REVIEW OF POTENTIAL AIR EMISSIONS FROM BURNING POLYETHYLENE PLASTIC SHEETING WITH PILED FOREST DEBRIS

FINAL REPORT

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Executive Summary

URS reviewed the available scientific literature regarding emissions from burning polyethylene (PE), and burning silvicultural piles of woody debris. Few papers report measuring emissions from polyethylene burned in an open pile, and none has assessed emissions from silvicultural piles with and without a PE covering. Thus the literature review must draw from bench-scale studies of PE pyrolysis and combustion. These are unlikely to duplicate the actual emissions from operational burns of silvicultural piles.

Bench-scale research investigating the pyrolysis and combustion chemistry and emissions from pure PE has identified a broad range of emissions, many of which are also identified in emissions from burning woody silvicultural debris. Carbon dioxide (CO_2), carbon monoxide (CO), water and particulate matter are major emissions from both sources. Polycyclic aromatic hydrocarbons (PAHs) are found in emissions from both materials, and at widely varying concentrations. Many partially oxygenated products of incomplete combustion (PICs) have been quantified in woody debris emissions, and identified but not quantified in PE emissions—these along with PAHs and other PICs are known to have adverse effects on human and nonhuman receptors when they are exposed at significant concentrations. There is no evidence that unique classes of chemicals are, or should be found in emissions from burning PE, in comparison to burning wood debris.

The relative impacts from PE and silvicultural debris cannot be accurately estimated from these diverse data sources, but the expected ranges can be summarized. The literature suggests that the emissions to the atmosphere contributed by the sheet of PE covering are chemically similar to the emissions from the underlying pile of silvicultural debris. For many of these emissions, such as CO, CO_2 and particulate matter, the amount emitted from the woody debris will of course overwhelm the contribution from the PE. Some studies indicate that PE does not produce a great deal of PAHs, while others indicate that it may be an efficient producer of PAHs, and in theory could produce almost as much PAH as the silvicultural pile, but only when two unlikely assumptions are made: 1) that PE emissions from pellets in high-temperature furnaces replicate the emissions of PE covering a silvicultural pile where temperatures increase more slowly and half or more of the PE is likely to be volatilized or burned at lower temperatures before it reaches the high temperatures required to form PAHs, and 2) that the relatively complete spectrum of individual PAHs identified in PE combustion studies is directly comparable to the smaller subset of PAHs monitored from burning woody debris.

The literature, and anecdotal evidence, clearly indicates that silvicultural piles burn more efficiently and produce fewer PICs when they are allowed to cure to a dryness that readily supports combustion. Inasmuch as regions in Oregon where silvicultural burning occurs are exposed to significant amounts of precipitation, there is an overall emissions reduction benefit from covering silvicultural piles. Polyethylene does not include chlorinated compounds or significant amounts of other chemicals likely to form uniquely toxic emissions, nor have these been demonstrated in the literature. As a covering material, it is reportedly much less expensive than coated or uncoated kraft paper, an alternative product used to cover piles in central and southern California at the request of

local air quality management districts. There are no literature studies of the emissions from coated kraft paper, but the cellulose should be similar to woody debris and the waxy coating, when melted, should burn very similarly to melted polyethylene. In Oregon, some 314 grams of PE are burned on a typical pile covered with 4-mil PE sheeting. If 1 or 2-mil sheeting were used, the PE emissions would be cut by half or more. In terms of overall emissions from the pile and the cover, the benefit of cutting PE emissions by only covering the center of the pile may be offset by higher emissions from uncovered wood which has attained higher fuel moistures during the curing period.

All the bench-scale studies suffer from a weakness in extrapolating from very controlled combustion conditions to those found in operational burns. A definitive answer as to whether emissions from a PE-covered or partially-covered pile are measurably different from the uncovered or paper-covered pile can only be obtained from actual open burning of the piles. The available literature does not support a contention that burning PE sheeting would produce unique chemicals or classes of chemicals that are not also found in emissions from burning wood debris.

1.0 INTRODUCTION

Polyethylene (PE) plastic sheeting has long been used by the forest products industry to prevent the accumulation of excessive moisture within silvicultural debris piles as they cure over a timeframe of several months to a year or more. The curing process dries the piled woody debris and enhances the combustion process, making ignition easier and producing fewer products of incomplete combustion. Timber harvest residues (branches and small woody fuels) and woody debris from silvicultural thinning and fire hazard reduction projects are collected, piled and partially covered with PE sheeting. The sheeting (typically six to ten foot squares) is draped over a pile and anchored with sticks, logs and rocks to prevent removal by the wind. The sheeting protects the piles from rain and snow until they cure. These piles are then ignited with a drip torch and burned, usually achieving 100% consumption of the piled debris. The PE sheeting is usually left on the pile, to burn, along with the woody debris. Most regulatory agencies enforce ordinances against the combustion of plastics in silvicultural debris piles because of concerns that the emissions may have an adverse affect on air quality.

This paper reviews the available literature on the pyrolysis and combustion products of PE and assesses whether burning the typical amount of PE produces significantly more or different emissions than the woody debris piles themselves. This work has been undertaken at the request of the Smoke Management Review Committee of the Oregon Smoke Management Plan Citizens Advisory Group. The Committee is a multiparty association comprised of parties interested in smoke management and forestry issues in Oregon, including the USDA-Forest Service, the U.S. Department of the Interior-Bureau of Land Management, the Oregon Department of Forestry, the Oregon Department of Environmental Quality, Oregon State University Cooperative Extension, the Nature Conservancy, the Oregon Forest Industries Council, Lane Regional Air Pollution Control Authority, Jackson County, and small woodland owners and public representatives. The Committee has posed the following specific questions to the authors:

- Is there such a thing as pure PE? And, if so, is pure PE readily available (commercially) and how would one tell PE from other polymer products on the market that are known to contain toxic materials (PVC, styrene, etc.) and heavy metals?

- What is the basic chemistry of PE and how does it combust and react within a pile in an ambient environment?

- How will PE volatilize by itself, and as part of a slash pile?

- Are there any material safety data sheets that include a combustion test of PE?

- Is there a difference in PE emissions between a pile that is completely covered and one that uses PE in the center to create a dry spot for ignition?

- Does it make a difference in the emissions if 1-mil or 4-mil PE sheeting is used?

- Is there any benefit to requiring the PE to sit in the environment for a period of time (weather) prior to burning?

- What are the alternatives to PE and what is the chemical makeup of "impregnated" paper product?

- Is the use of PE cost effective compared to alternative products?

2.0 BACKGROUND

Polyethylene is the most commonly used plastic, worldwide. It is produced by the free radical polymerization of ethylene, 1-propene, 1-butene, 1-hexene or 1-octene. There are three main types of PE: high-density PE (HDPE), low-density PE (LDPE) and linear low-density PE (LLDPE). The majority of PE produced is either HDPE or LDPE. HDPE chains are not branched while LDPE contains about 50 branches for every 1000 carbon atoms[1].

Commercially manufactured PE is a relatively pure material. Pure PE is translucent; the opaque black sheeting used to cover woody debris piles is produced by adding carbon black to the polymer. Carbon black, an amorphous form of carbon, does not possess a long-range, or macrocrystalline structure. It does exhibit a short-range crystal structure that deviates from both the diamond lattice and graphite lattice with respect to the interatomic distances and bond angles[2]. Water, polycyclic aromatic hydrocarbons (PAHs), metallic oxides, salts and other contaminants may be present in trace amounts within carbon black[3].

