain level pitch and roll. However, the controller permits the pilot to override the autonomous stability commands, allowing for manual maneuvering. All flight patterns were completed in this altitude hold mode with the flight path controlled manually by the pilot.

Verification experiments were performed to evaluate the functionality of our air sampler while on a UAV. Chemical exposure experiments were performed inside of an airport hangar located at the University of California, Davis University Airport (**Figure 2A**). Briefly, a large open space was in the center of the back wall, and limited air circulation was present within the hangar. All turbulent airflow present during experimentation is assumed to be generated by the UAV propellers while in flight.

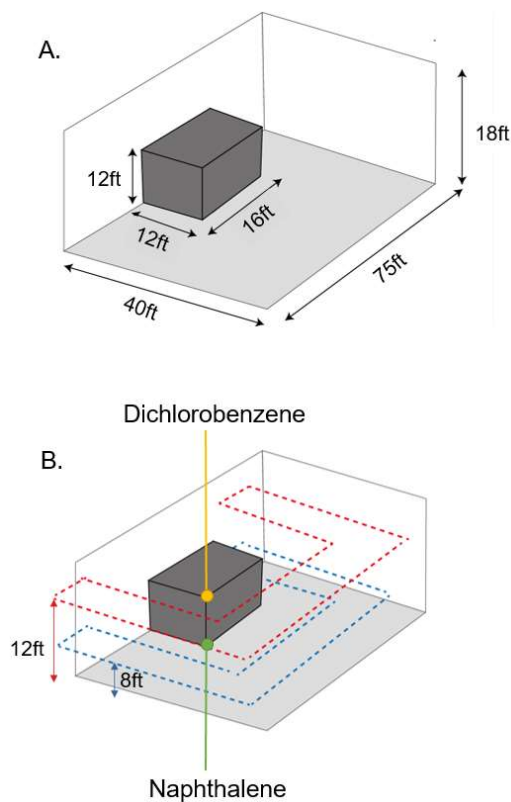


Figure 2: (A) Airport hangar dimensions; and (B) verification flight pattern and VOC source location within airport hangar.

A series of three repeated UAV sampler tests were performed exposed to two different VOCs in the form of commercial emission sources (e.g. moth balls) which contained either dichlorobenzene or naphthalene. One field test was performed per day to allow for the dissipation of the VOCs between experiments. A flight pattern was chosen to mimic a forensic sampling of the indoor hangar airspace. Flights were 10 min duration, which was the maximum flight time for our given sampler payload. The flight pattern as well as the location of the VOC sources is shown (**Figure 2B**). The flight pattern was a peripheral path around the hangar approximately 5 ft from the walls at two different height altitudes. Three and a half cycles at a height of 8 ft were flown, then the drone increased its height to 12 ft for another three and a half cycles.

During a hangar sampling episode, a background air sample was first performed before the introduction of the VOCs to evaluate residual presence of the target VOCs from previous experiments. The same flight pattern performed during experimentation was also performed for the background sample. This background measure (if any) was subtracted from that day measurement. VOCs were then brought into the hangar and stationed at their designated location. Naphthalene moth balls were placed onto the ground, and dichlorobenzene moth balls were placed on top of the open area 12 ft above the ground. The moth balls were exposed for 10 min before the start of experiments to allow for chemical dispersion. The sampler was then attached to the UAV containing a new chip, powered on, and flight was initiated. After flight completion and chip retrieval, the chips were transported to the lab for analysis.

### **Mobile VOC sampling during an experimental fire.**

To evaluate the performance of the mobile sampler in a fire environment, three field experiments were performed in which the UAV sampler flew through smoke from a controlled grill fire. The fire was ignited at the Woodland-Davis Aeromodelers (WDA) field on 07/19/2019. UC Davis researchers were granted permission by WDA management, the Davis Fire Department, and the Yolo-Solano Air Quality Management District to perform this experiment. Also, designated researchers were equipped with fire extinguishers for the duration of these experiments.



A 30 min background air sample was first taken in the gravel area in which experiments took place. A commercial outdoor charcoal grill (Aussie Walk-A-Bout 2.0 model 4250; MECO Corporation, Greeneville, TN) was loaded with various biomass and industrial substances laid upon a layer of charcoal. Materials were chosen to mimic some of the materials that can be expected to burn during a wildfire that spreads over both natural land and municipal areas. Biomass materials included: wood from indoor flooring, hickory firewood, and dried grass/vegetation. Industrial materials included: carpet, sponge rubber carpet underlay, and broken printed circuit boards. The fire was then ignited and left to burn for 5 min to ensure the combustion of materials before chemical sampling (**Figure 3A**).

A loaded sampler was attached to the UAV and powered on. A 10 min flight was initiated in which the UAV sampler repeatedly flew through the smoke at a consistent height of approximately 12 ft from ground (**Figure 3B**). Once the flight was completed, the sampler was removed from the drone and the  $\mu$ PC chip was placed into a sealed container. The fire was replenished with a portion of each material before the initiation of the remaining two flights containing unused chips. After the completion of the three flights, the fire was extinguished, and the  $\mu$ PC chips were transported to the laboratory for analysis.

