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## Characterization of PM<sub>2.5</sub> collected during broadcast and slash-pile prescribed burns of predominately ponderosa pine forests in northern Arizona

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### Abstract

Prescribed burning, in combination with mechanical thinning, is a successful method for reducing heavy fuel loads from forest floors and thereby lowering the risk of catastrophic wildfire. However, an undesirable consequence of managed fire is the production of fine particulate matter or PM<sub>2.5</sub> (particles  $\leq 2.5$   $\mu\text{m}$  in aerodynamic diameter). Wood-smoke particulate data from 21 prescribed burns are described, including results from broadcast and slash-pile burns. All PM<sub>2.5</sub> samples were collected in situ on day 1 (ignition) or day 2. Samples were analyzed for mass, polycyclic aromatic hydrocarbons (PAHs), inorganic elements, organic carbon (OC), and elemental carbon (EC). Results were characteristic of low intensity, smoldering fires. PM<sub>2.5</sub> concentrations varied from 523 to 8357  $\mu\text{g m}^{-3}$  and were higher on day 1. PAH weight percents (19 PAHs) were higher in slash-pile burns ( $0.21 \pm 0.08\%$  OC) than broadcast burns ( $0.07 \pm 0.03\%$  OC). The major elements were K, Cl, S, and Si. OC and EC values averaged  $66 \pm 7$  and  $2.8 \pm 1.4\%$  PM<sub>2.5</sub>, respectively, for all burns studied, in good agreement with literature values for smoldering fires.

### Keywords

elemental carbon; fine particulate matter; organic carbon; PM<sub>2.5</sub>; polycyclic aromatic hydrocarbons; prescribed burn; wood-smoke particulate

## 1. Introduction

Prescribed fire is a useful method for reducing the buildup of fuels on forest floors in forestlands where wildfires have been suppressed, such as in the U.S. Southwest (Covington and Moore, 1994a). Prescribed fires reduce the risk of stand-replacing crown fires (Kilgore and Sando, 1975), control disease, and promote the growth of grasses and forbs, thereby restoring overgrown forests to presettlement (late 19th century) conditions (Allen et al., 2002). The need for managed fire has increased due to the rise in frequency and severity of

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**Supplementary material.**Supplementary data are included in Tables S1–S5.

wildfires. In 2009, nearly 70,000 wildland fires were reported nationally; in the same year, over 12,000 prescribed burns were conducted (National Interagency Fire Center, 2010).

Despite the benefits of prescribed fire, it is also a well-known source of particulate matter or  $PM_{2.5}$  (particles  $\leq 2.5 \mu\text{m}$  in aerodynamic diameter). These particles, most of which are submicron in size, are small enough to be inhaled into the lungs and have been linked to pulmonary disease and morbidity (Dockery, 2009; Dockery et al., 1993; Zmirou et al., 1998). Wood-smoke particulate is composed primarily of organic material (typically 80% of the particle mass), elemental carbon or soot (5–9%), and trace inorganic species (12–15%) (Reid et al., 2005). Approximately 250 compounds have been identified in the organic carbon (OC) fraction, comprising between 15 and 51% of the total OC mass (Fine et al., 2004). Major classes of compounds include alkanes, alkenes, alkanols, alkanolic and alkenolic acids, guaiacols, syringols, anhydrosugars (notably levoglucosan), resin acids, and diterpenoids (Fine et al., 2004; Hays et al., 2002; Lee et al., 2005; Mazzoleni et al., 2007; McDonald et al., 2000; Oros and Simoneit, 2001; Schauer et al., 2001). The OC fraction also contains polycyclic aromatic hydrocarbons (PAHs). Although the PAH mass fraction is small ( $<5\%$ ), PAHs in wood-smoke particulate have been highly studied because of their known or expected toxicities (Freeman and Cattell, 1990; Oanh et al., 1999; Robinson et al., 2008; Tan et al., 1992; Zou et al., 2003). The PAHs are formed during flaming and can serve as condensation nuclei for other pyrolyzed species (Reid et al., 2005). The elemental carbon (EC) fraction refers to refractory forms of carbon that are not volatilized at temperatures  $>700 \text{ }^\circ\text{C}$  (Birch and Cary, 1996). The inorganic components of wood-smoke particulate commonly include sulfate, nitrate, and soil elements such as aluminum, silicon, titanium, calcium, and iron (Malm and Hand, 2007). The inorganic and organic components of wood-smoke particulate are predominately light scattering (Malm and Hand, 2007), resulting in a cooling effect on earth's climate (Forster et al., 2007). Alternatively, the EC component is light absorbing, leading to a warming effect (McMeeking, 2008; Reid et al., 1998). The light scattering and absorbing properties of particulate can also degrade visibility, and fires are an important source of haze aerosols in the western United States (Jaffe et al., 2008; Malm et al., 2004; Spracklen et al., 2007).

