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Carcinogenesis, Vol. 3: Polynuclear Aromatic Hydrocarbons, **edited by P. W. Jones and**
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Polynuclear Aromatic Hydrocarbons in Forest Fire Smoke

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The occurrence of polynuclear aromatic hydrocarbons (PAH) in the combustion products of carbonaceous fuels is a well-known phenomenon. Several PAW are known to be carcinogenic in animals. Benzo[a]pyrene (BaP) is the most well-known and studied compound of those classified by the National Academy of Science (NAS) as strongly carcinogenic. Ambient BaP concentrations have been recorded for many years by the National Air Surveillance Networks (NASN) and found to range from less than 1 ng/m^3 in rural areas to a maximum of 50 ng/m^3 in some urban sites (12). The primary sources of PAH (measured as BaP) in the United States are heat generation, which produces 300 to 430 metric tons/year, and the open burning of refuse (primarily coal wastes), which produces 300 to 500 metric tons/year (12). Forest fires and agricultural burning were estimated by NAS to emit 127 metric tons/year in 1968, but that figure was revised to 9.5 metric tons/year in a 1972 estimate (6).

In general, the areas of uncertainty about BaP and PAH are often greater than the areas of knowledge. Although there are well over 1,000 publications on the subject, there still exists much uncertainty on sources, measurement techniques, and environmental effects. The lo-fold disparity in forest fire estimates for BaP is overshadowed by a 100-fold disparity in the estimates for forest fire total suspended particulate matter (TSP). Estimates range from a low of 0.5 x 10^6 tons/year to a high of 54 x 10^6 tons/year (17).

Some of the uncertainty in emission factors associated with forest fires is the result of several "estimates" made by early investigators that were simply off the mark. However, there is much natural variability resulting from the variety of fuels, fire types, and fire intensities. There is also a wide range of emissions within a given fire between the various combustion phases (i.e., flaming versus smoldering). Thus, it is essential to recognize that the emission characteristics of forest fires vary with the time history or burning phases of the fire. It is, therefore, important at the outset to briefly outline the concepts associated with forest fuels and fire types.

FOREST FUELS

Physical Characteristics

Forest fuels are divided into two broad classes-ground fuels and aerial fuels. Ground fuels include all combustible matter lying on the ground, immediately above the ground, or in the ground. The principal materials are dead leaves, needles, grass, fine dead wood, down logs, stumps, low brush and vegetation, and duff (partially decayed vegetative matter). Aerial fuels include all. live and dead material in the upper-forest canopy in the form. of tree branches, crowns, snags (standing dead trees), moss, and high brush.

Chemical Characteristics

The tree, grass, and herbaceous species of forest areas contain approximately 50% carbon, 6% hydrogen, and 44% oxygen.

Macronutrients (nitrogen, sulfur, phosphorus; potassium, calcium, magnesium, and iron) and micronutrients (manganese, zinc, copper, boron, to name a few) are found in small or trace quantities. Exact percentages for each of the elements vary slightly among and between species. For example, nitrogen, the most abundant of the madronutrients and of importance to air quality studies, ranges from 0.2% in the older wood of some species to 1 .0% in the needles of some pines to 2.0% in ‘fallen hardwood leaves (11) .

The elements found in plants are combined by the growth processes into many organic compounds—mainly cellulose, hemicellulose, and lignin. These three polymeric compounds account for over 90% of the dry weight of most forest fuels. The minor constituents, often called extractables, consist of several hundred individual organic chemical compounds that vary greatly among tree species and within various parts of the tree. In this group we find many terpenes, tannins, resins, oils, pectins, gums, free organic acids, and minerals.

The cellulosic content of most wood varies between 41% and 53 %, hemicellulose between 15 % and 25 %, and lignin between 16% and 33 % (3). Lignin is much higher (up to 65%) in decaying. (punky) wood in which the cell wall polysaccharides are partially removed by biological degradation.

CATEGORIZING FOREST BURNING

Wildfires and prescribed fires’ are the two general types that occur in the nation’s forests.

Wildfires

Wildtires, whethercaused by nature or by the accidental/malicious acts of man, are simply fires that are undesirable and bum uncontrolled. Wildfires can be of low intensity and cover only a few acres or can.be the catastrophic fires where depth of the flaming zone. can be hundreds of feet, with the fire energy exceeding that of -the wind field. Damage to the timber, wildlife, and water resources can be devastating.