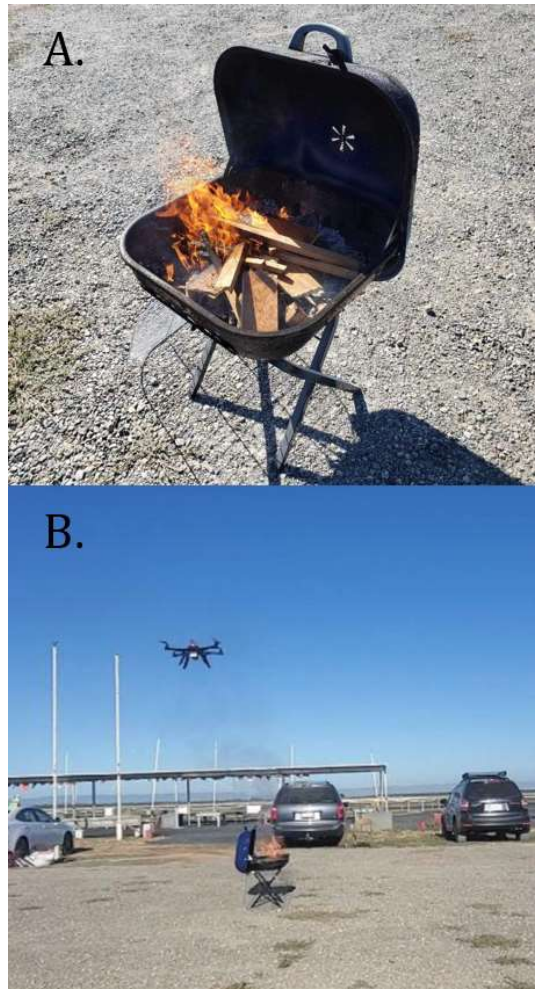


Figure 3: (A) Supervised experimental fire; (B) UAV sampler in flight through smoke generated by the experimental fire.

## Chapter 3. Results

### 2018 Camp Fire Environmental Ambient Air Sampling.

Ten two-hour air samples were collected over five days of the 2018 Camp Fire in Northern California, while the regional AQI was at its worst (**Figure 4**). The ten obtained Total Ion Chromatograms (TICs) show similar chemical profiles though all samples, with clear differences with their peak abundances on certain days. After peak deconvolution and alignment, 126 individual chemicals were identified. From those, 44 were tentatively identified by comparing their mass spectrum to a NIST reference database (**Table 2**). Each volatile has a corresponding match score value obtained from the database ID process. An additional confirmation was performed with available commercial standards, including benzene, toluene, ethylbenzene, ortho-xylene, (meta+para)-xylene (BTEX), naphthalene, and dichlorobenzene. The CAS ID, formula, retention time, experimental and literature Kovats Index (KI), and chemical family of all the detected compounds are described. The number of times a compound was detected through all measured samples is also listed. Each chemical has been linked to literature in which the ambient environment was chemically analyzed during a fire.

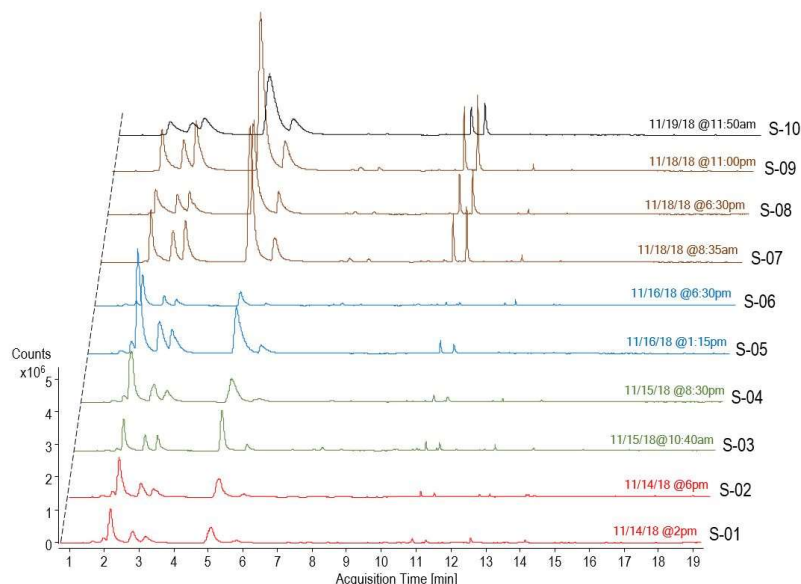


Figure 4: Total Ion Chromatograms (TICs) of ten two-hour air samples taken during the 2018 Camp Fire. Each color represents one of the five days in which samples were taken. All signals are shown using the same abundance scale.