Because of its potential affect on health, climate, and visibility, much effort has been devoted to studying particulate from various fire sources such as biomass burning (Andreae and Merlet, 2001; Crutzen and Andreae, 1990; Reid et al., 2005; Reid and Hobbs, 1998), residential firewood combustion (Fine et al., 2004; McDonald et al., 2000; Schauer et al., 2001), campfire burning (Simoneit et al., 2000), wildland fuel combustion (Chen et al., 2006; Chen et al., 2007; Hays et al., 2002; Mazzoleni et al., 2007), and prescribed burns (Lee et al., 2005; Mazzoleni, 2007; Robinson et al., 2004; Robinson et al., 2008). In this work, we summarize the characteristics of 21  $PM_{2.5}$  samples collected during prescribed burns of the Coconino and Apache-Sitgreaves National Forests in northern Arizona between 2001 and 2007. Both broadcast and slash-pile prescribed burns were studied. Broadcast burns are low-intensity burns that consume large areas of downed woody materials (e.g., dead branches, pine cones, and decaying pine needles). Slash-pile burns are high-intensity burns that consume stacked piles of logs and logging debris. Samples were collected in situ (within 50 m of the fire) on day 1 (ignition), when short flaming episodes were present, or day 2, when smoldering predominated. Concentrations of  $PM_{2.5}$ , OC, and EC are reported for all burns; PAH and elemental concentrations are reported for selected burns. Some values have been reported previously (Robinson et al., 2004; Robinson et al., 2008), but we repeat them here so that general trends can be highlighted. To our knowledge, this is the first paper to investigate  $PM_{2.5}$  from broadcast and slash-pile burns in ponderosa pine forestlands and only the second to study prescribed burns in situ (see also Lee et al., 2005).

## 2. Experimental

### 2.1. Prescribed fire sites

PM<sub>2.5</sub> samples were collected during 21 prescribed burns of the Coconino and Apache-Sitgreaves National Forests (Table S1). Both forests are predominately ponderosa pine (*Pinus ponderosa*) with a small fraction of oak, Douglas fir, and mixed conifers. Samples were collected during broadcast burns on day 1 (ignition) ( $n = 11$ ) and day 2 ( $n = 4$ ) and slash-pile burns on day 1 ( $n = 4$ ) and day 2 ( $n = 2$ ). Because sample numbers are small, comparisons across the different burn types are qualitative only, using the arithmetic mean ( $\pm$ stdev). Broadcast burns consumed 20–80 hectares, after the area had been mechanically thinned and prepared for prescribed fire. Slash-pile burns ignited between 300 and 2650 piles. On day 1, sampling began 1 to 2 h after initial ignition. Because it takes at least 4 h to ignite an entire area, at least some flaming was present on day 1, together with smoldering. On day 2, smoldering predominated and little to no flaming was observed. Note that “flaming” and “smoldering” are used qualitatively; CO and CO<sub>2</sub> levels were not monitored nor were combustion efficiencies calculated (Reid et al., 1998). Except for one maintenance burn of a grassland (conducted within 7 years of an earlier broadcast burn), all broadcast burns were first-entry fires; hence, the parcel had not experienced fire for at least 7 (and more typically 50) years. These areas all had heavy fuel loads composed of small diameter fuels (dead twigs and branches), pinecones, brown-dead pine needles, and decaying soil layers or duff. Relative humidity was typically 25–35% except at one pile burn, where it began to rain shortly after ignition. In addition to 21 prescribed burns, 2 experimental burns were also conducted. Both were open-air burns in which either dead ponderosa pine needles or wood was placed in a stainless steel container and ignited with a match. The fuel was continuously replaced and flaming was encouraged throughout the sampling period (2 h).

### 2.2. PM<sub>2.5</sub> collection and analysis

PM<sub>2.5</sub> samples were collected using a PM<sub>2.5</sub> chemical speciation sampler (SuperSASS, Met One Instruments, Inc., Grants Pass, OR). The monitor is equipped with eight sampling channels; up to four channels can be operated simultaneously. Each channel has its own sharp-cut cyclone (to remove particles  $> 2.5 \mu\text{m}$ ), automatic flow controller (flow rate  $6.7 \pm 0.5$  Lpm), filter holder, and selected filter media (47 mm). Samples analyzed by gas chromatography/mass spectrometry were collected on pre-fired (overnight at 650 °C) quartzfiber filters (PallFlex Tissuquartz). Samples analyzed gravimetrically or by X-ray fluorescence spectroscopy were collected on PTFE filters (2  $\mu\text{m}$ , Whatman).

Because no electrical sources were available at the burn sites, the sampler was battery operated, limiting collection times to between 1 to 3 h per sample (Table S1). On day 1, for safety reasons, the sampler was placed just outside the burn area, in a region expected to receive high levels of smoke. On day 2, the sampler was placed inside the burn area, typically near a smoldering log or slash pile. Once positioned, the monitor could not be moved again; hence, smoke intensities varied as the wind shifted during sampling. Filters were transported to and from the burn site in a cooler ( $<10$  °C). Quartzfiber filters were stored at  $-20$  °C until analyzed; PTFE filters were stored at room temperature. Two field blanks, one PTFE and one quartzfiber, were collected on each burn day.

### 2.3. Gravimetric analysis

PTFE filters were analyzed gravimetrically by RTI International (Research Triangle Park, NC) or Chester LabNet (Tigard, OR). Following conditioning in a control chamber (24 h, 20–25 °C, 30–40% relative humidity), filters were weighed ( $\pm 0.001$  mg) pre- and post-exposure. PM<sub>2.5</sub> concentrations ( $\mu\text{g m}^{-3}$ ) represent the particulate mass divided by the volume of air sampled. Average concentrations are reported in cases where two or more

PTFE filters were co-collected. PTFE field blanks increased in mass by <3.0% PM<sub>2.5</sub> mass. In cases where only quartzfiber filters were used, the PM<sub>2.5</sub> concentration was estimated from the OC concentration by multiplying [OC] by the average ratio of [PM<sub>2.5</sub>]/[OC] for the same burn type: [PM<sub>2.5</sub>]/[OC] = 1.59, 1.34, 1.58, and 1.44 for bc (day 1), bc (day 2), pile (day 1) and pile (day 2), respectively.