Small quantities of chemical additives are often used in order to enhance or attenuate some of PE's characteristics. PE is easily oxidized at temperatures as low as 180 °C. To minimize oxidation during processing, either phenol or phosphite based antioxidant chemicals are commonly added. Fatty acid amides are added to aid in the formation of plastic sheets. Polyethylene glycol esters, glycerol monostearate and ethoxylated secondary amines are sometimes added to reduce PE's propensity to collect a static charge[4]. The chemical composition and some of the physical properties of pure PE pellets are listed in Table 1.

Table 1. Polyethylene – Chemical Composition and Physical Properties

Volatiles (wt.%)	100
Ash (wt.%)	0
Carbon (wt.%)	85.4 – 86.4
Hydrogen (wt.%)	13.5 - 14.3
Sulfur (wt.%)	0 - 0.08
Nitrogen (wt.%)	0
Oxygen (wt.%)	0 - 0.2
Chlorine (wt.%)	0
Heat Value (MJ/kg)	40.5
Density (g/cm^3)	0.910 - 0.940
Degree of Crystallinity (%)	45 - 55
Melting Point Range (^{o}C)	105 - 115
Molecular Weight (Daltons)	10,000 - 50,000

Reference: 4, 5, 6, 9,

Poly-America is a manufacturer of the LDPE sheeting used in Oregon as a moisture barrier on silvicultural debris piles. Although the material safety data sheet provided by the company identifies the product as HDPE and linear LLDPE, the manufacturer's website, and subsequent phone conversations with a representative of Poly-America, have confirmed that the material is LDPE. It would be difficult, if not impossible to differentiate among the three varieties of polyethylene and most other types of plastics by a visual examination of the sheet material.

The density of LDPE ranges from 0.910 to 0.925 grams per cubic centimeter. Guidance from the USDA-Forest Service stipulates that silvicultural debris piles are to be covered with a sheet of 4-mil polyethylene plastic of 6-foot by 6-foot minimum dimensions. A sheet of LDPE with these dimensions would have an approximate mass of 314 grams (11.1 ounces).

3.0 CHEMISTRY OF POLYETHYLENE PYROLYSIS AND COMBUSTION MECHANISMS

Polyethylene combustion is more akin to the combustion of a liquid, rather than a solid. PE melts and the liquid pyrolyzes, then burns, producing a visible flame[7, 8]. The combustion of PE, and all polymers (including wood) is a complex process that is still not fully researched. Pyrolysis and combustion reactions occur simultaneously in both the liquid and gas phases. Volatile components can continue to thermally degrade, oxidize and/or react with other chemical species to produce a complex mix of chemicals[9, 10].

The first step in the pyrolysis of PE is random scission of the polymer into smaller subunits, which in HDPE produces a wide range of primary radicals; because LDPE contains varying proportions of side chains, it can initially produce secondary and tertiary radicals as well [1, 11]. Low reaction temperatures favor the formation of long-chain radicals, while a higher temperature leads to the formation of a greater number of short-chain radicals. Primary radicals can either undergo β-scission to produce ethene, or

intramolecular hydrogen transfer to form more stable secondary radicals. The latter path dominates at low temperatures. High temperatures also increase the rate of volatilization of longer chains, where they undergo β-scission at a rate much higher than that found in the liquid phase[12, 13].

The rate of pyrolysis increases as the extent of the branching increases. LDPE pyrolyzes at a faster rate than that of HDPE, primarily as a result of the stability of the radicals formed during the initial step. The exposure of PE to ultraviolet radiation has been shown to lower its thermal stability. This trend is less pronounced for branched polymers, because they already exhibit significantly lower activation energies[11].

The formation of aromatic rings in the PE pyrolysis/combustion gas is believed to occur at higher temperatures due to the rapid thermal degradation of the polymer. The cracking of heavy olefins produces gaseous compounds of lighter molecular weight, which at temperatures above 730 ^{o}C, can react to generate aromatic compounds via the Diels Alder mechanism[13, 14, 15].

Chromatographic evidence has determined that at temperatures below 750 ^{o}C significant pyrolytic degradation of PE occurs, however, complete combustion of PE would not occur[9]. This may provide some insight into the expected emissions from burning PE with a silvicultural debris pile. Immediately after pile ignition, especially considering the low thermal conductivity of plastics, the combustion temperature would not be intense enough to heat the PE to a temperature high enough to initiate combustion. Because PE melts and thermally degrades at relatively low temperatures (105 and 180 ^{o}C), pyrolysates would be formed and emitted before the temperature can rise high enough to ensure more complete combustion. At temperatures below 755 ^{o}C, as much as 18 to 41 percent of the mass of PE is lost and volatilized prior to particle ignition[16].

In the context of a burning silvicultural debris pile, PE pyrolysis chemistry would be of far greater importance than combustion chemistry. The temperature of the pile surface would rise from ambient to about 1000 ^{o}C over roughly one to five minutes. Thus, the PE is likely to undergo thermal degradation and melt during the early stage of combustion, when the pile temperature is between 250 and 600 ^{o}C. These temperatures are not high enough to allow PE combustion. The emissions from this early phase of the pile burn would contain a high percentage of aliphatic hydrocarbons and radicals, as well as a low percentage of aromatic and polycyclic aromatic hydrocarbons (PAHs). As the biomass pyrolysis and oxidation rates accelerate, the temperature of the pile will increase high enough to make PE combustion an important process, but by this time most, if not all of the PE would have already been pyrolyzed and lost to the atmosphere. The temperature of the plume at the time of PE pyrolysis would be lower due to cooling by entrained air, precluding the downwind formation of aromatic compounds because there is not enough heat to overcome the activation energy of the Diels Alder reaction.

4.0 CHEMICAL COMPOUNDS EMITTED FROM THE PYROLYSIS AND COMBUSTION OF POLYETHYLENE

Most of the data regarding the emissions from the pyrolsis/combustion of PE were measured at temperatures ranging from 500 to 1000 ^{o}C. The experiments were conducted in various apparatus' that could be described as horizontal laminar flow reactors, vertical tube-type furnaces or fluidized bed reactors. In many cases the device had a secondary combustion chamber and exhaust samples were collected and analyzed from both the primary and secondary stages. Only results reported from a primary combustion stage are discussed here, as they are more comparable to the conditions under which PE sheeting would burn on a silvicultural debris pile. There is one major difference between the pile and the furnace conditions; the temperature of the furnace is maintained at a set temperature, while the silvicultural debris pile begins at ambient temperature. This means that the pyrolysates and combustion products in a furnace at 800 ^{o}C are exposed to that temperature immediately upon initiation of the experiment until the samples are collected. In contrast, a silvicultural debris pile will exhibit a temperature gradient. Compounds emitted from the thermal degradation of PE will not remain at that temperature indefinitely.

The US EPA lists emission factors for some PAHs due to the burning of agricultural plastic[17]. Specifically, Chapter 2.5.2.4 of the widely used document "AP-42" discusses the burning of "agricultural plastic film." The type of plastic is not expressly stated, however, agricultural plastic film is almost always black PE. These experimental conditions under which these emission factors were calculated are more similar to those expected in silvicultural applications than those obtained under furnace conditions. The AP-42 emission factors are rated a "C." This indicates that there is no known statistical bias present in the data, however, the data may not represent a random sample population.