Compound	CAS ID	Formula	RT (min)	KI (exp.)	KI (Lit)	Freq.	Family	Score	Reference
2-methylbutane	78-78-4	C5H12	1.65	<850	462	2	alkane	87.7	[22, 23]
2-methyl-1-butene	563-46-2	C5H10	1.93	<850	490	3	olefin	87.5	[22-26]
ethoxyacetylene	927-80-0	C4H6O	1.97	<850	498	2	ether	86.1	
vinyl acetate	108-05-4	C4H6O2	2.13	<850	550	1	acetate ester	86.4	
dimethoxyborane	4542-61-4	C2H7BO2	2.14	<850	-	9	borane	81.1	
2-butanone	78-93-3	C4H8O	2.25	<850	600	2	ketone	78.8	[22, 27]
benzene*	71-43-2	C6H6	2.80	<850	650	10	aromatic	90.0	[15, 22-37]
2-pentanone	107-87-9	C5H10O	3.16	<850	680	3	ketone	72.9	[22, 24-27, 32, 36]
1,6-heptadien-3-yne	5150-80-1	C7H8	5.06	<850	71.5	3	alkyne	75.9	
toluene*	108-88-3	C7H8	5.12	<850	760	10	aromatic	84.3	[15, 22-26, 28, 29, 31-36]
acetyl valeryl	96-04-8	C7H12O2	5.76	<850	800	2	ketone	77.9	
2-hexanone	591-78-6	C6H12O	5.81	<850	785	5	ketone	73.7	[22]
(Z)-4-(acetyloxy)-3-penten-2-one	38365-58-1	C7H10O3	5.83	<850	-	1	ketone	78.8	
hexanal*	66-25-1	C6H12O	6.15	<850	81.5	5	aldehyde	73.1	[22, 24-27]
butyl acetate*	123-86-4	C6H12O2	6.62	<850	810	1	acetate ester	74.5	
furfural*	98-01-1	C5H4O2	7.16	<850	830	1	aldehyde	80.6	[15, 22, 23, 27, 29, 32]
4-hydroxy-4-methyl-2-pentanone	123-42-2	C6H12O2	7.42	<850	835	2	ketone	83.4	
ethylbenzene*	100-41-4	C8H10	7.80	<850	860	10	aromatic	89.4	[15, 22-26, 28, 29, 31, 32, 34-36]
(m+p)-xylene*	106-42-3	C8H10	8.05	892	890	10	aromatic	91.3	[15, 22-26, 28, 29, 31, 32, 36]
o-xylene*	95-47-6	C8H10	8.61	898	890	10	aromatic	86.7	[15, 22-29, 31, 32]
methylphenethyl sulfoxide	7714-32-1	C9H12OS	8.66	898	-	2	sulfoxide	78.1	
3-thujene	353313	C10H16	9.54	935	921	4	terpene	75.3	[25]
1-ethyl-3-methylbenzene	620-14-4	C9H12	10.15	958	960	6	aromatic	87.4	[23, 24, 27, 29]
benzaldehyde*	100-52-7	C7H6O	10.35	974	970	1	aromatic	86.7	[22-24, 26, 27, 29]
β-pinene*	127-91-3	C10H16	10.51	982	993	4	terpene	77.4	[24-27, 31]
isopropylbenzene	98-82-8	C9H12	10.53	982	925	4	aromatic	77.6	
ethyl 3-ethoxypropionate	763-69-9	C7H14O3	10.69	990	1000	1	ester	85.3	
1,2,3-trimethylbenzene	526-73-8	C9H12	10.87	999	1010	4	aromatic	74.1	[23-26, 31, 32]
octanal*	124-13-0	C8H16O	11.06	1009	1010	4	aldehyde	85.3	[24, 27, 37]
3,6,6-trimethyl-2-norpinene	4889-83-2	C10H16	11.13	1013	980	2	olefin	76.4	
1,4-dichlorobenzene*	106-46-7	C6H4Cl2	11.31	1023	1020	5	aromatic	77.0	[23, 28]
1,5-dimethyl-1,5-cyclooctadiene	3760-14-3	C10H16	11.54	1035	1047	4	olefin	73.7	
d-limonene*	138-86-3	C10H16	11.54	1035	1030	4	terpene	81.0	
β-cimene*	3779-61-1	C10H16	11.82	1051	1050	1	olefin	71.9	[24-27]
2-phenylpropanal	93-53-8	C9H10O	11.92	1057	1090	3	aldehyde	81.4	
(1R,2R,4S,5S)-8-methylenecyclo[3.2.1.0(2,4)]octane	38310-48-4	C9H12	12.03	1063	-	6	olefin	76.0	
3,4-dimethylstyrene	27831-13-6	C10H12	12.50	1089	1100	1	aromatic	70.5	
nonanal*	124-19-6	C9H18O	12.87	1111	1105	2	aldehyde	86.3	[24]
2-nitro-phenol	88-75-5	C6H5NO3	13.44	1146	1150	2	aromatic	75.4	
naphthalene*	91-20-3	C10H8	14.32	1201	1175	10	aromatic	75.4	[15, 23, 24, 27, 29, 34]
methyl salicylate*	119-36-8	C8H8O3	14.39	1207	1220	8	aromatic	83.9	
2-methyl-naphthalene	91-57-6	C11H10	16.20	1336	1300	1	aromatic	78.4	
2-ethyl-3-hydroxyhexyl 2-methylpropanoate	74367-31-0	C12H24O3	16.91	1386	1375	7	ester	80.1	
oxo-tremorine	4630-07-3	C15H24	17.54	1437	1470	3	aromatic	81.2	

