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TECHNICAL PAPER

Effect of low-density polyethylene on smoke emissions from burning of simulated debris piles

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Low-density polyethylene (LDPE) plastic is used to keep piled debris from silvicultural activities—activities associated with development and care of forests—dry to enable efficient disposal by burning. The effects of inclusion of LDPE in this manner on smoke emissions are not well known. In a combustion laboratory experiment, 2-kg mixtures of LDPE and manzanita (Arctostaphylos sp.) wood containing 0, 0.25, and 2.5% LDPE by mass were burned. Gaseous and particulate emissions were sampled in real time during the entire flaming, mixed combustion phase—when the flaming and smoldering phases are present at the same time—and during a portion of the smoldering phase. Analysis of variance was used to test significance of modified combustion efficiency (MCE)—the ratio of concentrations of fire-integrated excess CO_2 to CO_2 plus CO—and LDPE content on measured individual compounds. MCE ranged between 0.983 and 0.993, indicating that combustion was primarily flaming; MCE was seldom significant as a covariate. Of the 195 compounds identified in the smoke emissions, only the emission factor (EF) of 3M-octane showed an increase with increasing LDPE content. Inclusion of LDPE had an effect on EFs of pyrene and fluoranthene, but no statistical evidence of a linear trend was found. Particulate emission factors showed a marginally significant linear relationship with MCE (0.05 < P-value < 0.10). Based on the results of the current and previous studies and literature reviews, the inclusion of small mass proportions of LDPE in piled silvicultural debris does not appear to change the emissions produced when low-moisture-content wood is burned. In general, combustion of wet piles results in lower MCEs and consequently higher levels of emissions.

Implications: Current air quality regulations permit the use of burning to dispose of silvicultural piles; however, inclusion of lowdensity polyethyelene (LDPE) plastic in silvicultural piles can result in a designation of the pile as waste. Waste burning is not permitted in many areas, and there is also concern that inclusion of LDPE leads to toxic air emissions.

Introduction

Mechanical cutting and piling of woody shrubs and suppressed trees in forests is a common silvicultural practice to reduce fire hazard in the United States (Wenger, 1984). Postlogging debris (branches and foliage) is also often piled. These piles are burned during periods of low fire danger to dispose of the material. In order to improve consumption of the piled debris when burned, low-density polyethylene plastic (LDPE) is placed over part or all of the pile to keep water out so that the pile can be burned to reduce the fire hazard while minimizing hazardous air pollutants due to incomplete combustion. LDPE, also known as agricultural plastic, has been used for many years to conserve moisture and reduce weeds in row crops (Linak et al., 1989).

In the western United States, if silvicultural activities generate approximately 15,000 piles per year (M. McCorison, U.S. Forest Service, personal communication, April 2010), this would be

equivalent to 9000 metric tons per year, assuming an average of 600 kg fuel per pile. Recent analysis of hand-piled debris reported pile mass ranging from 150 to 670 kg (Wright et al., 2010). The interested reader is referred to Wright et al. (2010 and references therein) for a description of current and past research regarding pile construction, composition, and smoke emissions. Assuming that the piles burned at 90% combustion efficiency, burning might produce 95 tons of particulate matter of which 59 tons is particulate matter less than 2.5 µm in size (Hardy, 1998). Similar calculation tools and information can be found in Prichard et al. (2007) and Wright et al. (2010) and at http:// depts.washington.edu/nwfire/piles. A greater number of piles burned annually would produce more gaseous and particulate emissions. The emissions produced by burning piled debris are a component of wildland fire emissions inventories, which is an area of active research. Current air quality regulations permit the burning of piled wood debris from land management operations. However, if low-density polyethylene (LDPE) plastic is used to cover the piles to keep the piles dry and improve consumption, they may be redesignated as piled waste and not allowed to be burned, since there is a concern that LDPE produces toxic air emissions.

Due to the widespread presence of polyethylene (and other plastics) in municipal waste and the use of combustion as a waste disposal mechanism, several studies have examined the pyrolysis and combustion products of PE (Conesa et al., 1994; Kolb et al., 1965; Paabo and Levin 1987; Shemwell and Levendis, 2000; Wheatley et al., 1993). Paabo and Levin (1987) concluded in their literature review that "the toxicity of the combustion products from various samples of polyethylenes [is] not highly or unusually toxic." Linak et al. (1989) measured emissions produced by burning piled black LDPE (agricultural plastic) under no-wind and simulated air-curtain incineration conditions and found little difference in the variety and quantity of organic compounds between the burning techniques. Mutagenicity of organic extractives from particulate matter was also similar to that of residential wood smoke. Salvador et al. (2004) examined the combustion rate and production of polycyclic aromatic hydrocarbons (PAHs) from cardboard and polyethylene mixtures compressed into fuel bricks of various densities and burned in a cone calorimeter. Mass percentage of LDPE in the mixtures was 0, 5, 10, 20, 33, 70, or 100. Brick density and size of the fuel elements had no effect on PAH emissions. The percentage of LDPE in the brick was related to the PAH emissions; PAH emissions were high when the percentage of LDPE in the composite fuel exceeded 30. Wrobel and Reinhardt (2003) performed a review of bench-scale studies of combustion and pyrolysis of PE and wood to estimate the impact of PE in silvicultural burn piles on emissions. They concluded that the literature did not provide "an unequivocal answer to whether burning PE plastic would have any greater impact on air quality than the burning of biomass" and suggested that empirical studies be performed to determine the effect of PE on emissions from burning piled debris.

We designed a laboratory study to simulate the burning of silvicultural debris piles that contained low-density polyethylene plastic under a dry condition (30% moisture). First-time smoke emission measurements using real-time, state-of-the-art instrumentation for this type of wildland burning are reported.

Methods

Experimental design and fuel description

A typical silvicultural debris pile in the western United States is 2.4 m in diameter and height and may contain approximately 600 kg of woody debris (Wrobel and Reinhardt, 2003). Assuming a cylindrical shape for the pile, we estimated an exposed surface area of 22.6 m² for a solid cylinder; the mass of a 4-mm LDPE sheet of this size was estimated at 0.87 kg. This yields a mass ratio of PE (shorthand for LDPE) to woody debris of approximately 0.001. Other configurations will produce different pile surface areas. In order to determine whether inclusion of PE in debris piles has any effect on smoke emissions, mass ratios of 0, 0.0025, and 0.025 were selected to cover the range of possible mass ratios. Note that the 0.025 mass ratio

(50 gm LDPE) is 25 times the mass ratio we estimated. Our estimate may in fact be greater than actual field mass ratios. Idealized debris piles were composed of a 2-kg mixture of PE and manzanita wood (Arctostaphylos sp.); the mixture contained 0, 5, or 50 g of PE. Foliage and soil, components of debris piles depending on how they are constructed, were not included so that we could detect the effect of inclusion of LDPE to burning wood. The 4-mm PE was shredded and mixed with the manzanita sticks to provide a homogeneous mixture; in actual use, the PE sheet either covers the inner core of a pile or covers the entire pile. Piles in which only the inner core is covered contain a much smaller mass proportion of PE than the completely covered piles. Moisture content (oven-dry basis) of two 5-g samples of manzanita wood was determined using a Computrac XL1000 moisture analyzer. (The use of trade names is provided for informational purposes only and does not constitute endorsement by the U.S. Department of Agriculture.) Density of the PE and that of manzanita were assumed to be 900 and 700 kg m⁻³, respectively. Elemental composition of LDPE was assumed from the literature. Elemental composition of the manzanita wood was determined using ultimate analysis. Approximately 5 g of the fuel sample was finely ground and analyzed with a Thermo Fisher Scientific FlashEA 1112 Series elemental analyzer. The results of the elemental analysis of manzanita as a part of a larger study are reported in Table 1 of Hosseini et al. (2013).