AP-42 emission factors are based on the research performed by Linak *et al.* at the US EPA's Air and Energy Engineering Research Laboratory. The experimental methodology used kerosene to initiate the pyrolysis of 1-lb samples of used and unused PE. The clean unused PE was balled in a manner similar to the way in which used agricultural film is prepared for incineration in the field. The used PE samples contained varying quantities of soil, biomass and water[18].

The thermal decomposition and combustion of PE, as with the combustion of any carbonaceous fuel, produces carbon monoxide (CO), carbon dioxide (CO_2), water (H_2O) and a plethora of alkanes, alkenes and aromatic compounds[9]. At least 140 chemical species have been tentatively identified in the emissions from the pyrolysis and gasification of PE[19]. The pyrolysis energy of activation is approximately 260 kilojoules (kJ)/mole, and a range of reaction orders between 0.5 and 1.5 has been reported[12, 20].

Some general trends regarding the types and quantities of emission products from the combustion of PE have been identified. CO_2 emissions are maximized at around 600 to 700 ^{o}C, while the minimum concentrations tend to occur near 1000 ^{o}C[5, 21]. CO and

particulate matter concentrations exhibit little variability over the 500 to 1000 ^{o}C temperature range and CO concentrations peak at around 800 ^{o}C. Particulate matter emissions are almost identical at both ends of the temperature range (500 and 1000 ^{o}C), with little variation found at the temperatures between, although the chemical mechanisms and compounds responsible for this observation are different. As much as 70 to 97 percent of the particulate matter formed was found to have a mean aerodynamic diameter of 2 micrometers (μm) or less[22].

The proportions of organic chemicals emitted can vary widely with the PE combustion temperature, although most chemicals can be found at some concentration at all temperatures[23]. Emissions of benzene and its derivatives are maximized around 700 to 800 ^{o}C. From 800 to 900 ^{o}C, alkenes, naphthalene, fluorene and phenanthrene were the predominant organic compounds detected. At a combustion temperature of 950 ^{o}C, the production of light hydrocarbons was reduced, while PAH concentrations increased[5]. PAH concentrations were found to increase along with combustion temperature[5, 19, 14]. Of those PAHs analyzed for; naphthalene was found in the largest concentrations followed by acenaphthylene, phenanthrene, pyrene, fluoranthene, fluorene, biphenyl, anthracene, cyclopenta[*c*,*d*]pyrene, benzo[*a*]pyrene, acephenanthrylene, benzo[*b*]fluoranthene, chrysene, benzo[*g*,*h*,*i*]fluoranthene, benzo[*g*,*h*,*i*]perylene, and perylene[5].

Hydrocarbon emissions tend to exhibit a trend opposite to that of PAHs. Hydrocarbon emissions peak in the temperature range of 600 to 800 ^{o}C[19, 14]. The concentration of ethylene was the greatest, due to the β-scission of primary radicals. The mole fractions of methane, ethane, and ethylene all reached maximums around 700 °C. At temperatures greater than 700 °C the concentrations of methane, ethane, and ethene all decrease[5].

The research suggests that synthetic polymers produce as much as one to two orders of magnitude more soot than cellulosic material at typical heating rates (10 –100 K/s). Soot production has been found to increase with the combustion temperature for all plastic polymers. PAH concentrations in the soot vary, however, soot from PE was found to have the greatest concentration of benzo[a]pyrene (1.5 mg/g) among the common plastics. Soot production was found to be very low in experiments using very high heating rates (~10,000 K/s) and combustion temperatures in excess of 1000 ^{o}C[24, 22].

Oxygenated organic compounds have been identified in the combustion gases of PE. The species positively identified include acetaldehyde, acrolein, propionaldehyde, acetone, methyl ethyl ketone and acetic acid[23, 24].

Emission factors for those compounds quantified during the pyrolysis/combustion of PE have been compiled in Tables 2 and 3. The minimum and maximum emission factors found in the literature are reported. It is important to note that the emission factors reported were determined under controlled laboratory conditions. The procedures generally involved dropping pure PE pellets into a furnace maintained at a known temperature. Experimental conditions and sources of error should be expected to vary among the cited experiments. The overall conditions at which the emission factors were

obtained may provide values that differ from those produced under the uncontrolled, open burn conditions experienced in the field.

Some additional chemical species that have been qualitatively identified are listed in Table 4. A large number of organic chemicals have been reported in PE combustion emissions, however, only those chemicals confirmed to be emitted from the pyrolysis/combustion of PE are listed.

Tables 2 and 3 also list the anticipated range of each chemical quantified. These values were calculated using the minimum and maximum emission factors for each chemical compound and assuming a sheet of PE with a mass of 314 g (6-foot by 6-foot by 4-mil) is burned. The mass emissions are only intended to provide an estimate of the range and magnitude of the emissions produced from the combustion of the PE sheet. As discussed previously, the values from among those studies that reported emission rates were used in the calculations. The accuracy of the emission rates is not known, and too few studies have been conducted to allow for a meaningful statistical analysis of these data.

Table 2. Emission Factors and Mass Emissions from Polyethylene Covering a Typical Silvicultural Pile – Inorganic, Alkane, Alkene, Aromatic and Total Suspended Particulate Matter

Chemical	Emission Factor			Mass Emitted[1]			
	Minimum	Maximum	Units	Minimum	Maximum	Units	Reference
CO	100	175	mg/g[a]	31	55	g	5
CO_2	400	1500	mg/g	126	471	g	5
Acetylene	ND	2.9	mg/g	ND	0.9	g	5
Methane	0.2	7	mg/g	0.1	2.2	g	5
Ethane	0.175	0.6	mg/g	0.1	0.2	g	5
Ethene	1.5	12	mg/g	0.5	3.8	g	5
Propene	0.4	1.5	mg/g	0.1	0.5	g	5
Benzene	1.23E-02	4.78E-02	µg/g[b]	3.86E-03	1.50E-02	mg	17
Toluene	3.30E-03	4.60E-03	µg/g	1.04E-03	1.44E-03	mg	17
Ethylbenzene	6.00E-04	1.20E-03	µg/g	1.88E-04	3.77E-04	mg	17
1-Hexene	1.00E-03	4.30E-03	µg/g	3.14E-04	1.35E-03	mg	17
TSP (soot)	8	36	mg/g	2.5	11.3	g	5, 22

ND = not detected
[1] Mass emissions were calculated using the minimum and maximum emission factors for each chemical compound and assuming a sheet of PE with a mass of 314 g is burned.
[a]Milligrams of emission per gram of polyethylene
[b]Micrograms of emission per gram of polyethylene

Table 3. Emission Factors and Mass Emissions from Polyethylene Covering a Typical Silvicultural Pile – Polycyclic Aromatic Hydrocarbons