\* Compounds confirmed using commercial standards. RT: retention time; KI (exp.): experimental Kovats Index; KI (Lit) Kovats Index from the literature; Freq.: frequency of the compounds in the ten obtained samples; Score: average number between detected replicates, which considers the mass spectrum score based on a NIST database.

**Table 2. List of putatively identified volatile compounds collected from 2018 Camp Fire air samples. Bolded compounds correspond to VOCs used for quantification of concentrations.**

We recognize that several of the identified volatile compounds in Table 2 have been reported in other studies that sought to evaluate chemicals in various types of fires, ranging from experimental fires to wildfires around the world. Specifically, the BTEX mixture was detected multiple times and has been highly studied [15, 22-37]. Also, other aromatic compounds commonly detected in fires were observed in our data, such as benzaldehyde, 1,4-dichlorobenzene, naphthalene, 1,2,3-trimethylbenzene and 1-ethyl-3-methylbenzene. Other compounds frequently identified include aldehydes (hexanal, furfural, octanal and nonanal), ketones (2-pentanone and 2-hexanone), 2-methyl-butene and d-limonene. Although some of the compounds are common VOCs present in normal ambient air, compounds with high toxicity that have been previously related to wildfires have been identified in our data set. Additionally, these results indicate that our  $\mu$ PC device can work functionality to capture VOC compounds that indicate the presence of fire emissions.

BTEX compounds were detected in all samples collected during the Camp Fire. Because these compounds are commonly used to measure air quality, we wanted to determine the concentration captured by our device (**Table 3**). BTEX concentration ratios are commonly used to determine emission sources and obtain information about the photochemical reactivity of compounds, given different component degradation rates in air. For example, toluene to benzene (T/B) ratios are largely thought to designate the presence of traffic combustion sources. While toluene can come from industrial solvent usage, benzene (highly toxic) is not used in solvent formulations such as vehicle fuels. Therefore, higher T/B ratios ( $>2$ ) indicate a high amount of pollution generated by emission sources (mainly traffic). The ratio of (m+p)-xylene/ethylbenzene (m+p/E) can act as an indicator of the photochemical age. Values of 3.5 and higher indicate fresh local emissions, whereas lower values suggest the emissions originate some distance away [38]. Concentrations ( $\mu\text{g}/\text{m}^3$ ) were expressed as the amount ( $\mu\text{g}$ ) of the corresponding VOC per volume of air ( $\text{m}^3$ ) during the collection exposure. In this case, the  $\mu$ PC chip was exposed for two hours under laboratory conditions using a flow rate of 30 mL/min. We also included other VOCs such as 1,4-dichlorobenzene and naphthalene for their quantification. These compounds are also commonly detected in

fires and were present in most of the samples. We also used 1,4-dichlorobenzene and naphthalene to validate the later UAV sampler testing.

Compound	Concentration ( $\mu\text{g}/\text{m}^3$ )										Avg.
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	
Total BTEX	7.1	8.7	8.8	12.7	22.2	4.0	23.5	37.2	48.5	29.2	20.2
Benzene	2.9	3.5	2.5	4.9	8.9	1.5	4.5	6.5	7.2	4.9	4.7
Toluene	4.1	5.1	5.9	7.5	13.1	2.2	18.6	30.1	40.6	24.1	15.1
Ethylbenzene	0.023	0.042	0.121	0.111	0.051	0.101	0.120	0.177	0.196	0.074	0.102
m+p-xylene	0.021	0.065	0.161	0.137	0.050	0.110	0.143	0.227	0.237	0.080	0.123
o-xylene	0.011	0.029	0.085	0.085	0.027	0.070	0.134	0.196	0.225	0.056	0.092
1,4-dichlorobenzene	<lod	0.069	0.066	<lod	<lod	0.073	0.084	0.073	<lod	<lod	0.073
Naphthalene	0.004	0.009	0.019	0.014	0.005	0.009	0.010	0.011	0.011	0.006	0.010
Ratio T/B	1.4	1.5	2.3	1.5	1.5	1.4	4.2	4.6	5.6	4.9	2.9
Ratio m+p/E	0.9	1.5	1.3	1.2	1.0	1.1	1.2	1.3	1.2	1.1	1.2

lod: limit of detection of the method for 2h collection ( $4.2 \times 10^{-4}$  ng/L =  $0.42$  pg/m<sup>3</sup>)

Ratio T/B: toluene/benzene; Ratio m+p/E: m+p=xylenes/ethylbenzene

Table 3. Quantification of the VOCs collected with the  $\mu\text{PC}$  chip during the 2018 Camp Fire.