The experiments were conducted in the fire laboratory at the U.S. Forest Service Pacific Southwest Research Station facility in Riverside, CA. All fires were burned on the same day. Three replications of the three LDPE treatments (0, 5, 50 g) were arranged in a randomized complete block experimental design to control for possible effects due to changing ambient conditions throughout the day. The fire laboratory is a $12.2 \times 12.2 \times 11.1$ m (L \times W \times H) metal building with an unconditioned environment. Total air volume of the building is approximately 1380 m³; a high volume (2.4 m³ sec⁻¹) of air is introduced at low velocity into the building through ducts located along the base of the walls to vent smoke through openings in the roof. This aeration rate results in a complete exchange of air approximately every 9.6 min; however, the slight positive pressure, natural buoyancy of smoke, and building height result in smoke accumulation in the building several meters above the sampling inlet used in this study. Each mixture was ignited with a small quantity of ethanol (<10 mL), which was consumed in the first 10 sec or so of the 10-min burns, burned in a 30-cm-diameter meshwalled basket, and the smoke was collected using a small hood and ducting of galvanized steel as shown in Figure 1. In practice, silvicultural piles are often ignited using a mixture of gasoline and diesel fuel. The entrance to the 0.2 m diameter \times 3 m long sampling duct was a 0.30 to 0.20 m reducer. Holes made in a capped T formed the ports of the sampling duct. The L-shaped sampling probe was oriented with the flow with the sampling opening oriented downstream to prevent large particles from entering the sampling probe. A 0.2-m single-speed duct fan inducted 7 m/sec airflow inside the duct. Each test lasted 10 min, after which the fire was extinguished.



Figure 1. Examples of fuel beds of manzanita (Arctostaphylos sp.) wood and low-density polyethylene plastic: (a) 0.25 wt% PE and (b) 2.50 wt% PE.

The randomized complete block design of the experiment can be represented as a fixed effects linear model (eq 1) that assumes that effects of various factors on the measured emission factor are additive. One of the important factors, named the modified combustion efficiency (MCE), is a relative measure of completeness of combustion process and is defined as the ratio of fireintegrated excess concentrations of CO_2 to CO plus CO_2 (MCE, eq 1, Ward and Hao, 1991). While MCE has been shown to be linearly related to EF (e.g., Ward and Radke 1993), it was included as a covariate in this analysis to account for possible differences in the burning characteristics of each test in order to improve the ability to detect differences due to LDPE. Inclusion of MCE as a covariate and not as a response variable implicitly assumes that MCE is unaffected by the LDPE treatment (Mason et al. 1989, p. 397). We verified this assumption by performing an analysis of variance in which MCE was the response variable and no effect due to LDPE was observed (P = 0.64).

$$EF_{ij} = \mu + MCE_{ij} + \beta_i + \tau_j + \epsilon_{ij} \tag{1}$$

where EF_{ii} (unit mass of pollutant per unit mass of CO₂ produced) is the observed emission factor for a particular chemical species, μ is the overall mean emission factor, MCE_{ii} is the modified combustion efficiency, β_i is the effect due to block *i* $(i = 1, 2, 3), \tau_i$ is the effect due to polyethylene (j = 1, 2, 3; 0, 5, 5)50 g), and ε_{ii} is random error, which is assumed to be normally distributed with mean 0 and constant variance. We chose not to test the validity of the normality assumption due to the small number of observations (9). The Friedman test (Friedman, 1937, 1939) is a distribution-free (nonparametric) test similar to analysis of variance (ANOVA) and can be used for randomized complete block experimental designs (SAS Institute, 2002).

$$MCE = \frac{\Delta CO_2}{\Delta CO_2 + \Delta CO}$$
(2)

where ΔCO_2 and ΔCO are the differences between the concentration measured in the smoke and the ambient background values.

The PROC GLM routine in SAS 9.3 (SAS Institute, 2002) was used to estimate the terms in eq 1 and to test various hypotheses using analysis of covariance (ANCOVA) with $\alpha = 0.05$ as the significance level (Table 1). The objective of the study was to determine whether the presence of polyethylene affected EF, and the null hypothesis (H₀) expresses this. If LDPE has no effect, then $\tau = 0$. The alternative hypothesis (H₁) is accepted (but not proven) if the null hypothesis is rejected. The effect of LDPE on the time to flaming and emission factors for alkanes, cycloalkanes, alkenes, cycloalkenes, diolefins, and monocyclic aromatic hydrocarbons was also tested using the same ANCOVA model.

$$\begin{cases} H_0: \tau_1 = \tau_2 = \tau_3 = 0\\ H_1: \tau_i \neq 0 \text{ for at least one } i \end{cases}$$
(3)

To statistically isolate the tests of the effects in the experiment, we used Type III sums of squares to test the null hypothesis. Pairwise comparisons of the treatment effect $(\tau_i: \tau_1 - \tau_2, \tau_1 - \tau_3)$ were performed if the null hypothesis was rejected to determine how LDPE affected the emission factor while keeping the experiment-wise Type I error rate at $\alpha = 0.05$ (Table 1). The PROC FREQ routine in SAS 9.3 performed the nonparametric Friedman test, and the Cochran-Mantel-Haenszel statistic (CMH2) tested the equality of the ranks of the emission factor given the presence of a block effect.

Source	burce df°		Mean square (MS)	F-statistic	
Model	5	SS _{model}	SS_{model} / df	MS _{model} /MS _{error}	
MCE	1	SS_{MCE}	SS_{MCE} / df	MS _{MCE} /MS error	
Block	2	SS_{β}	SS_{β}/df	MS_{β}/MS_{error}	
Polyethylene	2	SS_{τ}	SS_{τ}/df	MS_{τ}/MS_{error}	
Error	3	SS _{error}	SS _{error} / df		
Total corrected	8	SS _{total}			

Table 1. General form of analysis of variance used to test effect of polyethylene plastic on emission factors produced by the burning of manzanita (Arctostaphylos sp.) wood

Notes: ^aDegrees of freedom. The interested reader is referred to any general statistics text (e.g., Mason et al. 1989) for further explanation of the composition of an analysis of variance table.