#### 2.4. PAH analysis

Quartzfiber filters were analyzed for 21 PAHs using gas chromatograph/mass spectrometry (GC/MS) as described elsewhere (Brown et al., 2002; Engling et al., 2006). Briefly, filters were spiked with a series of deuterated internal standards (including naphthalene-d<sub>8</sub>; pyrene-d<sub>10</sub>; chrysene-d<sub>12</sub> and perylene-d<sub>12</sub>; all Cambridge Isotope laboratories, Andover, MA) then extracted three times (3 × 25 mL) with methylene chloride (Fisher, Optima grade) under sonication. Extracts from co-collected filters were combined into a single sample and reduced to 250 μL under a gentle flux of purified nitrogen. A 2 μL aliquot of the sample was injected into the GC/MS system (Agilent 6890/5973inert). PAHs were identified and quantified by comparison with retention times and peak areas of 21 PAH calibration standards. Nineteen PAHs were monitored: phenanthrene, anthracene, fluoranthene, acephenanthrylene, pyrene, benzo[ghi]fluoranthene, cyclopenta[cd]pyrene, benz[a]anthracene, benzo[c]phenanthrene, chrysene+triphenylene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[e]pyrene, perylene, benzo[ghi]perylene, indeno(1,2,3) cd pyrene, and dibenz[ah]anthracene. (Naphthalene and fluorene were also monitored, but their particle-phase concentrations were negligible and are not discussed further.) The limit of detection (LOD) per sample was 0.5 ng. In calculations that involved samples below the detection limit, LOD/√2 (0.3535 ng) was used. Field blanks showed little to no contamination; samples were not blank corrected. In two instances, the sampling filter was followed by a second prebaked, quartzfiber backup filter to test for semivolatile PAH filter adsorption artifacts. Two PAHs (phenanthrene and anthracene, MW = 178) were detected on the backup filters, in roughly equal amounts as the sampling filters. No other PAHs were detected on the backup filters. Reported concentrations were not corrected for these artifacts.

#### 2.5. Elemental analysis

PTFE filters were analyzed for 38 elements with atomic numbers 11 (sodium) through 82 (lead) by X-ray fluorescence (XRF) spectroscopy by RTI International (Research Triangle Park, NC) or Chester Lab Net (Tigard, OR) according to Method U.S. EPA-3.3. Elements with concentrations <3 times the instrumental uncertainty are reported as non-quantifiable (NQ). Elements with concentrations below limits of detection are reported as LOD.

#### 2.6. Organic and elemental carbon analysis

Organic and elemental carbon masses were determined using thermal-optical transmission methods (Birch and Cary, 1996) with corrections for charring (Sunset Laboratory, Inc., Tigard, OR). One-quarter of one quartzfiber filter was used per burn event. The OC or EC mass (μg cm<sup>-2</sup>) was multiplied by the approximate deposit area (11.3 cm<sup>2</sup>) and divided by the volume of air sampled (m<sup>3</sup>). Error bars were calculated by propagating the reported uncertainty in mass (or ±15%) and volume (estimated to be ±5%). In two instances, the sampling filter was followed by a second prebaked quartzfiber backup filter to test for semivolatile adsorption artifacts; OC/EC analysis suggested that artifacts comprised roughly 6% of the OC mass. Reported OC values were not corrected for these artifacts.

### 3. Results and Discussion

#### 3.1. PM<sub>2.5</sub> mass concentrations

Wood-smoke PM<sub>2.5</sub> concentrations (Table 1) varied from a low of 523  $\mu\text{g m}^{-3}$  in a grassland maintenance burn (entry 5) to an estimated high of 8357  $\mu\text{g m}^{-3}$  during a broadcast burn (entry 7). (See Table S2 for PM<sub>2.5</sub> masses and air volumes.) This variability reflects both true differences in particle concentrations at various burn events and fortuitous differences resulting from the placement of the monitor at the start of each burn. In most instances, PM<sub>2.5</sub> concentrations were higher on day 1, and the arithmetic means ( $\pm$ stdev) of day 1 concentrations were roughly the same for both broadcast ( $2800 \pm 2500$ ) and slash-pile burns ( $3000 \pm 2800 \mu\text{g m}^{-3}$ ). Smoke levels and particulate concentrations were noticeably lower on day 2 and during the maintenance grassland burn (entry 5).

#### 3.2. PAH analysis of wood-smoke particulate

Because of their potential toxicity, PM<sub>2.5</sub> samples were analyzed for 19 different PAHs. Fig. 1 shows the average mass fraction of each PAH (mg PAH/g OC) according to burn type: broadcast (day 1,  $n = 6$ ), broadcast (day 2,  $n = 1$ ), pile (day 1,  $n = 4$ ), and pile (day 2,  $n = 2$ ), as well as two experimental burns. (See Table S3 for individual PAH concentrations in each burn.) In general, PAH levels were lower in broadcast burns of pine needles and duff than in slash-pile burns of logs, although variability was large. Corresponding results were observed in the experimental burns: dead pine needles produced lower PAH levels than dead pine wood. Tan et al. (1992) report similar findings in laboratory burns of split firewood (lodgepole pine) versus duff; PAHs were significantly higher in the firewood burns, although a more complex array of PAHs was identified in the duff burns.

PAH levels are predicted to be higher in flaming than smoldering fires (Reid et al., 2005). Thus, we expected to observe higher PAH levels on day 1, when the fires were ignited, than on day 2, when smoldering predominated. However, as shown in Fig. 1, the levels were roughly the same on both days. This result can be explained by the short duration of flaming combustion in the burns studied and in prescribed burns in general. By design, prescribed fires are low-intensity (low-flaming) burns. Each area (or pile) is typically ignited only once; it flames for a few minutes, and then enters a smoldering phase. Thus, in any given area, smoldering predominates, even on day 1. Because we sampled smoke produced over the entire burn area and for several hours, our results are more representative of smoldering fires.