All BTEX compounds were detected in all ten samples, benzene and toluene being the most abundant compounds (**Table 3**). The average concentration of benzene and toluene was  $4.7$  and  $15.1$   $\mu\text{g}/\text{m}^3$ , respectively. Toluene concentrations reached as high as  $40$   $\mu\text{g}/\text{m}^3$ . These high values are common when there are episodes of high contamination due to smoke or other pollutants [38]. Total BTEX values ranged from  $4.0$  to  $48.5$   $\mu\text{g}/\text{m}^3$ , with an average value of  $20.2$   $\mu\text{g}/\text{m}^3$ . However, most of these came from benzene and toluene, and the total averaged concentrations of (m+p)-xylenes, o-xylene and ethylbenzene were low, with values close to  $0.1$   $\mu\text{g}/\text{m}^3$  in all cases. Those results are commonly reported in semirural areas like Davis, California mainly during warm weather [38]. These aromatic compounds with higher-molecular weight are largely removed by the reaction with OH radical in the atmospheric content, which can be higher in the conditions of the study. Additionally, the ratio T/B higher than 2 indicates high levels of pollution from the emission sources, which can include nearby traffic or fuel sources from the 2018 Camp Fire. However, an average value of 1.2 was calculated for the m+p/E ratio, which indicates that the samples contained compounds originating at large distances from the collection area. This is consistent with our location 150 km away from the Camp Fire origination site.

Finally, the presence of 1,4-dichlorobenzene and naphthalene was below the limit of the detection (lod) of the analysis technique for some samples. Considering the total volume collected, the lod for all the compounds was set at 0.42  $\mu\text{g}/\text{m}^3$ . These compounds were averaged at 0.073  $\mu\text{g}/\text{m}^3$  for 1,4-dichlorobenzene and 0.01  $\mu\text{g}/\text{m}^3$  for naphthalene.

All concentrations of BTEX, 1,4-dichlorobenzene, and naphthalene were averaged by day and compared to the daily AQI values from the nearest reporting site in Sacramento, California [21] across the 5 days of our sampling (**Table 4**). AQI values increased to a maximum value of 314 between day 1 and day 2 and decreased each day after that. Correlation regression analyses were performed for the AQI with each of the listed compounds. Highest correlation values ( $R^2 \sim 0.75$ ) were observed with toluene, total BTEX and ratio T/B, all influenced by the high toluene presence.

Compound	Concentration ( $\mu\text{g}/\text{m}^3$ )					Correlation ( $R^2$ )
	Day 1	Day 2	Day 3	Day 4	Day 5	
Total BTEX	7.9	10.8	13.1	36.4	29.2	0.73
Benzene	3.2	3.7	5.2	6.1	4.9	0.33
Toluene	4.6	6.7	7.7	29.8	24.1	0.76
Ethylbenzene	0.03	0.12	0.08	0.16	0.07	0.03
m+p-Xylene	0.04	0.15	0.08	0.20	0.08	0.01
o-Xylene	0.02	0.09	0.05	0.18	0.06	0.13
1,4-dichlorobenzene	0.07	0.07	0.07	0.08	< lod	0.27
Naphthalene	0.01	0.02	0.01	0.01	0.01	0.29
Ratio T/B	1.4	1.9	1.4	4.8	4.9	0.77
Ratio m+p/E	1.2	1.3	1.0	1.2	1.1	0.10
AQI	253	314	275	189	176	

Table 4. Average concentration by day of some detected VOCs during the 2018 Camp Fire and their comparison to daily AQI values.

The correlation between AQI and toluene, benzene, and the T/B ratios were plotted and is shown in **Figure 5**. In all three cases, a moderate negative correlation was found, especially for the toluene concentrations. Considering that the total AQI values during the Camp Fire were dominantly described by  $\text{PM}_{2.5}$  AQI (**Table 1**), the negative correlations could indicate that the source of  $\text{PM}_{2.5}$  is different than the sources that generate toluene and benzene. One possible explanation is the varying levels of traffic related pollutants, described by T/B ratio, during the periods with lower AQI during the study. For example, as the AQI became hazardous, decreased vehicle usage due to evacuations and people staying indoors may have

resulted in lower toluene and benzene concentrations. Oppositely, as the AQI improved (decreased), vehicle usage may have increased in the area, resulting in increased toluene and benzene concentrations. For context, the UC Davis campus was closed for two weeks during the dangerous air quality period of the Camp Fire, which coincided with the 5-day duration of our study.