Sampling media and instrumentation

Schematic of sampling setup is shown in Figure 2. A multigas analyzer (PG-250, Horiba) was used to measure NO_x, CO, and CO₂ concentrations. The PG 250 ranges were selected as 50 ppm for NO/NOx, 200 ppm for CO, and 5% for CO₂. For quality control, analyzer checks with U.S. Environmental Protection Agency (EPA) protocol calibration gases were made to the selected ranges both before and after each test to check for drift. The measured values were usually between 10% and 90% of the selected range. Carbonyls were collected at 1.0 lpm onto 2,4-dinitrophenylhydrazine (DNPH)-coated silica cartridges (Water Corp., Milford, MA). Volatile organic compounds (VOC) were collected at 100 mL min⁻¹ onto prebaked 6 mm OD Gerstel Carbotrap 300 Multi Bed glass thermal desorption (TDS) tubes (GERSTEL). Both the DNPH cartridge and the TDS tube were located downstream of a Teflon filter. PAHs were collected sequentially: first on a quartz filter and then in a column packed with polyurethane foam (PUF) and XAD-4 resin. Particulate matter (PM) was collected on a 47mm quartz (2500QAT-UP Tissuquartz, Pall Co.) filter and a preweighed Teflo (2 μ m pore, Pall Co.) filter. The quartz filter was preconditioned at 600°C for 5 hr in an oven. Measured flow rates through Teflon and quartz filters were 15.6 and 20.1 lpm, respectively.

Particle size distributions (5.6 to 560 nm) were sampled at 1 Hz using an engine exhaust particle sizer (EEPS) (TSI, model 3090). Prior to entering the EEPS, the exhaust sample was diluted with a two-stage ejector (TD-110H, Air-Vac Engineering Co.) diluter (Khalek et al., 2000) to a final dilution ratio of 17:1. Dilution air was cleaned in a series of units that removed water, hydrocarbons, and particles (Agrawal et al., 2008).

Off-line analytical methods

Samples collected in the fire laboratory were analyzed for carbonyls, VOCs, PAHs, PM mass, and composition using the following protocols:



Figure 2. Schematic illustration of experimental setup.

- Carbonyls: DNPH cartridges were analyzed for carbonyls following a modified SAE 930142 HP protocol (Siegel et al., 1993). The cartridges were extracted with acetonitrile and injected into an Agilent 1200 series high-performance liquid chromatograph (HPLC) equipped with a diode array detector. The column used was Deltabond AK resolution (200 cm \times 4.6 mm ID) with an upstream guard column.
- C₃-C₁₀: CarboTrap 300 Multi Bed tubes were injected into an Agilent 6980 GC-FID system via a Gerstel thermal desorption system (TDS) by ramping the injector from –40 to 250°C at a rate of 6°C/min. Chromatographic separation and hydrocarbon quantification followed the methods outlined in the SAE 930142 HP protocol (Siegl et al., 1993).
- PAHs and C₁₀-C₃₀ hydrocarbons: Quartz filters and PUF/ XAD resin were analyzed according to a modified U.S. EPA TO-13A protocol. Both substrates were spiked with deuterated standards and extracted with methylene chloride using a Dionex automated solvent extractor (ASE-200) (60 min, 250°C). The extracts were Roto-evaporated and further concentrated with an ultra-high-purity nitrogen or helium stream. Samples were introduced into an Agilent 5973 GC-MS using a programmable temperature vaporizer (PTV) large volume inlet (7683 Series).
- Elemental and organic carbon: A 1.5 cm² quartz filter punch was analyzed for elemental and organic carbon with a Sunset Laboratory (Forest Grove, OR) thermal/optical aerosol analyzer according to the NIOSH 5040 reference method (NIOSH 5040: NIOSH, 1999).
- Particulate mass: The PM mass was determined from the Teflon filter pre and post weights. Both tare and final weights were measured with a Cahn C-35 (Madison, WI) microbalance in a temperature- and humidity-controlled room following the Code of Federal Regulations (40 CFR Part 1065).

Results and Discussion

Fire and smoke characteristics

The nine manzanita wood/LDPE mixtures were burned on November 4, 2008. Mean moisture content of the manzanita wood was 30% (dry weight basis), which resulted in wellsustained combustion once ignited. Initially, the smoke was observed to be white in color indicating the presence of water vapor. During the early stage of the burn (<60 sec) the LDPE typically melted and combusted. Approximately 3 min after ignition, the opacity of the white smoke was greatly reduced and the smoke plume became transparent with active flaming up to 2 m in height. We refer to the elapsed time until the plume became transparent as "time to flaming." LDPE and MCE did not affect time to flaming (P = 0.28, 0.75, respectively). Ten minutes after ignition the amount of visible smoke was reduced significantly and sampling ceased. The 10-min period captured emissions from the flaming and mixed phases and some of the smoldering phase. Mean MCE of the 9 fires was 0.988 with a standard deviation of 0.0036. The presence of LDPE did not significantly affect MCE (P = 0.64); there was no significant block effect indicating that the fires burned similarly throughout the day.

Fuel composition analysis

Reported carbon content of manzanita ranges from 48 to 53% (Burling et al., 2010; Fletcher et al., 2007; Jenkins and Ebeling, 1985; McMeeking et al., 2009). These samples were wood only, foliage only, and mixtures of wood and foliage. Ultimate analysis of the manzanita wood yielded carbon content of 41%. The literature reports LDPE carbon content of 86% (Wrobel and Reinhardt, 2003). Using 41 and 86% carbon content for manzanita wood and PE, respectively, the total carbon present in the three mixtures was 820.0, 824.3, and 863.0 g, respectively; addition of 50 g of PE to 2 kg of manzanita wood added 43 g carbon to the 820 g carbon in the wood. The difference between carbon content of the mixture and the wood is ~5%; therefore, we assume that the fuel composition of the simulated debris pile did not significantly change due to addition of 5 or 50 g of PE.

Emission factors

Emission factors are normally calculated and reported based on the amount of emissions per kilogram of fuel burned; however, the approach typically taken is to determine emission factors based on kilograms of CO_2 produced and adjusting the values based on the amount of carbon contained in the fuel (Ward et al., 1979; Burling et al., 2011).

In this study we did not measure the amount of residual carbon in the char; therefore, emission factors are calculated based on the amount of carbon dioxide released over the entire 10-min measurement period. As all the emission factors in this study were based on kilograms CO_2 ; a factor of 1.8 can be used to convert all the emission factors from per kg CO_2 to per kg fuel assuming 41% carbon content.

From the variety of real-time and off-line sampling equipment deployed in this experiment, we calculated emission factors for 195 compounds. Results of both the parametric ANCOVA and the nonparametric Friedman test were in agreement for three species, pyrene (particle phase), fluoranthene (particle phase), and 3M-octane (gas phase), indicating that LDPE significantly affected the emissions. The data for 3Moctane gas suggested an increasing trend with LDPE. MCE was a significant covariate for only two gas-phase species: 3,3-DMhexane and M-cycpentane. The Friedman test indicated that LDPE significantly affected the ranking of the emission factors of anthracene (particle), fluorene (particle), NOx, and c-1*3-DM-CycPentane. While we decided that LDPE did not affect emissions of anthracene (particle) and fluorene (particle) because the probability of the ANOVA F-test fell between 0.05 and 0.1, if one were willing to accept $\alpha = 0.1$ as the significance level, then both the ANCOVA and Friedman test results would be in agreement for anthracene (particle) and fluorene (particle) as well.