Prescribed Fires

Some burning in the nation's forest lands takes place according to planned decisions made by forest managers. When fire is used in a forest to achieve a planned silvicultural objective, within a defined area, under exacting weather and fuel conditions, the process is called prescription burning-sometimes referred to as managed or controlled burning.

The major uses of prescribed fire are for the reduction of hazardous fuel accumulations (a form of fire prevention), wildlife habitat improvement, disease control, and disposal of the logging slash debris preparatory to forest regeneration. There is increasing interest in prescribing tires in wilderness areas to maintain near-natural' conditions.

Over two million acres of forest land are treated annually in the Southern States using low-intensity prescription fires. These. fires do not damage or destroy the crop trees but are surface fires that bum the litter of fallen leaves, needles, twigs, low brush, 'and vegetation on the forest floor. Various firing techniques are available to help accomplish a prescribed fire objective. Based on behavior and spread rate, fires move either with the wind (heading fire) or against the wind (backing fire). The heading fire is the most intense because of its faster spreading rate; wider burning zone, and greater flame lengths. The backing fire is characterized by slow spread rates, narrow burning zones, and short flames and is generally the safest firing technique—especially in heavy fuels. Burning on slopes has an effect similar to wind on rate of spread. Downslope fires burning in the foothills, for example, would give much the same results as backing fires in flat country.

RELATIONSHIPS OF FUELS AND TEMPERATURE ON PAH PRODUCTION

Although all organic compounds that contain carbon and hydrogen may serve as precursors of PAH, pyrolysis experiments have shown certain compounds to'be extremely efficient precursors to PAH—especially BaP. These findings (Table. 1) demonstrate the relative unimportance of carbohydrates in the generation of BaP as compared to other less-oxygenated organic precursors.

The hexane-soluble or lipid fraction of tobacco that comprises 6% of the dry-leaf weight accounts for about 60% of the BaP produced by pyrolysis of tobacco (14). These results demonstrate the relative unimportance of. highly oxygenated compounds such as the carbohydrates compared to the less-oxygenated precursors found in a hexane or petroleum ether extract.

TABLE 1. Levels of benzo[a]pyrene produced on pyrolysis (40°C, N_2)

Substance pyrolyzed	μg BaP/g pyrolyzed
Glucose	47.5
Fructose	90.5
Cetlulose	288.8
Steoric acid	1,200
Dotriacontane	3,130
β-Sitosterol	3,750

From ref. 14.

The formation of PAH has been found to be greatly diminished in tobacco with high nitrate concentrations of 1% to 5% (14). It is believed that pyrolytically formed and thermally activated nitrogen oxides react as scavengers of .C,H-radicals, thereby inhibiting PAH formation.

Temperature factors also play a major role in PAH formation. Many experiments (7,14,16) have determined, the optimum formation temperatures for PAH from a wide variety of organic fuels. Some experiments show optimum temperature ranges of 700 to 850°C. However, PAH have been formed in much lower yields at 400°C (4).

In some experiments pure organic compounds have been exposed to pyrolytic conditions and, depending on volatilization, will either distill or pyrolyze. Those same compounds, when mixed in a substrate rich in other organics, behave quite differently. For example, tracer studies (9) have shown that pure dotriacontane in pyrolysis experiments generates substantial quantities of BaP. However, in a burning cigarette dntriacontane is transferred essentially intact into the smoke. Phytosterols, which are high-yield precursors of PAH in the pure state, yield much lower amounts of PAH when burned in a cigarette (14).

The formative mechanism of PAH in the pyrolytic/combustion process is known as pyrosynthesis (1,2,5,13), which is a buildup of carbon fragments into larger molecules in the reducing zone of the burning fuel. Often, the thermal degradation process rather than the chemical nature of the carbonaceous fuel is the controlling factor in the production of PAH compounds. This is illustrated by the low BaP emission factor found in high-efficiency power plants that burn crushed or pulverized coal; whereas lower efficiency, hand-stoked, residential coal furnaces have emission factors of several higher orders of magnitude (8) .

With fuel and temperature influencing PAH formation, it is easy to see that a comprehensive and systematic study will be required to determine PAH production in forest fires. A simple examination of just a few samples from one or two fires will not portray the wide range of thermal environments that are possible for the different kinds of forest fuels and fires.