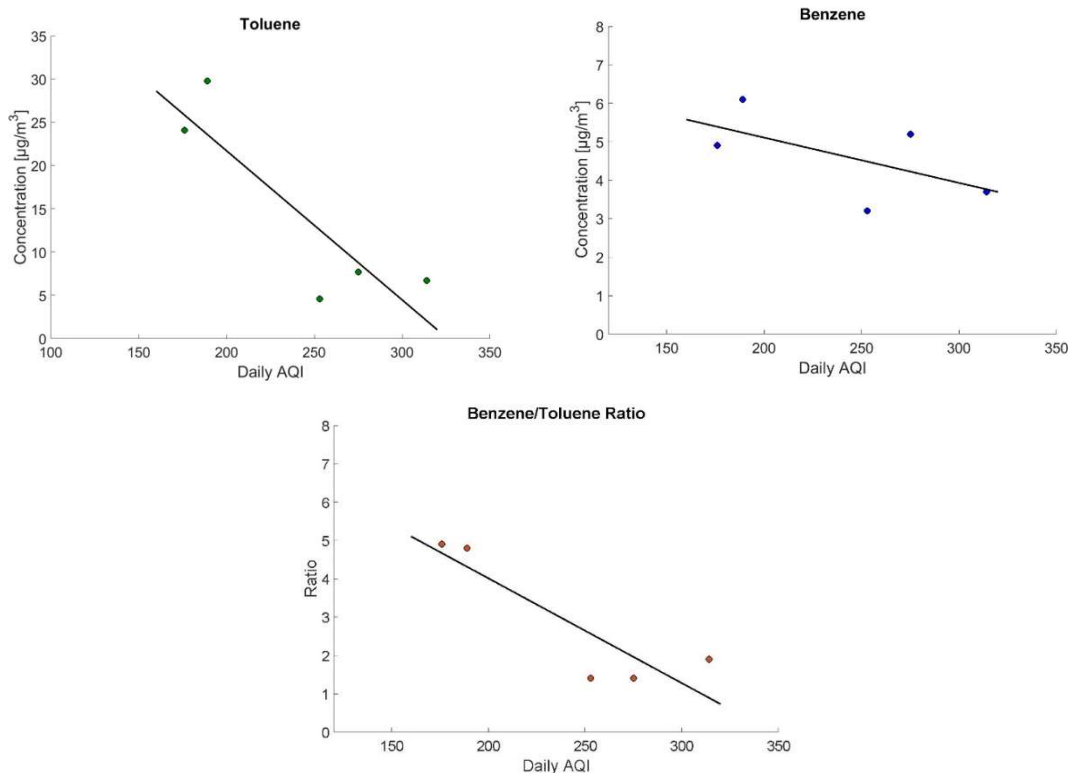


Figure 5. Correlation between AQI and major chemical compounds. We observe that both benzene and toluene are well-correlated with other measures of air quality captured by the AQI composite score.

### Mobile VOC Sampling Verification on an Airborne Platform.

Once the environmental sampler was shown capable of capturing ambient fire-related compounds during the 2018 Camp Fire, the same sampler was functionality verified on a mobile UAV platform. This was to determine possible localized mobile VOC analysis in future wildfires in a safe and practical manner. Two VOC sources (1,4-dichlorobenzene and naphthalene) were placed at differing altitudes in an airport hangar and air samples were taken as the drone flew in a specified flight pattern discussed previously (**Figure 2**). A background sample was taken before all measurements. For both chemicals, the concentration detected by the device increased after ambient exposure (**Figure 6**). Naphthalene was detected at higher



concentrations, achieving more than twice the initial concentration, going from 0.39 to 0.95  $\mu\text{g}/\text{m}^3$ . Dichlorobenzene increased from 0.10 to 0.18  $\mu\text{g}/\text{m}^3$ . One possible explanation of higher naphthalene concentrations is due to the increased mixing of naphthalene in the air during flight. Turbulent airflow was directed downward towards the emission source which was located on the ground of the airport hangar. These results demonstrate the successful operation of the environmental sampler while on an aerial platform.

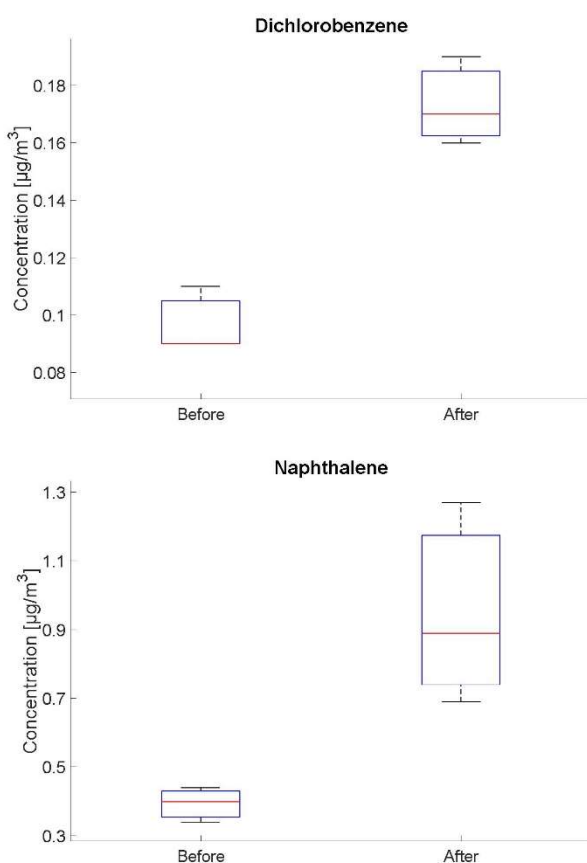


Figure 6: Concentration readings before and after chemical introduction for verification of mobile sampler functionality.