Given that the analyses just presented did not find differences in EFs for the bulk of the 195 compounds, in this section and also in Tables 2–5 (shown in the following) we present EFs in terms of raw data to compare with other studies. For those five gases in which we detected differences due to LDPE, we provide further discussion. The mean EFs presented in the following tables are known as "least-squares means" (SAS) or population marginal means (Searle et al., 1980). These means are based on the linear model of the experiment (eq 1). From eq 1, the population marginal mean for the 2.5 wt% treatment is $PMM(\tau_2) = \mu + \tau_2$. The population marginal means are adjusted for the covariate MCE. When the experimental design is balanced (same number of replications per treatment), the population marginal mean is equal to the arithmetic mean of the replications; when the number of replications per treatment differs, the population marginal mean will not equal the arithmetic mean of the replications. The experiment we present was balanced.

Carbon monoxide and nitric oxides. Gas-phase emissions were integrated over each burn and normalized against fireaverage integrated CO₂. As shown in Table 2, average CO emission factors were 13.5, 12.6, and 9.9 g/kg CO₂ for 0, 0.25, and 2.5 wt% PE, respectively (average). Note that the multi-gas analyzer got saturated for a portion of 0 wt% PE tests for CO. Therefore, we speculate that actual CO emission factors in case of 0% PE should be higher than reported here and the reduction of CO emissions with inclusion of PE against 0 wt% PE burn may be higher than we report. The CO coefficients of variation for this study were 18, 21, and 14%; the high values reflect the difficulty of replicating burn conditions. Note that reduction of CO emission factor due to the use of PE cover for actual silvicultural piles is very effective due to the fact that fuel without PE is exposed to moisture, which causes more smoldering combustion and ultimately CO emissions (refer to Figure 2 of Hosseini et al., 2013). In this study, we did not consider moisture effects caused by the PE cover.

Table 2 presents NO_x emission factors as NO of 1.53 ± 0.09 , 1.83 ± 0.05 and 1.95 ± 0.07 g/kg CO₂ for 0, 0.25, and 2.5 of PE, respectively. Past research suggested that NO_x emissions in biomass burning depend on fuel nitrogen content (Andreae and Merlet, 2001; McMeeking et al., 2009). However, the manzanita nitrogen content was (~1 wt%) (Hosseini et al., 2013), and Linak

et al. (1989) measured no NO_x formation from combustion of agricultural plastic. On the other hand, Burling et al. (2010) showed that for a specific fuel type, NO_x emissions normalized to fuel nitrogen are a function of modified combustion efficiency. In our case the differences in MCE were not significant. ANOVA results also suggested NO_x emissions are not affected by PE content.

Gaseous C_3 - C_{12} . In addition to criteria pollutants, emission factors for selected volatile and semivolatile hydrocarbons with carbon numbers between C3-C13 were measured as shown in Table 3. Overall, the results show that propane, t-2 pentene, and 2-methyl-propene made up ~19-30% of the total aliphatic hydrocarbons. These emission factors fall within the lower range of the values reported in the literature. For example, EF of butane in this study was 5.0-8.5 mg/kg fuel burned, while McDonald et al. (2000) reported 1.7-17.4 mg/kg fuel for wood combustion (ponderosa pine, oak, etc.) in fireplace/woodstove and Schauer et al. (2001) reported 28.9 mg/kg fuel burned for Australian woods. Pentene ranged between 4.4 and 9.9 mg/kg, compared to 8.69-13.12 mg/kg of McDonald et al. (2000) and 4.7 mg/kg of Schauer et al. (2001). Our EFs are lower most likely due to high MCE values of the burns in the current study and more complete combustion of the fuel. Only 3M-octane was significantly affected and increased by the increase in PE content (P < 0.01), and the emissions of the rest of alkanes, cycloalkanes, alkenes, and cycloalkenes were independent of the amount of PE added to the fuel.

Diolefins. Diolefins were 1-3% of total VOC mass, and the emission factor of 1,3-butadiene was in the range of 2.6–15.7 mg/kg CO₂ released with an average of 7.21 mg/kg CO₂ (Table 3). In milligrams per kilogram fuel burned, the 1,3-butadiene emission value is almost half of the lower range of McDonald et al. (2000) for 2.5 wt% PE (28.7 vs. 62 mg/kg fuel burned) and a factor of 10 smaller for the other two cases. The 0.25% PE case is one-third of the 1,3-butadiene EF of 117 mg/kg

Table 2. Emission factors of selected components measured from burning mixtures of manzanita (Arctostaphylos sp.) wood and LDPE in g/kg CO₂; other references in g/kg fuel burned

Species	0% PE	0.25% PE	2.50% PE	RMSE (SD)	Other references
MCE ^a	0.98	0.98	0.99		$0.948 \pm 0.007^{^{\mathrm{b}}}, 0.930 \pm 0.029^{^{\mathrm{c}}}$
Time to flaming	283	226	168	69	
СО	13.5	12.6	9.9	4.6	$64.3\pm8.0^{\tt b}$
NO _x as NO	1.53	1.83	1.96	0.15	$2.67\pm0.21^{\tt b}$
PM	1.97	1.85	2.01	0.59	$3.61 \pm 1.17^{\text{b}}, 23.5 \pm 25.9^{\circ}, 2.7-11.4^{\circ}, 0.1-2.5^{\circ}, 5.1-9.5^{\circ}$
EC	0.38	0.54	0.58	0.26	$0.51 \pm 0.18^{\text{b}}, 0.35 \pm 0.31^{\circ}, 0.22 - 3.56^{\circ}, 1.4 - 3.2^{\circ}$
OC	0.91	0.91	0.97	0.50	$0.85 \pm 0.71^{\circ}$, $14.8 \pm 17.3^{\circ}$, $2.34-8.37^{\circ}$, $43.7-56.0^{\circ}$

Notes: ^aMCE, modified combustion efficiency. ^bHosseini et al. (2013). ^cPM_{2.5}: McMeeking et al. (2009). ^dFine et al. (2001), red maple, northern red oak, paper birch, eastern white pine, eastern hemlock, and balsam fir grown in northern United States. ^cHedberg et al. (2002), birch wood combustion in a woodstove. ^fSchauer et al. (2001), residential fireplace combustion of pine, oak, and eucalyptus.

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Table 3. Estimated emission factors of alkanes, cycloalkanes, alkenes, cycloalkenes, diolefins, and monocyclic aromatic hydrocarbons produced by the burning of
manzanita (Arctostaphylos sp.) wood-polyethylene plastic mixtures in mg/kg CO ₂