The five most abundant PAHs in the prescribed burns were the lowest in molecular weight: phenanthrene (178), anthracene (178), fluoranthene (202), acephenanthrylene (202), and pyrene (202). Benz[a]anthracene (228) and chrysene + triphenylene (228) were also relatively high in concentration; both are classified as probable human carcinogens by the U.S. Environmental Protection Agency (2010). Phenanthrene, anthracene, fluoranthene, and pyrene are reported as “not classifiable as to human carcinogenicity”; acephenanthrylene has not yet been characterized. The 12 remaining PAHs (MW 226 to 278) were also detected in all burns except for one (entry 11). Among these 12, four are probable human carcinogens: benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, and indeno[1,2,3]cd pyrene (U.S. EPA, 2010). Despite the potential health risks, occupational exposure to particle-phase PAHs during prescribed burns is likely to be small, even in pile burns, both because the firefighters can avoid areas of intense smoke (Robinson et al., 2008) and because the overall PAH levels are typically <1% of the particulate mass (Reid et al., 2005). The 19 particle-phase PAHs described in this work averaged only  $0.07 \pm 0.03\%$  of the OC mass for broadcast burns ( $0.08\%$  OC for the pine needle burn) and  $0.21 \pm 0.08\%$  OC for the pile burns ( $0.21\%$  OC for the pine wood burn). Our broadcast burn data are in good agreement

with the broadcast burn data of Lee et al. (2005), who reported 0.11% OC for a slightly different set of 18 PAHs. Similarly, Simoneit et al. (2000) reported PAHs as only a minor component in campfire wood-smoke particulate. Campfire wood is expected to be similar to the dead wood consumed in prescribed fires.

In Fig. 2, the concentrations of selected PAHs are compared across six different wood-burning studies, including this work. The PAHs include (from highest to lowest concentration) fluoranthene, pyrene, benzo[b+j+k]fluoranthene (grouped together), benz[a]anthracene, chrysene+triphenylene, benzo[a]pyrene, benzo[e]pyrene, and benzo[ghi]perylene. A fireplace combustion study of hardwoods produced the highest PAH levels (McDonald et al., 2000) followed by three fireplace combustion studies of softwood (pine) (Fine et al., 2004; McDonald et al., 2000; Schauer et al., 2001). These softwood studies are in reasonable agreement with our open air slash-pile burns of ponderosa pine. Lower PAH levels were observed in the two authentic broadcast burns (Lee et al., 2005; this work) and in a simulated broadcast burn of brown-dead pine needles (Hays et al., 2002). Collectively, these data support the general trend that burning wood (hardwood then softwood) generates higher PAH levels than burning dead pine needles or duff, likely due to the flaming and higher temperatures associated with wood burning (Reid et al., 2005). The lowest PAH levels were observed in a simulated logging slash-pile burn (Hays et al., 2002). This last result does not support the general trend; however, fresh green logging slash was consumed in this burn, possibly affecting the results.

### 3.3. Elemental analysis of wood-smoke particulate

XRF analysis was used to determine particulate-phase elemental concentrations in 15 of the 21 prescribed burns investigated (Table 2, Table S4). In accord with the literature (e.g., see Reid et al., 2005), K, Cl, S, and Si dominated the inorganic composition. The abundance of K and Cl in wood-smoke particulate has made them useful tracer species (Reid et al., 2005). Bromine was also detected but at lower levels (<0.01% of PM<sub>2.5</sub> mass). The soil elements Ti, Ca, and Fe were observed at quantifiable levels, as were zinc and copper. Heavy metals such as lead, chromium, and arsenic were detected but not quantifiable.

Unlike PAH levels, which were roughly the same on days 1 and 2, several elements varied with burn day. For example, the average wt% of Cl, K, and Br decreased on day 2 for both broadcast and pile burns (Table 2). Conversely, the average wt% of Si and Ca increased on day 2 for both burn types. Day 1 values are in accord with the broadcast burns of Lee et al. (2005) and the fireplace burns of Schauer et al. (2001), with a few exceptions. For broadcast burns, Lee et al. (2005) measured higher values for K ( $0.57 \pm 0.37$ ) and Cl ( $0.42 \pm 0.23\%$  PM<sub>2.5</sub>) than we observed. Even higher values of K ( $0.71 \pm 0.21$ ) and Cl ( $1.71 \pm 0.01\%$  PM<sub>2.5</sub>) were detected in a simulated pile burn of fresh green logging slash (Hays et al., 2002). Conversely, in a simulated understory burn of brown-dead pine needles K and Cl were non-quantifiable (Hays et al., 2002). A possible explanation for this variability, and for our larger day 1 than day 2 values, is fuel moisture content and humidity. K and Cl levels appear to increase with moisture content. For example, higher levels of K and Cl were observed in the “wet” pile burn, which was conducted in the rain, and in the maintenance burn, which consumed live grasses and brush seedlings rather than dead wood. A South American grassland burn (Ferek et al., 1998) produced essentially the same values for K ( $2.9 \pm 1.5$ ) and Cl ( $1.7 \pm 1.0\%$  PM<sub>2.5</sub>) that we observed in the grassland burn. Collectively, these data suggest that burning grasses or other fresh fuels may be a more significant source of K and Cl than dead wood or logs.