### Mobile VOC Sampling During a Controlled Experimental Fire.

The drone sampling platform was then operated during a controlled experimental fire containing various industrial and biomass materials as described earlier (**Figure 3**). Compounds were measured during

10 min flights before the fire (blank controls) and during the fire (in triplicate). BTEX and other VOCs were detected at lower concentrations compared to the 2018 Camp Fire, and we measured the average concentrations of BTEX before and after fire ignition (**Figure 7**). Initial collections show the presence of only toluene and (m+p)-xylene, which had concentrations of 0.014 and 0.008  $\mu\text{g}/\text{m}^3$ , respectively. Toluene presence can be indicative of the traffic present in the area, and a high initial T/B ratio of 9.8 confirms the presence of vehicular sources close to the sampler. However, after fire ignition, the T/B ratio decreases drastically to 3.9 due to the increasing presence of benzene from the smoke. Overall, BTEX compounds had a significant increase in concentration once the fire was ignited. Total BTEX concentration increased from 0.03 to 0.27  $\mu\text{g}/\text{m}^3$ . Ethylbenzene had an average of 0.015  $\mu\text{g}/\text{m}^3$  and has been shown to be unusually high in industrial fires involving electronics [23]. Benzene, toluene, (m+p)-xylene, and o-xylene had average values of 0.042, 0.163, 0.027, and 0.018  $\mu\text{g}/\text{m}^3$ , respectively.

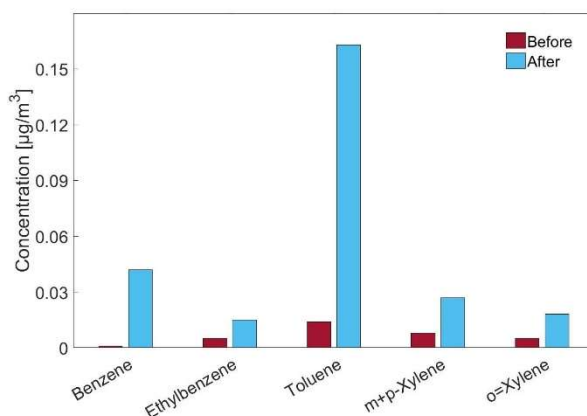


Figure 7. Comparison of concentrations obtained for the BTEX compounds during the experimental fire.

Finally, the VOC profile obtained during the 2018 Camp Fire was compared to the VOC profile of the experimental fire (**Figure 8** and **Table 5**). We were able to detect nine common compounds between both cases, including BTEX, limonene, naphthalene and aldehydes such as octanal and nonanal. The GC-MS chromatograms showed different profiles at different scales, with the signals from the Camp Fire (**Figure 8A**) having higher intensities than the experimental figure (**Figure 8B**). These differences may be

due to the nature of the samples collected, the sampling methodology (static versus mobile), and sampling times. However, many compounds could be detected in both cases (**Figure 8**).

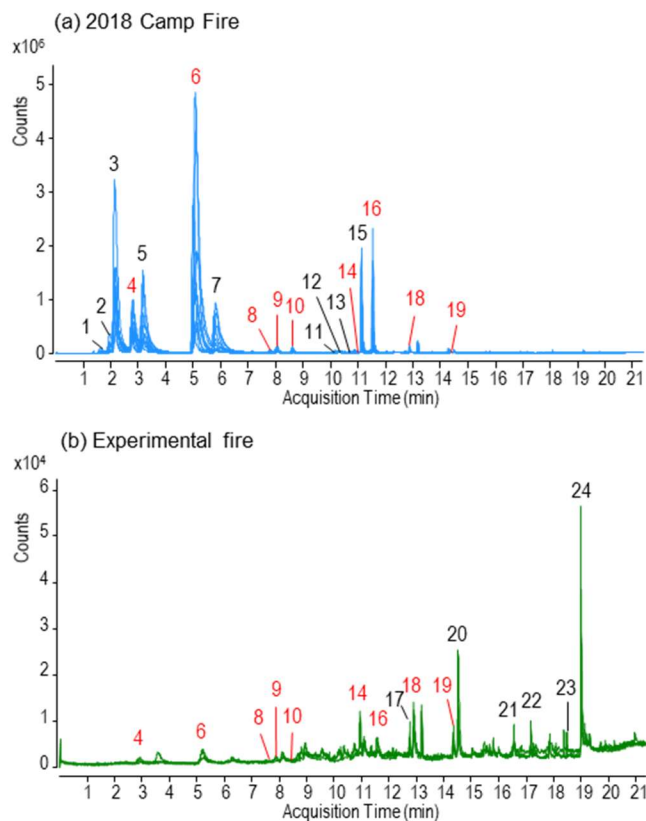


Figure 8. Comparison of the Total Ion Chromatogram (TIC) profiles obtained during (A) the 2018 Camp fire; and (B) the experimental fire. The matching compounds in both experiments are colored in red and unique peaks for each experiment are colored black. The compound names corresponding to the numbers are displayed in Table 5.