Species	0 % PE	0.25 % PE	2.50 % PE	RMSE (SD)	Other references (mg/kg fuel)
Alkanes					
Propane	14	45	9	19.9	$107 - 167,^{*}169^{b}$
2M-Propane	2.4	1.2	2.1	1.4	
2M-Propene	7.4	13.5	11.4	10.3	
Butane	4.7	2.8	3.3	6.3	1.68–17.36, ^a 25.9 ^b
2,2-DM-Propane	3.5	3.5	1.4	2.3	
Pentane	5.9	5.8	2.5	3.9	8.69–13.12, ^a 4.7 ^b
2,2-DM-Butane	3.3	8.7	1.8	5.8	
CycPentane	3.1	0.1	0.6	2.8	
2,3-DM-Butane	7.6	11.3	1.9	15	
2M-Pentane	2.1	1.6	3.0	0.9	
3M-Pentane	1.7	2.0	2.6	1.1	
Hexane	2.5	3.2	5.5	7.2	$6.01 - 12.30^{\circ}$
2,2-DM-Pentane	0.1	0.3	0.3	0.3	
2M-Butane	3.5	5.9	11.7	12.8	
2,4-DM-Pentane	0.9	0.7	0.3	0.9	
2,2,3-TM-Butane	0.3	0.4	0.6	0.8	
3,3-DM-Pentane	1.5	0.7	0.2	1.0	
CycHexane	0.3	0.3	1.0	1.0	
2M-Hexane	0.6	1.9	0.4	1.7	
2,3-DM-Pentane	0.3	0.2	0.6	0.4	
3M-Hexane	0.3	0.4	0.6	0.7	
c-1,3-DM-CycPentane	0.1	0.1	0.8	0.5	
3E-Pentane	0.6	0.3	0.3	0.6	
2,2,4-TM-Pentane	0.4	0.4	0.5	0.6	
Heptane	0.3	0.3	0.7	0.8	3.71–5.36, ^a 28.9 ^b
2,2-DM-Hexane	0.2	0.1	0.1	0.1	0.000, 200
2,5-DM-Hexane	0.2	0.1	0.1	0.2	
2,4-DM-Hexane	0.1	0.0	0.6	0.6	
3,3-DM-Hexane	0.0	0.1	0.0	0.0	
2,3,4-TM-Pentane	0.0	12.3	0.1	13.6	
2,3,3-TM-Pentane	0.1	0.1	0.1	0.1	
2,3-DM-Hexane	1.6	0.7	1.2	1.6	
2M-Heptane	0.8	0.3	0.4	0.8	
4M-Heptane	0.1	0.3	0.2	0.2	
3M-Heptane	0.1	0.1	0.2	0.2	
2,2,5-TM-Hexane	0.3	0.2	0.5	0.1	
Octane	0.5	0.2	0.8	0.5	$2.54-14.94$, ^a 1.7^{b}
2,3,5-TM-Hexane	0.2	0.2	0.2	0.2	2.54 14.94, 1.7
2,4-DM-Heptane	0.2	0.2	0.2	0.2	
E-CycHexane	0.0	0.1	0.1	0.3	
3,5-DM-Heptane	0.0	0.0	0.1	0.3	
2,3-DM-Heptane	0.0	0.0	0.1	0.1	
2M-Octane	0.0	1.1	1.1	1.2	
3M-Octane	0.4	0.1	0.2	0.0	
		0.1			$1.09-5.13$, $^{a}3.9^{b}$
Nonane 2,2-DM-Octane	0.2 0.1	0.2	0.4 0.2	0.3 0.1	1.09-3.13, 3.9
-					
2,4-DM-Octane	0.1	0.1	0.1	0.1	0.92–2.10 ^ª
Decane	0.5	0.4	0.2	0.4	
Undecane	0.4	0.3	0.2	0.3	$1.29-2.92^{a}$
Dodecane	0.1	0.2	0.2	0.2	$0.93-2.54^{a}$
Tridecane	0.3	0.3	0.2	0.4	$0.40 - 1.60^{\circ}$
Sum	74	128	70	51	

Species	0 % PE	0.25 % PE	2.50 % PE	RMSE (SD)	Other references (mg/kg fuel)
Cycloalkanes					
M-CycPentane	0.4	0.2	0.3	0.1	
t-1,2-DM-CycPentane	0.1	0.2	0.2	0.2	
M-CycHexane	0.2	0.2	0.2	0.2	
1c,2t,3-TM-CycPentane	0.0	0.1	0.0	0.0	
c-1,3-DM-CycHexane	0.1	0.7	0.3	0.7	
t-1,4-DM-CycHexane	0.0	0.1	0.2	0.1	
t-1,3-DM-CycHexane	0.1	0.1	0.1	0.0	
c-1,2-DM-CycHexane	0.1	0.0	0.1	0.1	
Sum	0.9	1.5	1.3	1.2	
Alkenes					a b
1-Butene	6.8	11.2	13.4	11.4	$84-148, ^{a}_{b}90.7^{b}$
t-2-Butene	2.0	4.2	2.1	2.1	66.5 ^b
c-2-Butene	0.2	0.2	0.1	0.1	35.4°
3M-1-Butene	5.5	1.9	1.4	4.0	6.9 ^b
1-Pentene	10.4	0.7	2.0	6.9	$10-19,^{a} 8.6^{b}$
2M-1-Butene	6.0	3.4	0.9	3.7	13.8^{b}
t-2-Pentene	9.4	5.9	18.1	9.7	16.0 ^b
3,3-DM-1-Butene	1.5	8.0	16.8	11.6	to t ^b
c-2-Pentene	1.4	3.7	3.8	4.2	10.4^{b}
2M-2-Butene	12.8	2.4	1.6	13.6	13.4°
4M-1-Pentene	5.3	2.8	1.6	5.2	
3M-1-Pentene	2.0	3.7	0.2	2.2	
4M-c-2-Pentene	5.7	14.2	0.4	13.8	
4M-t-2-Pentene	9.3	4.9	4.7	5.7	
2M-1-Pentene	1.4	2.4	0.7	1.9	11 20 ^a
1-Hexene	3.1	5.5	3.7	7.2	$11 - 20^{a}$
t-3-Hexene	1.1	2.9	0.5	1.7	
c-3-Hexene	0.8 0.3	1.6	0.1	0.9	8.6 ^b
t-2-Hexene 3M-t-2-Pentene	0.5	0.6 1.0	1.0 0.8	1.2 1.4	8.0
2M-2-Pentene	0.1	0.8	0.8	0.7	6.9°
c-2-Hexene	0.1	0.8	0.3	0.4	0.9
3M-c-2-Pentene	0.0	0.3	0.2	0.4	
3,4-DM-1-Pentene	0.2	0.4	0.1	0.3	
3M-1-Hexene	0.3	1.3	0.6	0.2	
1-Heptene	0.9	0.6	2.5	1.3	3.71–5.36 [°]
t-3-Heptene	0.9	0.7	0.1	0.6	5.71-5.50
2M-2-Hexene	0.2	0.2	1.2	0.8	
3M-t-3-Hexene	0.2	0.2	0.4	0.3	
t-2-Heptene	0.1	0.1	0.4	0.5	
3E-c-2-Pentene	0.1	0.3	0.4	0.2	
2,4,4-TM-1-Pentene	0.2	0.0	0.4	0.5	
2,3-DM-2-Pentene	0.1	0.2	0.2	0.2	
c-2-Heptene	0.1	0.2	0.2	0.2	
2,4,4-TM-2-Pentene	0.0	0.1	0.3	0.3	
1-Octene	0.0	0.3	0.5	0.5	$0.43 - 1.49^{\circ}$
t-4-Octene	0.1	0.2	0.5	0.5	0.10 1.17
t-2-Octene	0.1	0.1	0.6	0.6	
c-2-Octene	0.1	0.1	0.0	0.0	
1-Nonene	0.9	0.9	2.1	1.7	0–0.49 ^ª
Sum	91	88	85	55	0 0.12
Cycloalkenes	~ 1	00			
- ,	0.3	0.6	0.3	0.3	

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Table 3. (Cont.)