Chemical	Emission Factors (µg/g)[a]		Mass Emitted[1] (g)		Reference
	Minimum	Maximum	Minimum	Maximum	
1-(2-Propenyl)naphthalene	6.2E-01	1.2E+02	1.9E-04	3.8E-02	14
1,1-Diphenylethylene	ND	1.5E+01	ND	4.7E-03	14
1,2:7,8-Dibenzophenanthrene	2.1E+01	1.5E+02	6.6E-03	4.7E-02	14
1,2-Binaphthalene	1.7E+00	6.1E+02	5.3E-04	1.9E-01	14
1,6-Dimethylnaphthalene	3.4E+00	1.8E+02	1.1E-03	5.7E-02	14
1-Ethylidene indene	6.3E+01	1.5E+02	2.0E-02	4.7E-02	14
1-Ethylnaphthalene	2.0E+00	6.2E+01	6.3E-04	1.9E-02	14
1H-Phenalene	2.5E+01	7.4E+02	7.9E-03	2.3E-01	14
1-Methylanthracene	ND	2.8E+01	ND	8.8E-03	14
1-Methylene indene	6.2E+01	1.2E+02	1.9E-02	3.8E-02	14
1-Methylfluorene	1.7E+01	1.2E+02	5.3E-03	3.8E-02	14
1-Methylnaphthalene	2.8E+01	1.5E+03	8.8E-03	4.8E-01	14
1-Phenylnaphthalene	2.8E+01	1.3E+03	8.8E-03	3.9E-01	14
1-Phenylphenanthrene	4.0E+01	8.4E+02	1.3E-02	2.6E-01	14
2,2-Binaphthalene	2.1E+00	4.1E+02	6.6E-04	1.3E-01	14
2,6-Dimethylnaphthalene	ND	2.9E+00	ND	9.1E-04	14
2-Ethenylnaphthalene	7.5E+01	5.1E+03	2.4E-02	1.6E+00	14
2-Ethylnaphthalene	2.6E+00	9.0E+01	8.2E-04	2.8E-02	14
2-Methylanthracene	1.2E+00	4.1E+02	3.8E-04	1.3E-01	14
2-Methylbiphenyl	4.9E-01	1.9E+02	1.5E-04	6.0E-02	14
2-Methylfluorene	2.9E+01	5.3E+02	9.1E-03	1.7E-01	14
2-Methylnaphthalene	2.2E+01	1.8E+03	6.9E-03	5.6E-01	14
2-Methylphenanthrene	1.6E+01	6.2E+02	5.0E-03	1.9E-01	14
2-Phenylnaphthalene	7.9E+01	2.8E+03	2.5E-02	8.9E-01	14
3,4-Dihydrocyclopenta[cd]pyrene	2.7E+01	5.1E+02	8.5E-03	1.6E-01	14
3-Methylbiphenyl	2.5E+00	2.8E+02	7.9E-04	8.8E-02	14
3-Methylphenathrene	1.7E+01	7.2E+02	5.3E-03	2.3E-01	14
4H-Cyclopenta[def]phenanthrene	9.6E+00	3.5E+03	3.0E-03	1.1E+00	14
4-Methylbiphenyl	1.7E+01	5.5E+01	5.3E-03	1.7E-02	14
9-Ethenylanthracene	3.0E+00	2.8E+02	9.4E-04	8.8E-02	14
9-Methylanthracene	1.4E+00	2.3E+02	4.4E-04	7.2E-02	14
9-Methylphenanthrene	2.8E+01	4.7E+02	8.8E-03	1.5E-01	14
Acenaphthalene	3.1E+02	9.1E+03	9.7E-02	2.9E+00	5, 14
Acenaphthene	2.0E+01	1.2E+03	6.3E-03	3.7E-01	14
Acenaphthylene	NO DATA				
Acephenanthrylene	1.3E+02	4.7E+03	4.1E-02	1.5E+00	5, 14
Anthracene	1.3E-03	3.1E+03	4.1E-07	9.6E-01	5, 14, 17
Benz[a]anthracene	1.4E-02	5.3E-02	4.5E-06	1.7E-05	17
Benzo[a]anthracene	8.5E+01	1.3E+03	2.7E-02	4.0E-01	14
Benzo[a]fluorene	6.2E+01	2.2E+03	1.9E-02	6.8E-01	14
Benzo[a]pyrene	7.5E-03	1.6E+03	2.4E-06	5.1E-01	5, 14, 17
Benzo[b]chrysene	2.6E+01	1.2E+02	8.2E-03	3.8E-02	14

Table 3. (Continued)

Chemical	Emission Factors (µg/g)[a]		Mass Emitted[1] (g)		Reference
	Minimum	Maximum	Minimum	Maximum	
Benzo[b]fluoranthene	ND	3.0E+02	ND	9.4E-02	5
Benzo[b]fluorene	2.2E+01	1.8E+03	6.9E-03	5.6E-01	14
Benzo[b]pyrene	9.3E-03	3.5E-02	2.9E-06	1.1E-05	17
Benzo[c]phenanthrene	3.6E+02	2.0E+03	1.1E-01	6.2E-01	14
Benzo[e]pyrene	9.7E-03	1.2E+03	3.0E-06	3.9E-01	14, 17
Benzo[g,h,i]perylene	1.5E-02	4.9E-02	4.7E-06	1.6E-05	17
Benzo[ghi]fluoranthene	4.7E+01	1.3E+03	1.5E-02	4.2E-01	5, 14
Benzo[ghi]perylene	3.2E+01	7.5E+02	1.0E-02	2.4E-01	5, 14
Benzo[j]fluoranthene	3.3E+01	2.5E+02	1.0E-02	7.9E-02	14
Benzo[k]fluoranthene	2.5E-03	4.7E+02	7.9E-07	1.5E-01	14, 17
Bibenzo[def,mno]chrysene	8.6E+00	3.3E+02	2.7E-03	1.0E-01	14
Biphenyl	7.9E+01	4.1E+03	2.5E-02	1.3E+00	5, 14
Chrysene	1.7E-02	2.8E+03	5.4E-06	8.7E-01	5, 14, 17
Coronene	4.7E-01	1.5E+02	1.5E-04	4.7E-02	14
Cyclopenta[cd]pyrene	1.7E+02	2.8E+03	5.3E-02	8.7E-01	5, 14
Dibenz[ah]anthracene	NO DATA				
Dibenzopyrene	ND[b]	2.4E+02	ND	7.5E-02	14
Dihydronaphthalene	4.4E+00	4.5E+01	1.4E-03	1.4E-02	14
Diphenylethylene	1.8E+01	2.4E+02	5.7E-03	7.5E-02	14
Diphenylethyne	2.3E+01	9.5E+02	7.2E-03	3.0E-01	14
Ethylbiphenyl	5.3E+00	3.9E+02	1.7E-03	1.2E-01	14
Fluoranthene	1.1E-01	8.6E+03	3.4E-05	2.7E+00	5, 14, 17
Fluorene	1.5E+02	3.7E+03	4.7E-02	1.2E+00	5, 14
Indene	3.9E+01	6.5E+02	1.2E-02	2.0E-01	14
Indeno[1,2,3-cd]pyrene	1.1E-02	8.5E+02	3.4E-06	2.7E-01	14, 17
Methylanthracene	7.9E-01	2.2E+02	2.5E-04	6.9E-02	14
Methylbiphenyl	2.5E+00	3.3E+02	7.9E-04	1.0E-01	14
Methylfluorene	ND	2.6E+01	ND	8.2E-03	14
Methylpyrene	1.1E+02	1.2E+03	3.5E-02	3.7E-01	14
m-Terphenyl	5.5E-01	1.6E+02	1.7E-04	5.0E-02	14
Naphthalene	6.7E+01	9.0E+03	2.1E-02	2.8E+00	5, 14
Perylene	9.2E+00	3.5E+02	2.9E-03	1.1E-01	5, 14
Phenanthrene	2.4E-02	1.8E+04	7.6E-06	5.7E+00	5, 14, 17
Phenylindene	4.9E+00	3.3E+02	1.5E-03	1.0E-01	14
Picene	ND	1.4E+02	ND	4.4E-02	14
Pyrene	5.9E-02	1.4E+04	1.8E-05	4.5E+00	5, 14, 17
Retene	1.9E-02	3.2E-02	5.9E-06	1.0E-05	17
Total PAH			**0.77**	**39**	