### 3.4. Organic and elemental carbon analysis of wood-smoke particulate

Wood-smoke particulate is largely carbonaceous consisting of both organic carbon and elemental carbon or soot. The OC fraction is more volatile, comprising compounds that evolve in a helium-only environment at temperatures  $<700$  °C. The EC fraction desorbs at higher temperatures (800–1200 °C) in a helium-plus-oxygen environment. Because these definitions are empirically based, results can vary with the method used (Chow et al., 1993; Chow et al., 2007). In this work, OC and EC measurements were made using a thermo-optical method that corrects for “charring” caused by refractory organic carbon (Birch and Cary, 1996). In Table 1, ambient OC and EC concentrations are reported for each burn (see Table S5 for OC and EC masses and air volumes). In Fig. 3, OC and EC concentrations are reported as a wt% of  $PM_{2.5}$  mass and compared to literature values (all determined by thermo-optical methods). OC values ranged from 63 to 75%  $PM_{2.5}$  (57 to 69%  $PM_{2.5}$  after correcting for semivolatile adsorption artifacts), regardless of burn type or day, consistent with Reid et al. (2005) for smoldering fires ( $62 \pm 6\%$   $PM_{2.5}$ ). Two literature values were outside of this range: the fireplace study by Fine et al. (2004) ( $90.1 \pm 4.8\%$   $PM_{2.5}$ ) and the prescribed burn study by Mazzoleni et al. (2007) ( $35.7 \pm 7.7\%$   $PM_{2.5}$ ). EC values ranged from 1.7 to 3.4%  $PM_{2.5}$ , again consistent with the range reported by Reid et al. (2005) for smoldering fires (2–5%  $PM_{2.5}$ ). Only the fireplace study by Fine et al. (2004) ( $7.3 \pm 0.7\%$   $PM_{2.5}$ ) was outside of this range.

The ratio of organic carbon to elemental carbon is often used as a tracer for wood smoke. OC/EC values  $>12$  are indicative of wood burning (Malm et al., 2004), and wildfires typically report OC/EC ratios between 7 and 15 (Jaffe et al., 2008). For the 21 prescribed burns described in this work, the average OC/EC ratio was  $32 \pm 21$  (Table 1). A possible explanation for our higher values is the lack of flaming in the prescribed burns studied. Higher temperature, flaming fires have been shown to produce more soot (EC) than smoldering fires (Pósfai et al., 2003). Similarly, soot has been shown to be only a minor component in wildfires or biomass burnings without flaming (Ferek et al., 1998). Hence, the lack of flaming can explain our lower EC (higher OC/EC) values. The fact that we observed lower OC/EC ratios in our two experimental burns ( $11 \pm 1$  and  $6 \pm 1$ ), when flaming was encouraged, further supports this hypothesis (Table 1). Even lower OC/EC values ( $<3$  and often  $<1$ ) were reported when these same fuels were burned under intense flaming conditions (Chen et al., 2007; Mazzoleni et al., 2007). In the four prescribed burns conducted by Mazzoleni et al. (2007), an average OC/EC value of  $11 \pm 6$  was reported. This relatively small OC/EC ratio suggests the presence of flaming, and in a personal communication with Mazzoleni (2010), she indicated that firefighters were continuously igniting small patches of fire during sampling (30 min) and that a mixture of flaming and smoldering fires was present. These data suggest that OC/EC ratios may be useful indicators of flaming or smoldering fire conditions. Of course, other factors can also influence soot content, such as whether the smoke was sampled on the ground or above the fire.

By design, prescribed burns are low-intensity, low-flaming fires. Following ignition, flaming is short-lived and is soon replaced by smoldering, which can last for several days. Thus, works that study prescribed burns primarily during the flaming stages may overestimate the fractional amount of EC present in the wood-smoke particulate. The lower EC and higher OC/EC values presented in this work may provide a more accurate representation of the “average” smoke produced in a prescribed burn.

## 4. Conclusions

$PM_{2.5}$  was collected in situ during 21 prescribed burns of largely ponderosa pine forests in northern Arizona and analyzed for ambient concentration, PAH content, elemental composition, and OC and EC levels. Both broadcast and slash-pile prescribed burns were

studied, and samples were collected on the day of and the day after ignition. Smoldering predominated on both days. PAH concentrations were low (<0.2% PM<sub>2.5</sub> mass) but were nearly three times higher during slash-pile burns than broadcast burns. Elemental carbon concentrations were also low (<3.4% PM<sub>2.5</sub> mass), consistent with low-intensity, low-flaming fires.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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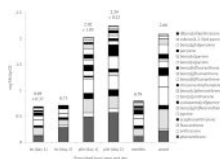
## References