Species	0 % PE	0.25 % PE	2.50 % PE	RMSE (SD)	Other references (mg/kg fuel)
3M-CycPentene	0.2	0.2	0.5	0.3	
1M-CycPentene	0.5	0.2	0.5	0.6	
CycHexene	0.4	0.3	1.0	0.9	
Sum	1.4	1.3	2.3	2.2	
Diolefins					a b
1,3-Butadiene	2.6	15.7	3.4	8.1	62–196, ^a 117 ^b
2M-1,3-Butadiene	0.7	3.4	5.4	4.9	2
CycPentadiene	1.4	0.1	1.0	1.9	26–127 ^ª
Sum	4.7	19.1	9.8	13.4	
Monocyclic aromatic hydrocar					2
Toluene	25	26	20	19	130–320 ^ª
m&p-xylene	6.6	4.1	5.6	7.8	40–72 [°]
Styrene	9.2	8.3	7.6	7.9	35–117 ^a
o-Xylene	2.2	1.5	1.4	1.6	16-27
Benzene	105	102	83	97	225–1190 ^a
Indan	0.0	0.1	0.1	0.1	$0.12 - 0.49^{a}$
Sum	148	142	118	103	
Ethyl Benzene	5.2	4.4	4.2	4.0	
i-PropBenzene	0.3	0.2	0.1	0.2	
n-PropBenzene	0.7	0.4	0.4	0.8	
1M-3E-Benzene	0.4	0.4	0.1	0.3	
1M-4E-Benzene	0.1	0.2	0.5	0.2	
1,3,5-TM-Benzene	0.4	0.5	0.3	0.5	
1M-2E-Benzene	0.7	0.1	0.6	0.9	
1,2,4-TM-Benzene	0.3	3.1	2.6	2.2	
i-ButylBenzene	0.1	0.2	0.0	0.1	
s-ButylBenzene	0.4	0.1	0.0	0.4	
1M-3-i-PropBenzene	0.0	0.3	0.1	0.2	
1,2,3-TM-Benzene	0.4	0.2	0.4	0.6	
1M-4-i-PropBenzene	0.2	0.1	0.1	0.1	
1M-2-i-PropBenzene	0.3	0.1	0.1	0.2	
1,3-DE-Benzene	0.1	0.4	0.1	0.4	
1,4-DE-Benzene	0.1	0.1	1.7	1.8	
1M-3-n-PropBenzene	0.2	0.7	0.3	0.4	
1M-4-n-PropBenzene	0.1	0.2	0.2	0.2	
1,2-DE-Benzene	0.1	0.3	0.1	0.3	
1M-2-n-PropBenzene	0.1	0.1	0.1	0.1	
1,4-DM-2-E-Benzene	0.2	0.4	0.1	0.3	
1,3-DM-4-E-Benzene	0.1	0.4	0.0	0.3	
1,2-DM-4-E-Benzene	0.2	0.3	0.1	0.3	
1,3-DM-2-E-Benzene	0.3	0.3	0.3	0.5	
1,2-DM-3-E-Benzene	0.1	0.1	0.2	0.2	
1,2,4,5-TetM-Benzene	0.1	0.1	0.1	0.1	
2-M-ButylBenzene	0.0	0.3	0.0	0.4	
1,2,3,5-TetM-Benzene	0.1	0.1	0.0	0.1	
tert-1-But-2-M-Benzene	0.0	0.1	0.1	0.1	
1,2,3,4-TetM-Benzene	0.1	0.1	0.0	0.1	
n-Pent-Benzene	0.3	0.2	0.1	0.2	
tert-1-But-3,5-DM-Benzene	0.1	0.1	0.1	0.1	
Sum	11.6	14.1	12.9	13.0	

Notes: ^aMcDonald et al. (2000) (fireplace softwood, hardwood, and woodstove), cottonwood, birch, aspen, and oak. ^bSchauer et al. (2001), residential fireplace combustion of pine, oak, and eucalyptus.

fuel burned reported by Schauer et al. (2001). No trend with increasing PE content was observed. No statistically significant trend or difference with increasing PE content was recognized in this group.

Monocyclic aromatics. Emission factors of monocyclic aromatic hydrocarbons are presented in Table 3. For this group, benzene is about 70% of the total monocyclic aromatic fraction, a value consistent with the findings of Schauer et al. (2001) in which there was no PE added to the wood. Although the average values decreased with increasing PE content, no significant differences were observed between different treatment groups.

Emission factors of benzene, toluene, and xylene isomers (m, p, and o) are shown in Table 3. The measured mass for the

sum of BTEX group (210–270 mg/kg fuel burned) is comparable with lower range values reported by McDonald et al. (2000) and Hedberg et al. (2002) of 420–1608 and 215–7481 mg/kg fuel burned, respectively. The average toluene/benzene ratio for this study was 0.24, 0.25, and 0.24 for 0, 0.25%, and 2.5% PE, respectively comparable with 0.26-0.58 reported by McDonald et al. (2000). The same ratio from the study of Hedberg et al. (2002) was 0.4, implying relatively higher toluene in that study.

PAH EFs are divided into two subcategories of particle-phase and gas-phase PAHs (Table 4). Among gas-phase PAHs, naphthalene, acenaphthylene, and phenanthrene are the most abundant, and among particle-phase PAHs benzo[ghi]perylene, benzo[a] pyrene, and indeno[1,2,3-cd]pyrene had the highest emission

Table 4. Gaseous emission factors for polyaromatic hydrocarbons (PAH) from the burning of manzanita (Arctostaphylos sp.) wood/LDPE mixtures (mg per kg CO2)