ND = not detected
[1] Mass emissions were calculated using the minimum and maximum emission factors for each chemical compound and assuming a sheet of PE with a mass of 314 g is burned.
[a]Micrograms of emission per gram of polyethylene
[b]Not Detected

Table 4. Additional Chemical Compounds Identified Qualitatively in Polyethylene Pyrolysis/Combustion Emissions

Chemical	Reference
Acetaldehyde	23
Acetic acid	23
Acetone	23
Acrolein	23
Methylethylketone	23
Propionaldehyde	23
4- and/or 9-Methylphenanthrene	9
4H-Benz[def]carbazole	9
4H-Cyclopenta[cd]pyrene	9
Acenaphthylene	9
Benzo[a]fluoranthene	9
Benzothiophene	9
Dibenz[a,h]anthracene	9
Dibenzofuran	9

5.0 BIOMASS EMISSIONS

5.1 MECHANISMS OF WOOD PYROLYSIS AND COMBUSTION

Forest (woody) biomass is mainly comprised of cellulose, hemicellulose and lignin polymers that burn via a series of steps: 1) fuel heating and drying, 2) solid fuel pyrolysis to volatiles and char, 3) pyrolysis and oxidation of the volatiles and 4) oxidation of the char.[25] Heat and mass transport processes are closely linked to, and affect the chemical reactions that occur; these chemical reactions in turn release or absorb heat and reaction products, which then feed back to the heat and mass transport mechanisms and can cause overall rates of combustion to increase or decrease.

After heat transfer drives off excess moisture and the fuel has reached a high enough temperature (150-190 °C), cellulosic materials decompose by two alternate pathways.[26] The first pathway is a reduction in the polymer length by bond scission and dominates at temperatures below 300 °C. The cellulosic polymer of wood is broken down into shorter subunits by bond scission, releasing water, forming free radicals and carbonyls, carboxyl and hydroperoxide groups, which then lead to decarboxylation and decarbonylation reactions. This first pathway converts the woody substrate into a reactive carbonaceous char and generates H_2O, CO_2 and CO as the major products, along with the free radicals. The char is characterized by a high surface area, a high degree of reactivity, and a large proportion of aromatic carbon. The aromatic content of the char increases with increasing temperature.

The second pathway, operating above 300 °C, breaks apart the remaining substrate molecules by transglycosylation, fission and disproportionation reactions. This second pathway produces tarry anhydro sugars (e.g., levoglucosan, 1,6-anhydro-ß-D-glucofuranose, and randomly linked oligosaccharides) and low molecular weight volatiles. At higher temperatures (300-500 °C), the tar-forming reactions accelerate and overtake the production of char and gases. At such temperatures, the heat of evaporation of levoglucosan is so endothermic that the pyrolysis process appears to be controlled by the rate of heat transfer rather than the chemical reaction kinetics.

Smoldering and glowing combustion are both characterized by oxidation of the reactive char created from the cellulosic substrate. Smoldering combustion operates at relatively low temperatures and involves the formation of reactive char by pyrolysis, chemisorption of oxygen on the char, production of CO and CO_2, and generation of new reactive sites. Incompletely oxidized volatile pyrolysis products are released, and smoldering combustion is characterized by a high proportion of these products of incomplete combustion. Glowing combustion, which burns the char more rapidly and at higher temperature, is incandescent and requires more oxygen than smoldering combustion, but both are solid-phase combustion processes.[26]

Flaming combustion is the result of oxidation of the gaseous volatiles, which are liberated in the breakdown of the cellulosic structure. These volatiles then are combusted in the gas phase. Flaming combustion is dominated by free radicals rapidly breaking apart larger molecules into simpler compounds and atoms. This involves a chain reaction mechanism that can be self-sustaining (e.g., regenerating the initiating radicals), or branching (generating more radicals). The relatively high rate of heat release created by the combustion of volatiles provides the energy for gasification of the substrate and propagation of the fire.

The rate of combustion is strongly influenced by fuel-specific factors, including the fuel bulk density, the arrangement (porosity) of the fuelbed (e.g., the deviation from the optimum ratio of air spaces to fuel material within the overall fuel array) and the fuel moisture content. This last factor is the driving force behind the use of plastic sheeting and other materials to cover piled forest biomass. At higher fuel moistures, more of the heat from a fire's exothermic reactions is used to vaporize excess water from the intact fuel matrix, resulting in lower temperatures within the fuelbed and enhancing the fuel consumption by smoldering combustion. This produces a much higher proportion of incompletely combusted products (e.g., CO and particulate matter). Conversely, at lower fuel moistures, less of the heat released is used to turn water to steam, and thus more is available to enhance gasification and liberation of volatiles. The volatile compounds burn in the gaseous phase with more oxygen available than in smoldering combustion, resulting in cleaner combustion and production of more completely oxidized combustion products (e.g., CO_2).

In summary, the mechanism of wood combustion is in many ways similar to that of polyethylene combustion. Glowing and smoldering combustion are wood-specific mechanisms that can produce significant products of incomplete combustion, whereas

flaming combustion results in much more complete, and cleaner, emissions. It is very difficult to precisely estimate emissions because they are dependent on the relative strengths of these various pyrolysis and combustion processes, which in turn depend on fuel moisture and pile arrangement.

5.2 Emissions from Wood Combustion

Burning forest biomass produces a diverse array of many hundreds of chemical species, ranging from gases to liquids and solid particulate matter. Relatively small amounts of sulfur oxides (SO_x) are formed due to the low sulfur content of forest fuels. Small amounts of oxides of nitrogen (NO_x) can be produced from endogenous plant nitrogen (e.g., chlorophyll), but temperatures are generally too low to dissociate atmospheric N_2.[27] Table 5 lists maximum mixing ratios for nitrogen species and SO_2 observed above a bench-scale burning system.[28]

Table 5. Nitrogen and Sulfur Species Measured in Forest Biomass Smoke

Compound	Maximum Mixing Ratio (ppm)	Combustion Phase
NO_x	100-160	Flaming
Nitrous oxide	2-19	Flaming
Ammonia	5	Smoldering
Hydrogen cyanide	4-30	Smoldering
Methyl cyanide	2-10	Smoldering
Sulfur dioxide	20-30	Flaming

Carbon by far dominates the emissions from forest biomass burning. The major carbon-bearing pollutants can be broadly broken down as shown in Table 6.[29]

Table 6. Percentage of Carbon Emissions by Phase of Combustion

Emission species	Carbon contribution (% by weight)	
	Flaming phase	Smoldering phase
Carbon dioxide	95.8	86.6
Carbon monoxide	3.0	10.1
Organic carbon particulate	0.7	2.3
Elemental carbon particulate	0.2	0.1
Methane	0.2	0.5
Nonmethane hydrocarbons	0.1	0.4