EXPERIMENTATION

Given the wide range of possible fuel and fire combinations, a preliminary screening experiment was conducted in a series of 12 laboratory fires using slash pine (*Pinus elliottii* Engelm.) needle litter as the fuel. Slash pine is one of the major fuel types involved in prescription burning in the Southeast and is well suited to laboratory burning methods. In the first set of experiments, the needles were 'burned by simulated heading fires and backing fires (three loadings and two replicates each) in the controlled-environment combustion room at the Southern Forest Fire Laboratory (Fig. 1) . The needles were uniformly distributed on a 3- by 4-foot wire basket "fuel bed" in a manner similar to the natural arrangement of fuel (Fig. 2). It should be noted that this procedure only partially simulates the natural fuel bed in that the needles rest on a thin asbestos sheet in the tray rather than a duff and soil layer as in the field. Also, the needles are conditioned to a uniform moisture level, whereas in the field the natural drying process results in a moisture gradient in the fuel.

The experiments are carried out on a bum table equipped with strain gauges in a large (30 ft^3) combustion room that is instrumented with monitors which measure fuel, fire behavior, and emission variables on a real-time basis. All emissions are channeled through a large stack where real-time monitors can be located or a sample withdrawn for subsequent analysis. The slope of the burn table can be adjusted to simulate the effect of wind on the

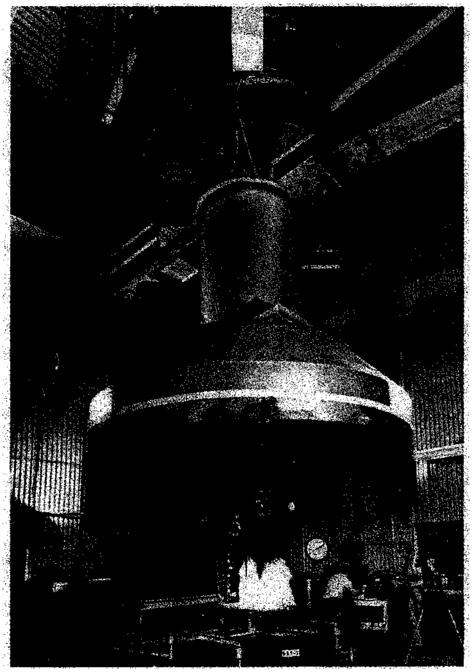

FIG. 1. Controlled-environmental combustion room at the Southern Forest Fire Laboratory.

FIG. 2. Test of a simulated heading fire consuming slash pine needle litter fuel on a weight-loss sensing slope table.

burning process. With ignition at the top of the table, a backing fire can be simulated in which the flame front moves slowly in the opposite direction of the airflow. Flames are low and tilt upslope while the fire moves downslope. With ignition at the bottom of the slope, a heading fire can be simulated. Here the fire moves upslope across the. surface of the fuel in the same direction of the airflow. Flames are much higher than in backing fires and flame tilt is in the same direction as the fire movement. In the backing fire the flames move slowly and efficiently, usually leaving less than 5% of the fuel to smolder behind the flame front. In heading fires the flame front moves rapidly, often skimming over the surface and leaving large amounts of fuel (up to 50%) to thermally decompose in a “residual” or smoldering burning process. During this phase, a heading tire is characterized by low intermittent flames and copious amounts of smoke.

In these experiments the burn table was adjusted to a 45” slope. Moisture content of the fuel was planned in the range of 22% to 24% (dry weight basis). However, a malfunction in the environmental chamber resulted in an 18% to 27% range. These initial screening experiments were designed principally to examine the effect of fire type (i.e., backing versus heading) and fuel loading (low, medium, high) on PAH production.

Sampling Procedure

Particulate matter samples were collected isokinetically on an 8- by 10-inch glass fiber filter in a modified “hi-vol” sampler. Temperature at the collection surface was maintained below 65°C to minimize breakthrough of

PAH. Less than 5% of the particulate matter collected on the filter was lost to the walls of the pickup tube and stack probe. Sampler flow was maintained at a constant 20 cfm. Flow through the stack was constantly monitored.

For the backing fire, one integrated sample over the entire fire history was collected. For the heading fire, one sample was collected during the flaming phase and one, during the smoldering phase. The flaming phase began at ignition and ended when the moving fire front reached the top of the bed; at this time there is a dramatic drop in flames, fire intensity, and temperature with a dramatic rise in smoke production. From a strict combustion science point of view, one might argue that the "flaming phase" should be sampled by a sampler probe in the flames, thereby eliminating any smoldering component from the sample. However, from an emission rate point of view, it is more useful to sample on a fire history basis.