Species	0% PE	0.25% PE	2.50% PE	RMSE (SD)	Other references (mg/kg fuel burned)			
Gas-phase polyaromatic hydrocarbons (PAH)								
Naphthalene	71	38	53	48	$21-54^{\circ}, 18.34 \pm 14.05^{\circ}, 38.1 \pm 31.9^{\circ}$			
Acenaphthylene	43	12	8	28	$5-9^{\circ}, 1.01-2.66^{\circ}, 14.2 \pm 12.2^{\circ}$			
Acenaphthene	0.8	0.5	0.3	0.4	$0.41 - 0.89^{\circ}$, $0.18 - 2.51^{\circ}$, $0.2 \pm 0.1^{\circ}$			
Fluorene	3.4	2.3	1.3	1.3	$2.153.50^{\text{a}}, 0.050.92^{\text{e}}, 0.2\pm0.1^{\text{r}}$			
Phenanthrene	10.5	5.7	3.4	5.7	$1.99-3.94^{\circ}, 5.8 \pm 1.8^{'}$			
Anthracene	1.2	0.9	0.4	0.3	$0.32 - 1.27^{\circ}, 6.3 \pm 1.4^{'}$			
Fluoranthene	1.0	1.1	1.0	0.5	$0.52 – 2.86^{\circ}, 1.2 \pm 0.2^{\circ}$			
Pyrene	1.0	2.2	1.1	1.4	$0.45 ext{-}1.47^{\circ}, 1.1 \pm 0.5^{'}$			
Benz[a]anthracene	0.04	0.05	0.02	0.02	$0.21 – 0.40^{\circ}, 0.04 \pm 0.06^{\circ}$			
Chrysene	0.03	0.03	0.02	0.01	$0.75 ext{-}1.14^\circ$, $0.21 ext{-}0.34^\circ$, 0.04 ± 0.05			
Benzo[b]fluoranthene	0.06	0.06	0.02	0.05	$0.40 – 0.79^{\circ}, 0 – 0.05^{\circ}, 0.09 \pm 0.12^{\circ}$			
Benzo[k]fluoranthene	0.01	0.02	0.02	0.01	$0.29-0.67^{\circ}, 0-0.13^{\circ}, 0.02 \pm 0.01^{\circ}$			
Benzo[a]pyrene	0.03	0.08	0.04	0.04	$0.25-0.71^{\circ}, 0.03 \pm 0.03^{\circ}$			
Indeno[1,2,3-cd]pyrene	0.01	0.05	0.02	0.02	n.d.°, $0.03 \pm 0.04^{'}$			
Dibenzo[a,h]anthracene	0.01	0.06	0.02	0.02	n.d.°, 0.05 ± 0.07^{r}			
Benzo[ghi]perylene	0.04	0.15	0.03	0.09	0–0.002 [°] , n.d. ^r			
Sum	132	63	68	78				
Particle-phase polyaromat	tic hydroca	rbons (PAH)						
Fluorene	0.06	0.12	0.11	0.02	$27.4^{\rm b}, 73269^{\rm d}, 0.04 \pm 0.06^{\rm f}$			
Phenanthrene	0.12	0.25	0.20	0.05	$10-17^{\circ}, 99.1^{\circ}, 0.21 \pm 0.20^{\circ}$			
Anthracene	0.01	0.03	0.02	0.01	19.3b, $1-50^{\circ}$, $0.04 \pm 0.03^{\circ}$			
Fluoranthene	0.10	0.28	0.13	0.05	$1.75 - 3.99^{a}, 19.3^{b}, 286 - 1083^{d}, 0.22 \pm 0.14^{f}$			
Pyrene	0.12	0.27	0.16	0.03	$1.49-3.39a$, 25.5b, 1.87–2.70c, 222–1080 ^d , 0.74 \pm 0.84 ^f			
Benz[a]anthracene	0.11	0.36	0.13	0.13	$\begin{array}{c} 0.31 - 0.56^{\circ}, 3.5^{\circ}, 127 - 249^{\circ}, 0.23 \pm 0.08^{\circ} \\ 0.28 - 0.61^{\circ}, 4.1^{\circ}, 107 - 253^{\circ}, 0.18 \pm 0.16^{\circ} \\ 0.51 - 1.05^{\circ}, 6.1^{\circ}, 36 - 157^{\circ}, 0.67 \pm 1.00^{\circ} \end{array}$			
Chrysene	0.10	0.28	0.14	0.10	$0.28-0.61^{\circ}, 4.1^{\circ}, 107-253^{\circ}, 0.18 \pm 0.16^{\circ}$			
Benzo[b]fluoranthene	0.26	0.40	0.21	0.29	$0.51 - 1.05^{\circ}$ *, 6.1° , $36 - 157^{\circ}$, $0.67 \pm 1.00^{\circ}$			
Benzo[k]fluoranthene	0.08	0.11	0.08	0.07	$0.51-1.05^{a}$ *, b.d. ^b , 3.23 ± 2.91^{f}			
Benzo[a]pyrene	0.18	0.57	0.50	0.18	$0.15 - 0.34^{\circ}, 0.09 \pm 0.10^{\circ}$			
Indeno[1,2,3-cd]pyrene	0.21	0.67	0.45	0.16	$0.07 – 0.19^{\circ}, 3.6^{\circ}, 39 – 164^{\circ}, 0.06 \pm 0.03^{\circ}$			
Dibenzo[a,h]anthracene	0.04	0.22	0.30	0.17	$0.07-0.19^{a}$, 3.6^{b} , $39-164^{d}$, 0.06 ± 0.03^{f} b.d. ^b , $3-11^{d}$, 0.02 ± 0.01^{f}			
Benzo[ghi]perylene	0.28	0.80	0.63	0.30	$0.07 – 0.22^{^{\mathrm{a}}}, 2.6^{^{\mathrm{b}}}, 0.44^{^{\mathrm{c}}}, 25 – 70^{^{\mathrm{d}}}, 0.11 \pm 0.07^{^{\mathrm{f}}}$			
Sum	1.66	4.36	3.07	1.01				

Notes: b.d. and n.d. indicate compound was below detection limit or not detected in that study, respectively. ^aMcDonald et al. (2000) (fireplace softwood, hardwood, and woodstove), cottonwood, birch, aspen, and oak. ^bHedberg et al. (2002), birch wood combustion in a woodstove. ^cSchauer et al. (2001), residential fireplace combustion of pine, oak, and eucalyptus. ^d Fine et al. (2001), red maple, northern red oak, paper birch, eastern white pine, eastern hemlock, and balsam fir grown in northern United States. ^cJenkins et al. (1996); included here of this study are wood from almond, walnut, and fir trees. ^fHosseini et al. (2013).

Species	0% PE	0.25% PE	2.50t% PE	RMSE (SD)	Other references (mg/kg fuel burned)
Acetone	51	40	46	19	$366^{^{\mathrm{b}}}, 749^{^{\mathrm{c}}}, 73.9 \pm 16.2^{^{\mathrm{d}}}$
Formaldehyde	206	330	147	227	$113-245^{\circ}, 422^{\circ}, 1165^{\circ}, 174.8 \pm 52.5^{\circ}$
Acetaldehyde	127	208	87	134	$301-425$ $^{\circ}$, 86 $^{\circ}$, 1704 $^{\circ}$, $92.7 \pm 21.9^{\circ}$
Propionaldehyde	20	31	14	19	$80-150\degree, 7.6, 255\degree, 7.5 \pm 15.1\degree$
Crotonaldehyde (butenal)	13	20	10	13	276 [°]
Methyl ethyl ketone (MEK)	39	60	27	21	8.3 ^b , 215 ^c
Methacrolein	23	27	15	37	1.8 [°] , 23 [°]
Butyraldehyde	5.4	7.9	5.9	6.0	$19-36^{\mathrm{b}}, 96^{\mathrm{c}}, 52.1 \pm 18.2^{\mathrm{d}}$
Benzaldehyde	8.4	12.5	7.8	7.4	12 ^b
Valeraldehyde	4.0	6.4	2.8	2.6	$7{-}18\degree, 1.1\degree, 85.9\pm 37.4\degree$
Tolualdehyde	4.5	6.6	2.4	3.5	0.9 ^b
Hexanal	120	183	91	121	$34.6^{b}, 89.0 \pm 37.5^{d}$
Acrolein	33	62	20	38	46–91 [°] , 63 [°]
Sum	618	940	452	487	

Table 5. Emission factors for aldehydes and ketones from the burning of manzanita (*Arctostaphylos* sp.) wood–LDPE mixtures derived from 2,4-dinitrophenylhydrazine (DNPH) coated silica cartridges; units are in mg/kg CO₂

Notes: ^aMcDonald et al. (2000) (fireplace softwood, hardwood, and woodstove), cottonwood, birch, aspen, and oak. ^bHedberg et al. (2002), birch wood combustion in a woodstove. ^cSchauer et al. (2001), residential fireplace combustion of pine, oak, and eucalyptus. ^dHosseini et al. (2013).

rates. Increase in polyethylene content had an effect on the emissions of fluoranthene and pyrene in particle form, but there was no statistical evidence of a linear trend in the effect. The sum of gasphase PAHs decreased for PE-containing mixtures; however, no significant difference was observed in ANOVA results. The probability values of the test for effect of LDPE on EFs of fluorene, phenanthrene, and anthracene fell in the range of 0.05–0.10. It is worth noting that Jenkins et al. (1996) showed that fires with higher MCE might lead to lower formation rate of PAH.