In flaming combustion, more of the fuelbed carbon is converted to CO_2 and elemental carbon in the particulate matter, while smoldering combustion produces proportionately more CO, organic carbon, methane and nonmethane hydrocarbons. Most of the particulate matter (82%) is smaller than 1 μm in aerodynamic diameter, and only 8% is

above 5 micrometers.[30] Thus, measurements of fine particles less than 2.5 μm in diameter (PM2.5) represent the bulk of particulate emissions. The production of CO is highly correlated to the production of particulate matter and PM2.5, with a coefficient of determination (r^2) between emission factors for these pollutants in the range of 0.8 to 0.84.[31] Combustion efficiency, a measure of how much of the carbon in the fuelbed is converted to CO_2, can range from less than 60% for smoldering-phase combustion to over 95% for flaming-phase combustion. Many of the pollutants emitted from forest fires are well-correlated to combustion efficiency, and algorithms have been developed to estimate their production.[32]

Table 7 lists some of the major air toxics measured in emissions from burning forest biomass, and algorithms for calculating their production as a function of combustion efficiency or a ratio to commonly-measured emissions such as CO or particulate matter.[32]

Table 7. Algorithms and Ratios for Estimating Emissions of Air Pollutants from Prescribed Burning

Pollutant	Regression or ratio	Emission Factor	Units	Mass Emitted[1]	Units	Reliability
Carbon dioxide	η ×1833[a]	1.7E+03	g/kg	1.0E+06	g	±5%
Carbon monoxide	961-η×984	2.6E+01	g/kg	1.6E+04	g	$r^2 = 0.95$
Methane	42.7- η×43.2	1.7E+00	g/kg	9.9E+02	g	$r^2 = 0.77$
Nonmethane hydrocarbons	0.76+EF CH4×0.616[b]	1.8E+00	g/kg	1.1E+03	g	$r^2 = 0.69$
Fine particles (PM2.5)	67.4-η×66.8	1.3E+02	g/kg	7.8E+04	g	$r^2 = 0.74$
Thoracic particles (PM10)	1.18×EF PM2.5	1.5E+02	g/kg	9.2E+04	g	±30%
Particulate Matter (TSP)	93.3-η×90.5	7.3E+00	g/kg	4.4E+03	g	$r^2 = 0.54$
Formaldehyde (HCHO)	0.0137×EF CO-0.0179	3.4E-01	g/kg	2.0E+02	g	±30%
Acrolein	0.0029×EF CO+0.0699	1.5E-01	g/kg	8.7E+01	g	±30%
Acetaldehyde	0.315×EF HCHO	1.1E-01	g/kg	6.4E+01	g	±50%
1,3-butadiene	0.00213×EF CO	5.6E-02	g/kg	3.3E+01	g	±40%
Benzene	0.00592×EF CO	1.6E-01	g/kg	9.3E+01	g	±40%
Toluene	0.00588×EF CO	1.5E-01	g/kg	9.2E+01	g	±40%
o-Xylene	0.00089×EF CO	2.3E-02	g/kg	1.4E+01	g	±40%
m,p-Xylene	0.00161×EF CO	4.2E-02	g/kg	2.5E+01	g	±40%
n-Hexane	0.00017×EF CO	4.5E-03	g/kg	2.7E+00	g	±40%
Benzo(a)pyrene	13×EF PM	9.5E+01	μg/kg	5.7E+04	μg	±50%
PAHs	345×EF PM	2.5E+03	μg/kg	1.5E+06	μg	±50%

[1] Mass emitted from burning one silvicultural debris pile with a diameter and height equal to eight feet (approximate mass = 598 kg).
[a]η = combustion efficiency (%)
[b]EF = emission factor

For woody fuels, piles have relatively high combustion efficiencies, and thus lower emissions of products of incomplete combustion, as compared to broadcast-burned slash. Table 8 lists emission factors for piled silvicultural debris from the Pacific Northwest.[33]

Table 8. Emission Factors for Major Pollutants from Piled Silvicultural Debris

Pile Type	Phase	Emission Factor (pounds per ton of fuel consumed)						
		PM	PM10	PM2.5	CO	CO_2	CH_4	NMHC
Tractor-piled	Flaming	11.4	7.4	6.6	44	3492	2.4	2.2
	Smoldering	25.0	15.9	14.0	232	3124	17.8	12.2
	Fire-average	20.4	12.4	10.8	153	3271	11.4	8.0
Crane-piled	Flaming	22.6	13.6	11.8	101	3349	9.4	8.2
	Smoldering	44.2	33.2	31.0	232	3022	30	20.2
	Fire-average	36.4	25.6	23.4	185	3143	21.7	15.2

Other measurements of emissions from bench-scale burning of forest biomass have identified a variety of PAHs; these are summarized in Table 9, along with an estimated mass of emissions from a typical silvicultural debris pile.[34] A list of quantified oxygenated organic chemicals and other various pollutants from bench-scale studies are presented in Tables 10 and 11. The quantities of each chemical species emitted are listed in Tables 9, 10 and 11. The mass range of each chemical was calculated from the widely-used Consume 2.1 fire consumption and emissions model, assuming a composition of 60 percent Douglas fir and 40 percent western hemlock and assuming a dome shaped pile eight feet high and eight feet in diameter. A fuel bulk density of 27.5 lb/ft^3 was assumed, along with a fuelbed porosity of 20%. A pile with these characteristics was determined to have a mass of 598 kg.

Table 9. Emission Factors and Mass Emissions – Polycyclic Aromatic Hydrocarbons from Fir and Pine Burns

Chemical	Emission Factor (µg/g)		Mass Emitted[1] (g)		Reference
	Minimum	Maximum	Minimum	Maximum	
1-(2-Propenyl)naphthalene	NO DATA				
1,1-Diphenylethylene					
1,2:7,8-Dibenzophenanthrene					
1,2-Binaphthalene					
1,6-Dimethylnaphthalene					
1-Ethylidene indene					
1-Ethylnaphthalene					
1H-Phenalene					
1-Methylanthracene					
1-Methylene indene					
1-Methylfluorene					
1-Methylnaphthalene					
1-Phenylnaphthalene					
1-Phenylphenanthrene					
2,2-Binaphthalene					
2,6-Dimethylnaphthalene					