- Allen CD, Savage M, Falk DA, Suckling KF, Swetnam TW, Schulke T, Stacey PB, Morgan P, Hoffman M, Jon T, Klingel JT. Ecological restoration of southwestern ponderosa pine ecosystems: A broad perspective. *Ecological Applications*. 2002; 12:1418–1433.
- Andreae MO, Merlet P. Emission of trace gases and aerosols from biomass burning. *Global Biogeochemical Cycles*. 2001; 15:955–966.
- Birch ME, Cary RA. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Science and Technology*. 1996; 25:221–241.
- Brown S, Herckes P, Ashbaugh L, Hannigan MP, Kreidenweis SM, Collett LL. Characterization of organic aerosol present at Big Bend National Park, Texas during the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study. *Atmospheric Environment*. 2002; 36:5807–5818.
- Chen L-WA, Moosmüller H, Arnott WP, Chow JC, Watson JG, Susott RA, Babbitt RE, Wold CE, Lincoln EN, Hao WM. Particle emissions from laboratory combustion of wildland fuels: In situ optical and mass measurements. *Geophysical Research Letters*. 2006; 33:L04803.
- Chen L-WA, Moosmüller H, Arnott WP, Chow JC, Watson JG, Susott RA, Babbitt RE, Wold CE, Lincoln EN, Hao WM. Emissions from laboratory combustion of wildland fuels: Emission factors and source profiles. *Environmental Science & Technology*. 2007; 41:4317–4325. [PubMed: 17626431]
- Chow JC, Watson JG, Pritchett LC, Pierson WR, Frazier CA, Purcell RG. The DRI thermal/optical reflectance carbon analysis system: description, evaluation and applications in U.S. Air quality studies. *Atmospheric Environment*. 1993; 27A:1185–1201.
- Chow JC, Watson JG, Chen L-WA, Chang MCO, Robinson NF, Trimble D, Kohl S. The IMPROVE\_A temperature protocol for thermal/optical carbon analysis: Maintaining consistence with a long-term database. *J. Air & Waste Manage. Assoc.* 2007; 57:1014–1023.
- Covington WW, Moore MM. Postsettlement changes in natural fire regimes and forest structure: ecological restoration of old-growth ponderosa pine forests. *J. Sustain. Forest.* 1994a; 2:153–181.
- Crutzen PJ, Andreae MO. Biomass burning in the tropics: Impact 389 on atmospheric chemistry and biogeochemical cycles. *Science*. 1990; 250:1669–1678. [PubMed: 17734705]
- Dockery DW. Health effects of particulate air pollution. *Ann. Epidemiol.* 2009; 19:257–263. [PubMed: 19344865]
- Dockery DW, Pope CA, Xu X, Spengler JD, Ware JH, Fay ME, Ferris BG, Speizer FE. An association between air pollution and mortality in six U.S. cities. *The New England Journal of Medicine*. 1993; 329:1753–1759. [PubMed: 8179653]

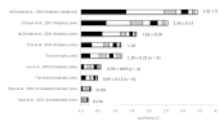


- Engling G, Herckes P, Kreidenweis SM, Malm WC, Collett JL. Composition of the fine organic aerosol in Yosemite National Park during the 2002 Yosemite Aerosol Characterization Study. *Atmospheric Environment*. 2006; 40:2959–2972.
- Ferek R, Reid J, Hobbs P, Blake D, Liousse C. Emission factors of hydrocarbons, halocarbons, trace gases and particles from biomass burning in Brazil. *J. Geophys. Res.* 1998; 103:D24.
- Fine PM, Cass GR, Simoneit BRT. Chemical characterization of fine particle emissions from the fireplace combustion of wood types grown in the midwestern and western United States. *Environmental Engineering Science*. 2004; 21:387–409.
- Forster, P.; Ramaswamy, V.; Artaxo, P.; Bernsten, T.; Betts, R.; Fahey, DW.; Haywood, J.; Lean, J.; Lowe, DC.; Myhre, G.; Nganga, J.; Prinn, R.; Raga, G.; Schulz, M.; Van Dorland, R. Changes in atmospheric constituents and in radiative forcing. In: Solomon, S.; Qin, D.; Manning, M.; Chen, Z.; Marquis, M.; Averyt, KB.; Tignor, M.; Miller, HL., editors. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press; 2007.
- Freeman DJ, Cattell FCR. Woodburning as a source of atmospheric polycyclic aromatic hydrocarbons. *Environmental Science & Technology*. 1990; 24:1581–1585.
- Hays MD, Geron CD, Linna KJ, Smith ND, Schauer JJ. Speciation of gas-phase and fine particle emissions from Burning of foliar fuels. *Environmental Science & Technology*. 2002; 36:2281–2295. [PubMed: 12075778]
- Jaffe D, Hafner W, Chand D, Westerling A, Spracklen D. Interannual variations in PM<sub>2.5</sub> due to wildfires in the western United States. *Environmental Science & Technology*. 2008; 42:2812–2818. [PubMed: 18497128]
- Kilgore M, Sando W. Crown-fire potential in a sequoia forest after prescribed burning. *Forest Sci.* 1975; 21:83–87.
- Lee S, Baumann K, Schauer JJ, Sheesley RJ, Naeher LP, Meinardi S, Blake DR, Edgerton ES, Russell AG, Mark Clements M. Gaseous and particulate emissions from prescribed burning in Georgia. *Environmental Science & Technology*. 2005; 39:9049–9056. [PubMed: 16382924]
- Malm WC, Hand JL. An examination of the physical and optical properties of aerosols collected in the IMPROVE program. *Atmospheric Environment*. 2007; 41:3407–3427.
- Malm WC, Schichtel BA, Pitchford ML, Ashbaugh LL, Eldred RA. Spatial and monthly trends in speciated fine particle concentration in the United States. *J. Geophys. Res.* 2004; 109:D03306.
- Mazzoleni LR, Zielinska B, Moosmüller H. Emissions of levoglucosan, methoxy phenols, and organic acids from prescribed burns, laboratory combustion of wildland fuels, and residential wood combustion. *Environmental Science & Technology*. 2007; 41:2115–2122. [PubMed: 17438751]
- McDonald JD, Zielinska B, Fujita EM, Sagebiel JC, Chow JC, Watson JG. Fine particle and gaseous emission rates from residential wood combustion. *Environmental Science & Technology*. 2000; 34:2080–2091.
- McMeeking, GR. Colorado State University; 2008. The optical, chemical, and physical properties of aerosols and gases emitted by the laboratory combustion of wildland fuels. PhD Dissertation
- Myhre G. Consistency between satellite-derived and modeled estimates of the direct aerosol effect. *Science*. 2009; 325:187–190. [PubMed: 19541952]
- National Interagency Fire Center. 2010. [http://www.nifc.gov/fire\\_info/ytd\\_state\\_2009.htm](http://www.nifc.gov/fire_info/ytd_state_2009.htm)
- Oanh NTK, Reutergrårdh LB, Dung NT. Emission of polycyclic aromatic hydrocarbons and particulate matter from domestic combustion of selected fuels. *Environmental Science & Technology*. 1999; 33:2703–2709.
- Oros DR, Simoneit BRT. Identification and emission factors of molecular tracers in organic aerosols from biomass burning: Part 1. Temperate climate conifers. *Applied Geochemistry*. 2001; 16:1513–1544.
- Pósfai M, Simonics R, Li J, Hobbs PV, Buseck PR. Individual aerosol particles from biomass burning in southern Africa: 1. Compositions and size distributions of carbonaceous particles. *J. Geophys. Res.* 2003; 108:8483.
- Reid JS, Hobbs PV. Physical and optical properties of young smoke from individual biomass fires in Brazil. *J. Geophys. Res.* 1998; 103:32013–32030.