Carbonyls. Formaldehyde, acetaldehyde, and hexanal made up 50% of the aldehydes and ketones for this study (Table 5). Inclusion of PE in the wood did not affect the ratio of carbonyls to VOCs. Formaldehyde was emitted at the highest rate of all carbonyls, with the average emission factors of 372 ± 138 , 594 \pm 288, and 265 \pm 79 mg/kg fuel for 0.0, 0.25, and 2.50 wt% PE. Emission factors for acetaldehyde and hexanal were next highest. Aldehydes and ketones were not affected by addition of LDPE.

Particulate matter. The fire average $PM_{2.5}$ emission factors for the three cases of 0.0, 0.25, and 2.50 wt% PE are presented in Table 2. On average, the PM emission factors did not show any decreasing or increasing pattern with increasing LDPE content and were 1.97 ± 0.50 , 1.85 ± 0.37 , and 2.01 ± 0.50 g/kg CO₂ for cases of 0.0, 0.25, and 2.5 wt% PE, respectively.

Reconstructed mass of particulate matter (PM) based on EC/ OC versus PM mass from gravimetric measurements of Teflon filters is shown in Figure 3. This was done assuming PM mass is equal to mass of organic matter (OM) added to mass of elemental carbon (EC) ($EF_{PM} = EF_{OC} \times factor + EF_{EC}$). Using an OM-to-OC ratio of 1.55 as suggested by McMeeking et al. (2009) and Levin et al. (2010) resulted in a best linear fit with slope of 1.00 and R² of 0.87 between the two variables of gravimetric PM mass EF and constructed PM mass EF. The



Figure 3. EF_{PM} is plotted versus reconstructed PM mass based on the emission factors of elemental carbon (EC) and organic carbon (OC); solid line shows the regression line with slope 1 and correlation coefficient of 0.87.

factor of 1.55 is within the range suggested by Reid et al. (2005) for biomass burning.

Particle size distribution. Figure 4 represents the particle number size distributions obtained by EEPS. These two contour graphs are for two typical burns. Hosseini et al. (2010) showed that the geometric mean diameter (GMD) of the particle size distribution is a function of instantaneous modified combustion efficiency, and that GMD decreases from flaming to smoldering phase. For 0% PE case, intermittent increase of GMD is shown until 80 sec, reflecting sporadic flame spread. From 80 to ~200 sec GMD shows continuous and smooth decrease due to more



Figure 4. Contour graphs shown for two different PE contents: (a) 0.0 wt% PE and (b) 2.5 wt% PE. The data were captured using a model 3090 engine exhaust particle sizer (EEPS).

stable flame spread and combustion phase change into vigorous flaming phase. Total particle concentrations decreased as the combustion progresses from flaming to smoldering phase. Note that this is not a particle concentration normalized by CO_2 concentration. For 2.5 wt% PE case the trend was similar. Past 100 sec, total particle concentrations decrease as combustion progresses from flaming to smoldering phase.

The simulated debris piles used in this study were uniform in composition, relatively dry, and free of foliage and soil, which produced high combustion efficiency and enabled us to test the effect of adding LDPE to burning wood on emissions. Increasing the moisture content of the wood and introducing other fuel and nonfuel components will alter the combustion efficiency and alter the emissions. LDPE as a cover to protect fuels from moisture is used to promote efficient burning; however, this study does not illustrate the gain in combustion efficiency or alteration of emissions due to this practice. To our knowledge, such research has not been performed. Extrapolation of the results of this study to the field should be limited to the fact that LDPE did not alter the emissions of a vast majority of compounds, including U.S. EPA criteria pollutants resulting from the burning of wood. The present study supports the conclusion reached by Wrobel and Reinhardt (2003), which was that inclusion of LDPE would not add additional toxics to the emissions from burning debris piles. Field testing of the results of the present study using actual debris piles, while desired, may be quite difficult and/or expensive to replicate given the heterogeneity of piles, the presence of moisture, and the range of environmental factors that affect combustion. Further testing of moisture effects, wood composition effects, and gain in combustion efficiency due to the presence of LDPE may be best tested in a laboratory setting where many of the factors that influence combustion can be controlled in a truly replicated study.

Summary and Conclusion

The effect of adding low-density polyethylene plastic to piled silvicultural debris on smoke emissions was examined using a simplified laboratory experiment. Shredded LDPE was mixed with manzanita wood to produce 2-kg piles containing 0, 0.25, and 2.5% LDPE by mass. The piles were ignited and gaseous and

particulate emissions were sampled during the entire flaming and mixed combustion phases and during a portion of the smoldering phase.

Based on tests using Type III sums of squares, we rejected the null hypothesis of no effect of adding LDPE for only 3 of the 195 compounds (Tables 2-5). Pairwise comparisons of the least-squares estimates of the treatment effects suggested that 3M-octane increased as LDPE increased. Increase in polyethylene content had an effect on the emissions of fluoranthene and pyrene in particle form, but there was no statistical evidence of a linear trend in the effect. MCE was a significant covariate for three compounds as well and ranged from 0.983 to 0.993. Although CO emissions reduced by 7 and 27% and NO_x emissions increased by 19 and 28% at 0.25 and 2.5 wt% PE, we could not find enough statistical proof to confirm that this was due to increase in PE content. We attributed this to better combustion efficiency when PE is added to debris piles. Particulate emission factors also showed statistically marginal significance in relation to MCE regardless of PE content. The rest of PAHs and carbonyls did not show any trend with PE contents. Diolefins were 1-3%of total VOC mass and showed no trend with PE contents.

In summary, changes in criteria pollutant concentrations and selected compounds might be attributed to improved combustion efficiency with addition of small amounts of PE. These results support the conclusion of an earlier study (Salvador et al., 2004) in which negligible effect of LDPE on PAH emissions was observed in compressed mixtures of cardboard and LDPE until LDPE comprised more than 10% of the mass of the mixture. The study also supports the conclusion reached by Wrobel and Reinhardt (2003) that LDPE does not add additional toxic compounds to burning wood. Based on the results of this study, previous studies, and literature reviews, inclusion of small proportions (<2.5% of total mass) of low-density polyethylene in piled silvicultural debris does not appear to significantly change the emissions produced when low-moisture-content wood is burned. The study did not examine the influence of LDPE on emissions of wet woody fuels, nor did it quantify effects on burning rates.

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