Peak	RT (min)	Compound	Formula	MW	CAS
11/14/18	1	2:00 pm	253	45	253
2	1.95	2-methyl-1-butene	C5H10	70	563-46-2
3	2.15	vinyl acetate	C4H6O2	86	108-05-4
4*	2.8	benzene	C6H6	78	71-43-2
5	3.2	2-pentanone	C5H10O	86	107-87-9
6*	5.1	toluene	C7H8	92	108-88-3
7	5.8	2-hexanone	C6H12O	100	591-78-6
8*	7.8	ethylbenzene	C8H10	106	100-41-4
9*	8.05	p-xylene	C8H10	106	106-42-3
10*	8.6	o-xylene	C8H10	106	95-47-6
11	10.15	1-ethyl-3-methylbenzene	C9H12	120	620-14-4
12	10.3	benzaldehyde	C7H6O	106	100-52-7
13	10.85	1,2,3-trimethylbenzene	C9H12	120	526-73-8
14*	11.05	octanal	C8H16O	128	124-13-0
15	11.13	1,4-dichlorobezne	C6H4Cl2	147	106-46-7
16*	11.5	limonene	C10H16	136	138-86-3
17	12.7	2,6-dimethyl-undecane	C13H28	184	17301-23-4
18*	12.8	nonanal	C8H18O	142	124-19-6
19*	14.35	naphthalene	C10H8	128	91-20-3
20	14.5	cyclodecanol	C10H20O	156	1502-05-2
21	16.5	terpinyl acetate	C12H20O2	196	80-26-2
22	17.2	2-ethyl-1-decanol	C12H26O	186	21078-65-9
23	18.5	butylated hydroxytoluene	C15H24O	220	128-37-0
24	19.0	2-pentyl-2-nonenal	C14H26O	210	3021-89-4

Table 5. Tentative identification of the main compounds detected in 2018 Camp Fire and experimental fire with mobile  $\mu$ PC chip. \* Compounds detected in both the 2018 Camp Fire and experimental fire.

Moreover, unique compounds were detected in the experimental fire including cyclodecanol, 2-pentyl-2-nonenal or 2-ethyl-1-decanol. Although their presence is not documented in literature related to wildfires, these compounds could have been present in the materials used in the experimental fire or their combustion. For example, butylated hydroxytoluene is commonly added to rubber or fuel industry products to prevent oxidation. Also, 2,6-dimethylundecane has been found to be an air contaminant that comes from new furnishing materials [39] and is present in petroleum fractions [40]. Terpinyl acetate has been used in air care products and is related to flooring materials like carpets or wood.

## **Chapter 4. Discussion**

The unique accomplishment of this work is the successful deployment of a novel VOC sampler to evaluate compounds produced by fires both ground-based and mobile via drone. Comparison of stationary air samples taken during the 2018 Camp Fire to mobile air samples taken during an experimental fire highlight the potential of preconcentration techniques to remotely monitor VOCs during wildfires. The composition of the air during wildfires is complicated and continuously changing, but certain toxic compounds can be measured and monitored on a mobile platform without endangering people. Future studies intend to establish VOC concentration maps of areas through time by operating multiple mobile samplers as wildfires persist. Future studies also intend to assess the value of using additional sorbents to generate a more extensive VOC profile.

## Chapter 5. Conclusion

We investigated volatile organic compounds in Davis, California during five days of the 2018 Camp Fire. Air samples were obtained using an in-house manufactured environmental sampler and micro-gas preconcentrator chips. Aromatic compounds that were detected and correlated to fire-related chemicals seen in the literature included benzaldehyde, 1,4-dichlorobenzene, naphthalene, 1,2,3-trimethylbenzene and 1-ethyl-3-methylbenzene. Compounds that were frequently identified included aldehydes such as hexanal, furfural, octanal and nonanal, ketones such as 2-pentanone and 2-hexanone, 2-methyl-butene, and d-limonene. We also reported a negative linear relationship between the daily AQI and both benzene and toluene, highlighting the possible impact of decreased vehicular activity as air quality became worse. We also assessed the performance of the environmental sampler on a mobile platform, namely a drone, and in the presence of an experimental fire. Analysis of the VOCs under the experimental fire were consistent with nine fire-related compounds detected during the Camp Fire, even at a much smaller sampling time. These included BTEX, octanal, limonene, nonanal, and naphthalene. BTEX concentrations increased upon fire ignition, notably toluene which increased from 0.014 to 0.163  $\mu\text{g}/\text{m}^3$ .

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