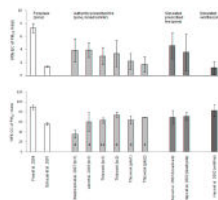
- Reid J, Hobbs P, Ferek R, Blake D, Martins J, Dunlap M, Lioussé C. Physical, chemical, and optical properties of regional hazes dominated by smoke in Brazil. *J. Geophys. Res.* 1998; 103:D24.
- Reid JS, Koppmann R, Eck TF, Eleuterio DP. A review of biomass burning emissions part II: Intensive physical properties of biomass burning particles. *Atmos. Chem. Phys.* 2005; 5:799–825.
- Robinson MS, Chavez J, Velazquez S, Jayanty RKM. Chemical speciation of PM<sub>2.5</sub> collected during prescribed fires of the Coconino National Forest near Flagstaff, Arizona. *J. Air & Waste Manage. Assoc.* 2004; 54:1112–1123.
- Robinson MS, Anthony TR, Littaw SR, Herckes P, Nelson X, Poplin GS, Burgess JL. Occupational PAH exposures during prescribed pile burns. *Ann. Occup. Hyg.* 2008; 52:497–508. [PubMed: 18515848]
- Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT. Measurement of emissions from air pollution sources. 3. C1–C29 Organic compounds from fireplace combustion of wood. *Environmental Science & Technology.* 2001; 35:1716–1728. [PubMed: 11355184]
- Simoneit BRT, Rogge WF, Lang Q, Jaffé R. Molecular characterization of smoke from campfire burning of pine wood (*Pinus elliotii*). *Chemosphere: Global Change Science.* 2000; 2:107–122.
- Spracklen DV, Logan JA, Mickley LJ, Park RJ, Yevich R, Westerling AL, Jaffe SA. Wildfires drive interannual variability of organic carbon aerosol in the western U.S. in summer. *Geophysical Res. Letters.* 2007; 34:L16816.
- Tan YL, Quanci JF, Borys RD, Martin J, Quanci MJ. Polycyclic aromatic hydrocarbons in smoke particles from wood and duff burning. *Atmospheric Environment.* 1992; 26A:1177–1181.
- U.S. Environmental Protection Agency. Integrated Risk Information System. 2010. <http://www.epa.gov/ncea/iris/>
- Zmirou D, Schwartz J, Saez M, Zanobetti A, Wojtyniak B, Touloumi G, Spix C, Ponce de León A, Le Moullec Y, Bacharova L, Schouten J, Pönkä A, Katsouyanni K. Time-series analysis of air pollution and cause-specific mortality source. *Epidemiology.* 1998; 9:495–503. Stable URL: <http://www.jstor.org/stable/3702525>. [PubMed: 9730027]
- Zou LY, Zhang W, Atkiston S. The characterisation of polycyclic aromatic hydrocarbons emissions from burning of different firewood species in Australia. *Environmental Pollution.* 2003; 124:283–289. [PubMed: 12713928]



**Fig. 1.** Average total ( $\pm$ stdev) and individual mass fractions of 19 PAHs in  $PM_{2.5}$  samples collected during broadcast burns on days 1 ( $n = 6$ ) and 2 ( $n = 1$ ), pile burns on days 1 ( $n = 4$ ) and 2 ( $n = 2$ ), and single laboratory burns of ponderosa pine needles and ponderosa pine wood.



**Fig. 2.** Total and individual PAH concentrations in selected wood-burning studies. From left to right the PAHs are as follows: fluoranthene, pyrene, benzo[b+j+k]fluoranthene, benz[a]anthracene, chrysene+triphenylene, benzo[a]pyrene, benzo[e]pyrene, and benzo[ghi]perylene. In the fireplace studies and simulated burn studies, error bars represent uncertainties. In Lee et al. (2005) and this work, error bars represent standard deviations.



**Fig. 3.** Comparison of OC and EC concentrations in selected wood-burning studies. In the fireplace and simulated burn studies, error bars represent uncertainties. In the authentic prescribed burns, error bars represent standard deviations ( $n$  is shown in the lower bar graph).

Table 1

PM<sub>2.5</sub> samples discussed in this work. CN = Coconino National Forest; AS = Apache Sitgreaves National Forest; bc = broadcast prescribed burn; pile = slash-pile prescribed burn; OC = organic carbon; and EC = elemental carbon. Co-collected filters were averaged in PM<sub>2.5</sub> measurements. PM<sub>2.5</sub> uncertainty is estimated to be ±10%.