Chemical	Emission Factor (µg/g)		Mass Emitted[1] (g)		Reference
	Minimum	Maximum	Minimum	Maximum	
2-Ethenylnaphthalene					
2-Ethylnaphthalene					
2-Methylanthracene					
2-Methylbiphenyl					
2-Methylfluorene					
2-Methylnaphthalene	2.265	2.575	1.35	1.54	34
2-Methylphenanthrene					
2-Phenylnaphthalene					
3,4-Dihydrocyclopenta[cd]pyrene					
3-Methylbiphenyl					
3-Methylphenathrene					
4H-Cyclopenta[def]phenanthrene			NO DATA		
4-Methylbiphenyl					
9-Ethenylanthracene					
9-Methylanthracene					
9-Methylphenanthrene					
Acenaphthalene					
Acenaphthene	1.868	2.518	1.12	1.51	34
Acenaphthylene	1.41	2.418	0.84	1.45	34
Acephenanthrylene			NO DATA		
Anthracene	0.429	0.723	0.26	0.43	34
Benz[a]anthracene	0.114	0.25	0.07	0.15	34
Benzo[a]anthracene			NO DATA		
Benzo[a]fluorene					
Benzo[a]pyrene	0.019	0.694	0.011	0.415	34, 35
Benzo[b]chrysene			NO DATA		
Benzo[b]fluoranthene	0.037	0.056	0.022	0.033	34
Benzo[b]fluorene					
Benzo[b]pyrene			NO DATA		
Benzo[c]phenanthrene					
Benzo[e]pyrene	0.024	0.054	0.014	0.032	34
Benzo[g,h,i]perylene			NO DATA		
Benzo[ghi]fluoranthene					
Benzo[ghi]perylene	ND	0.002	ND	0.0012	34
Benzo[j]fluoranthene			NO DATA		
Benzo[k]fluoranthene	0.039	0.136	0.023	0.081	34
Bibenzo[def,mno]chrysene			NO DATA		
Biphenyl					
Chrysene	0.1	0.217	0.06	0.13	34
Coronene			NO DATA		
Cyclopenta[cd]pyrene					
Dibenz[ah]anthracene	ND	ND	ND	ND	34
Dibenzopyrene			NO DATA		
Dihydronaphthalene					

Table 9 (continued)

Diphenylethylene					
Diphenylethyne					
Ethylbiphenyl					
Fluoranthene	1.351	1.766	0.81	1.06	34
Fluorene	0.68	0.857	0.41	0.51	34
Indene	NO DATA				
Indeno[1,2,3-cd]pyrene	ND	ND	ND	ND	34
Methylanthracene	NO DATA				
Methylbiphenyl					
Methylfluorene					
Methylpyrene					
m-Terphenyl					
Naphthalene	13.57	16.96	8.11	10.1	34
Perylene	ND	ND	ND	ND	34
Phenanthrene	2.594	3.938	1.55	2.35	34
Phenylindene	NO DATA				
Picene					
Pyrene	1.066	1.469	0.64	0.88	34
Retene	NO DATA				
Total PAH			**15.3**	**20.7**	

ND = not detected
[1] Mass emitted from burning one silvicultural debris pile with a diameter and height equal to eight feet (approximate mass = 598 kg).

Table 10. Emission Factors of Major Oxygenated Compounds Emitted from the Smoldering Combustion of Wood

Compound	Emission Factor (mg/kg)	Mass Emitted[1] (g)
Acetic acid	4.40E+03	2.63E+03
Methanol	4.30E+03	2.57E+03
Vinyl Acetate	3.00E+03	1.79E+03
1-Hydroxy-2-propanone	2.00E+03	1.20E+03
Pyruvic Aldehyde	2.00E+03	1.20E+03
Formic acid	9.70E+02	5.80E+02
2-Furaldehyde	7.90E+02	4.72E+02
3-Oxobutanoic acid, methylester	7.00E+02	4.19E+02
2-Furanmethanol	2.80E+02	1.67E+02
2-Methoxy-4-methylphenol	2.60E+02	1.55E+02
Propanoic acid	2.50E+02	1.50E+02
2-(5H)-Furanone	2.20E+02	1.32E+02
2-Cyclopenten-1-one	1.90E+02	1.14E+02
2-Methoxyphenol	1.80E+02	1.08E+02
gamma-Butyrolactone	1.70E+02	1.02E+02
5-Methyl-2-furaldhyde	1.50E+02	8.97E+01

Table 10 (continued)

Compound	Emission Factor (mg/kg)	Mass Emitted[1] (g)
Phenol	1.10E+02	6.58E+01
4-hydroxy-3-methoxybenzaldehyde	7.60E+01	4.54E+01
2-Methoxy-4-(1-prop-2-enyl)phenol	6.80E+01	4.07E+01
Crotonic acid	6.80E+01	4.07E+01
2-Acetylfuran	5.40E+01	3.23E+01
m- and/or p-Cresol	4.40E+01	2.63E+01
o-Cresol	4.20E+01	2.51E+01
Benzoic acid	2.00E+01	1.20E+01
o-Hydroxybenzaldehyde	1.50E+01	8.97E+00

Reference: 36

[1] Mass emitted from burning one silvicultural debris pile with a diameter and height equal to eight feet (approximate mass = 598 kg).

Table 11. Emission Rates and Mass Emissions for Various Pollutants from Burning a Silvicultural Pile

Compound	Emission Rate (g/kg)		Mass Emitted[1] (g)		Reference
	Minimum	Maximum	Minimum	Maximum	
Acetic Acid	1.6	4.4	963	2631	37, 38, 36
Acetylene	0.2	0.9	120	526	37, 38
Ethene	1.1	3.3	661	1961	37, 38
Ethane	0.2	0.2	140	140	37
Methane	1.2	19.4	739	11601	37, 39, 38, 40, 35
Carbon monoxide	28.2	359.0	16834	214682	37, 39, 38, 40, 35
Carbon dioxide	1146	1771	685308	1059058	37, 39, 38, 40, 35
Formaldehyde	ND	2.4	ND	1423	37, 39, 38
Formic acid	0.7	1.6	425	939	39, 38, 36
Hydrogen cyanide	0.6	0.6	365	365	38
Methanol	0.8	4.3	493	2571	39, 38, 36
Ammonia	0.3	1.5	169	891	39, 38
Nitric oxide	0.9	2.3	526	1357	37, 39, 38
Nitrogen dioxide	0.6	0.6	360	360	37
Sulfur dioxide	1.2	1.2	705	705	37
PM	6.0	34.2	3588	20452	33, 41, 42, 35, 43
PM10	6.2	12.8	3708	7656	28
PM2.5	2.8	17.6	1674	10525	33, 42, 35, 40, 43

ND = not detected
[1] Mass emitted from burning one silvicultural debris pile with a diameter and height equal to eight feet (approximate mass = 598 kg).

In summary, the burning of silvicultural debris produces a wide range of air emissions, many of which have toxic or reactive properties. The mass of pollutants emitted is quite

large for a typical pile, but piling has been shown to produce fewer emissions per ton of silvicultural debris burned, because it optimizes combustion conditions when compared to broadcast burning of debris in-situ.[44]

6.0 DISCUSSION

In this section, we specifically answer the questions posed by the Committee.

Is pure PE readily available (commercially) and how would one tell PE from other polymer products on the market that are known to contain toxic materials (PVC, styrene, etc.) and heavy metals?

Pure PE is commercially available; however, most of the PE manufactured will contain various types and amounts of additives. The quantities of these chemicals added to the PE would be small and should not significantly affect the types or amounts of chemicals emitted when PE is burned. The carbon black added to the polymer may contain trace amounts of PAHs, metal oxides and other contaminants. Again, this is unlikely to produce any detectable increase in emissions as carbon black comprises a few percent of the total mass of PE and the contaminants are present in only trace amounts in the carbon black itself. One study determined that there was no statistical difference in the heavy metal concentrations found in the residual ash of a coal-fired boiler with, or without the addition of PE waste to the fuel[45]. It would be difficult, if not impossible to differentiate among the three varieties of polyethylene and most other types of plastics by a visual examination of the sheet material.

What is the basic chemistry of PE and how does it combust and react within a pile in an ambient environment?