Entry	Type (day)	Forest	<sup>a</sup> PM <sub>2.5</sub> (µg m <sup>-3</sup> )	OC ± unc. (µg m <sup>-3</sup> )	EC ± unc. (µg m <sup>-3</sup> )	OC/EC ± unc.	Analysis	Ref.
1	bc (1)	CN	3986	2636 ± 182	108 ± 17	24 ± 4	XRF	<i>b</i>
2	bc (1)	CN	2541	1657 ± 136	66 ± 10	25 ± 4	XRF	<i>b</i>
3	bc (1)	CN	6060	3057 ± 180	239 ± 38	13 ± 2	XRF	<i>b</i>
4	bc (1)	CN	3309	2384 ± 140	60 ± 9	40 ± 6	XRF	<i>b</i>
5	bc (1)	CN(grass)	523	340 ± 35	23 ± 4	15 ± 3	XRF	<i>b</i>
6	bc (1)	CN	(1638)	1031 ± 75	43 ± 5	24 ± 3	GC/MS	this work
7	bc (1)	CN	(8357)	5260 ± 374	60 ± 7	87 ± 10	GC/MS	this work
8	bc (1)	CN	(1937)	1219 ± 88	38 ± 5	32 ± 4	GC/MS	this work
9	bc (1)	CN	(1230)	774 ± 57	42 ± 5	19 ± 2	GC/MS	this work
10	bc (1)	CN	(550)	346 ± 27	29 ± 4	12 ± 2	GC/MS	this work
11	bc (1)	AS	750	475 ± 35	26 ± 3	18 ± 2	XRF,GC/MS	this work
12	bc (2)	CN	618	423 ± 46	36 ± 6	12 ± 2	XRF	<i>b</i>
13	bc (2)	CN	666	540 ± 64	17 ± 3	32 ± 6	XRF	<i>b</i>
14	bc (2)	CN	904	682 ± 63	35 ± 6	19 ± 3	XRF	<i>b</i>
15	bc (2)	CN	(1541)	1150 ± 83	19 ± 4	62 ± 13	GC/MS	this work
16	pile (1)	AS	6976	3761 ± 268	88 ± 8	43 ± 4	XRF,GC/MS	<i>c</i>
17	pile (1)	AS	1047	674 ± 49	16 ± 3	41 ± 7	XRF,GC/MS	<i>c</i>
18	pile (1)	AS	1051	762 ± 55	23 ± 3	32 ± 5	XRF,GC/MS	this work
19	pile (1)	AS(wet)	2734	1806 ± 129	106 ± 9	17 ± 1	XRF,GC/MS	this work
20	pile (2)	AS	899	621 ± 45	8 ± 2	77 ± 23	XRF,GC/MS	<i>c</i>
21	pile (2)	AS	2889	2013 ± 144	74 ± 7	27 ± 2	XRF,GC/MS	<i>c</i>
22	lab needles		nd	1343 ± 97	122 ± 11	11 ± 1	GC/MS	this work
23	lab wood		nd	563 ± 42	89 ± 9	6 ± 1	GC/MS	this work

<sup>a</sup>For values in parentheses, PM<sub>2.5</sub> concentrations were estimated by multiplying the OC concentration by the average value of [PM<sub>2.5</sub>]/[OC] for burns of the same type. See section 2.3.

<sup>b</sup>Robinson et al., 2004.

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Table 2

Elemental concentrations under different burn conditions expressed as an average wt% of PM<sub>2.5</sub> mass ( $\pm$ stdev). NQ = ave less than  $3 \times$  unc. LOD = below limits of detection for all burns in group.

	Broadcast Burns			Pile Burns			Other	
	Day 1 n = 5	Day 2 n = 3	Day 1 n = 3	Day 2 n = 2	Day 1 n = 3	Day 2 n = 2	Maintenance n = 1	File (wet) n = 1
Na	NQ	NQ	NQ	NQ	NQ	LOD	LOD	NQ
Mg	NQ	NQ	NQ	NQ	NQ	NQ	LOD	LOD
Al	NQ	NQ	NQ	NQ	NQ	NQ	LOD	NQ
Si	0.029 (0.024)	0.054 (0.006)	0.027 (0.023)	0.034 (0.022)			0.147	NQ
P	0.021 (0.026)	LOD	LOD	NQ	NQ	LOD	LOD	LOD
S	0.076 (0.007)	0.080 (0.035)	0.047 (0.020)	0.023 (0.009)			0.520	0.185
Cl	0.130 (0.070)	0.028 (0.027)	0.095 (0.077)	0.012 (0.001)			1.540	0.143
K	0.096 (0.052)	0.035 (0.041)	0.203 (0.071)	0.031 (0.001)			2.805	0.649
Ca	0.019 (0.018)	0.028 (0.011)	0.009 (0.004)	0.018 (0.011)			0.489	0.032
Ti	0.002 (0.001)	NQ	NQ	NQ			NQ	NQ
V	NQ	NQ	NQ	NQ			NQ	NQ
Cr	NQ	NQ	LOD	LOD			LOD	LOD
Mn	NQ	NQ	NQ	NQ			NQ	NQ
Fe	0.007 (0.004)	0.027 (0.009)	0.003 (0.005)	0.004 (0.001)			0.026	NQ
Co	NQ	LOD	LOD	LOD			LOD	LOD
Ni	NQ	NQ	NQ	NQ			NQ	NQ
Cu	0.001 (0.001)	LOD	NQ	NQ			0.023	NQ
Zn	0.003 (0.001)	NQ	0.006 (0.002)	NQ			0.019	0.031
Ga	LOD	NQ	NQ	NQ			NQ	NQ
Ge	NQ	LOD	NQ	NQ			LOD	LOD
As	NQ	NQ	NQ	NQ			LOD	NQ
Se	NQ	NQ	NQ	LOD			NQ	NQ
Br	0.007 (0.003)	NQ	0.003 (0.002)	NQ			0.030	0.005
Rb	NQ	NQ	NQ	LOD			NQ	NQ
Sr	NQ	NQ	NQ	NQ			NQ	NQ
Pb	NQ	NQ	NQ	LOD			NQ	NQ