How PE will pyrolyze and combust within a slash pile can only be surmised based on the available research regarding its behavior when burned in a furnace or alone using kerosene as an accelerant. Several trends are evident in the pyrolysis/combustion behavior of PE. First, the production of PAHs will increase as the combustion temperature increases from 500 to 1000°C. Second, the emissions of light hydrocarbon will peak around 700°C. Third, particulate emissions are the highest at both low and high ends of the temperature range, although the emission factor does not deviate considerably throughout the range of temperatures. Third, complete combustion of PE will not occur at temperatures below 750°C.

How will PE volatilize by itself, and as part of a slash pile?

Based on the available data, it can be assumed that the volatilization of the PE will commence at a relatively low temperature. In the early stage of the pile burn, temperatures will quickly rise from ambient to around 350 to 400 ^{o}C. This is high enough to thermally degrade the PE, but not high enough to allow combustion. The pyrolysates will melt and drip into the hotter region of the fire and volatilize into the atmosphere. Since up to 41 percent of the PE is lost prior to ignition at temperatures lower than 750 ^{o}C, little PE will remain by the time the pile temperature becomes high enough to favor the formation of PAHs. This means the emissions of PAHs from the PE are likely to be low.

Are there any material safety data sheets that include a combustion test of PE?

Material Safety Data sheets do not contain detailed information regarding the products of incomplete combustion of PE because the raw material is not considered hazardous and burning is not an intended use of PE sheeting. The manufacturer provided material safety data sheet for the PE sheeting lists CO_2 and $H_2(O)$ as the compounds emitted during combustion and states CO would be produced under oxygen limiting conditions. The actual emissions from any fuel will vary considerably with the conditions under which it is burned, but are almost never limited to these three chemicals.

Is there a difference in PE emissions between a pile that is completely covered and one that uses PE in the center to create a dry spot for ignition?

A smaller amount of PE would of course produce a proportionately smaller mass of emissions. From the pile as a whole, research has documented that higher fuel moisture results in higher overall emissions due to the increased dominance of smoldering combustion processes. An uncovered pile that is left over a winter can take up to two drip torches of fuel to sustain ignition—this would increase overall emissions due to the excess fuel used. However, when piled forest materials are dry enough to sustain ignition, the combustion of the smaller-diameter materials in the fuelbed produce enough heat to drive off fuel moisture from the larger fuel pieces. This reduces the consumption-limiting effect of high fuel moisture, increases the combustion efficiency and consumes virtually all of the woody material in the pile.

Does it make a difference in the emissions if 1-mil or 4-mil PE sheeting is used?

The amount of PE used will proportionately affect on the overall amount of chemicals emitted from the PE. Using PE sheeting of only 1-mil thickness would cut the emissions by one quarter. If thinner PE is determined to work adequately, its use should be considered. Thinner PE would be more cost-effective, and each roll would be easier to handle since it would weight less per square foot. However, if the thinner PE sheet is easily torn on the fuel pile , it may not be quite as effective at drying the fuels beneath.

Is there any benefit to requiring the PE to sit in the environment for a period of time (weather) prior to burning?

There is no benefit to allowing the PE sheeting time to weather prior to burning. Exposure to ultraviolet radiation will begin to break the polymer down, but this will not have a significant affect on the overall combustion efficiency of the burn.

What are the alternatives to PE and what is the chemical makeup of "impregnated" kraft paper?

The only alternative to PE used by the forest products industry is kraft paper. The kraft paper is often treated with a waxy hydrocarbon (paraffin) to aid in its ability to resist water penetration. Anecdotal reports indicate some problems with the durability of the kraft paper, especially in high-precipitation climates. Paraffin is a long-chain hydrocarbon similar to some of the n-alkane emissions produced from the pyrolysis of PE. Kraft paper is made from cellulose and is therefore similar to the biomass contained in the silvicultural debris piles. The cellulose has been liberated from the lignin during the pulping process using heat, pressure, sodium hydroxide and sodium sulfide. The paper may contain trace amounts of residual sulfur compounds and could produce sulfur-containing emissions upon combustion. The quantity of sulfur emitted is not expected to be large.

Is the use of PE cost effective compared to alternative products?

From an economic standpoint, PE is more cost-effective than paper. The paper used to cover silvicultural debris piles may or may not be coated with paraffin. The coated paper costs about $160 per 3 ft by 200 ft roll, which is 26.7 cents per square foot. PE sheeting comes in numerous sizes, although Grayback Forestry in Oregon has indicated that they purchase the material in rolls 3 ft wide, weighing 22.9 lbs. A roll 3 ft by 400 ft would cost $14.40 (assuming at least 5000 lbs of PE is purchased per order) or about 1.2 cents per square foot.

7.0 CONCLUSION

The benefit obtained from the increased combustion efficiency commensurate with dry biomass fuel favors the use of some sort of moisture barrier to aid in the drying of logging slash piles. The articles reviewed provide no evidence that burning the PE plastic sheeting along with the slash pile would cause a significant impact to air quality, however, the limited amount of information regarding the pyrolysis/combustion of PE in conjunction with woody biomass precludes an ironclad statement. It is, however, likely that the emission factors for PAHs and single ring aromatic compounds obtained for the burning of PE in furnace type conditions overestimates the amount that would be formed during open burning. This is due to the fact that during an open burn, the pile temperature would be much lower than the 900 to 1000 ^{o}C temperatures that favor the formation of PAHs. By the time the higher temperatures are reached, most of the PE will have thermally degraded and volatilized.

Because the conditions under which PE pyrolysis and combustion have been studied are so varied, it is difficult to quantify the expected emissions of hazardous air pollutants. At least two researchers agree on the expected concentration range of TSP (soot) in the smoke from PE pyrolysis/combustion (8 to 36 mg per gram of material). However, other articles provide ranges for PAH emissions that are about 1000 times greater than those

listed in AP-42. The emission factors for the 77 PAHs found indicate that a sheet of 4 mil PE weighing 314 grams would produce between 2.5 and 11.3 grams of TSP and between 0.8 and 39 grams of PAH compounds when burned.

The literature is almost as ambiguous concerning biomass emissions as it is for PE. Using the lowest and highest emission factors for PM found in the literature gives a range of emissions between 3.6 and 20.5 kg per 598 kg pile. Empirical data from Table 8 for crane-piled debris (similar to hand piling) would lead to an estimate of 10.9 kg of PM. Using the TSP emission factor from Table 8 (converting units--18.2 g/kg) in the equation for PAHs listed in Table 7, returns a value of 3.8 grams of PAHs per slash pile. This mass of PAHs is considerably lower than the range of 15 to 21 grams per pile calculated using the emission factors for the 16 PAHs published by Jenkins *et al*. Further complicating the issue, because no published data exist for prescribed burning emissions of most of the 77 PAHs quantified in the PE research, a direct comparison of total PAH emissions can not be made between the two sources.

Unfortunately, the literature has not provided an unequivocal answer to whether burning PE plastic would have any greater impact on air quality than the burning of biomass. This is surprising given that AP-42 emission factors were determined in response to the agricultural industry's practice of burning PE sheeting material. If this is an ongoing practice across the country, then it seems contradictory to allow it for one industry, but not another. Unfortunately at this time, the only way to be sure burning PE with logging slash would not be detrimental to air quality is to conduct an experimental burn using the same type of fuel with and without PE sheeting and to quantify the emissions.

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