Filters containing the particulate matter were kept in the dark, weighed, and mailed in an aluminum foil wrapper to Battelle Columbus Laboratories for analysis.

PAH Analysis

The objective of the organic analysis was to obtain quantitative analytical data on all detectable PAH species with special regard to NAS‘ carcinogens (12).

At Battelle Columbus Laboratories, each filter was subjected to ultrasonic extraction with methylene chloride at about 50°C; the resulting solution was recovered by centrifugation. Internal standards were then added to the filter extract prior to volume reduction by rotary evaporation and Kuderna-Danish evaporation. Next, each extract was subjected to a Rosen-type liquid chromatographic separation to isolate the PAH fraction before carrying out gas chromatographic-mass spectrometric (GC-MS) analysis. Gas chromatographic separation was achieved using a 6 foot by 2 mm, 3% Dexsil[1] 300 column programmed from 170°C to 340°C at 4°C min^{-1}. Separation of the benzopyrene isomers was accomplished using a 1 foot 1% N,N′-bis(p-methoxybenzylidene)-α,α′-bi-p-toluidine (BMBT) column, isothermal at 120°C.

Mass spectrometric analysis was carried out with a Finnigan 3200 quadrupole mass spectrometer with a chemical ionization source; in: these analyses, methane was used as a carrier and reagent gas, Data acquisition was accomplished with a System Industries 150 data acquisition system, and quantification of the PAH compounds present was accomplished using a Digital PDP8 computer.

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[1] Mention of trade names throughout this chapter does not constitute endorsement by the U.S. Department of Agriculture.

All samples were analyzed using GC-MS with quantification by specific absolute ion current integration. The basis for this quantification procedure is to initially obtain the computer reconstructed gas chromatogram and mass spectrum in the normal fashion; this reconstructed gas chromatogram is then displayed on the CRT terminal and an overlay for the protonated molecular ion of the PAH of interest is superimposed. This overlay represents the ion current corresponding to that specific PAH molecular weight plus one mass unit. If there is an area in the reconstructed gas chromatogram where the overlay indicates that this mass number is prevalent, the mass spectrum of this chromatographic peak is displayed on the CRT unit and the presence of the PAN may be confirmed. If the PAH is found at a correct relative retention time to the internal standards, the computer then sums the ion current due to all important ions in the PAH mass spectrum which represents the area of the peak of interest. Quantification of each PAH was achieved by comparing its total ion current to that of an internal standard of known concentration. The relative ionization efficiencies of the internal standards and many PAN species have been previously determined, and the appropriate factor subsequently used in quantification.

In order to obtain optimum sensitivity during the gas chromatographic-mass spectrometric analyses, the ionization voltage was adjusted at various stages during the analysis. This adjustment necessitated the incorporation of three internal standards so that. an internal standard would elute between each ionization adjustment. The internal standards chosen were g-methylanthracene, 9-phenylanthracene, and 9, 10-diphenylanthracene. Results represent absolute quantification for the entire sample supplied. Detection limit for individual species was estimated to be slightly less than 20 ng. Glass fiber filter blanks and stack background samples gave negligible values for anthracene and phenanthrene. No other PAH compounds were detected.

RESULTS AND DISCUSSION

Emission factors for PAH species from anthracene to coronene are shown in Tables 2 and 3. Data represent the mean value of two replicates. Table 2 clearly shows that heading fires, in general, produce higher total particulate matter but lower PAH values than backing fires. Within heading fires (as shown in Table 3), the flaming phase has relatively low particulate matter and PAH levels as compared to the smoldering phase. A more dramatic comparison of backing versus heading fires is shown in Table 4. Here, total PAH as well ‘as BaP are in greater concentration in backing fire particulate matter by at least an order of magnitude. Thus, a high output of particulate matter, even with a corresponding high percentage of benzene-soluble organics (BSO), does not necessarily result in a high PAH level.

The PAH formation process is a complex series of pyrosynthetic steps involving the chemical condensation and cyclization of free radicals in a

TABLE 2. *PAN from burning pine needles by fire type (ng/g of fuel burned; dry weight basis)*[a]

	Backing fires			Headihg fires		
	0.1 lb/ft²	Cr.3 lb/ft²	0.5 lb/ft²	0.1 lb/ft²	0.3 lb/ft²	0.5 lb/ft²
Anthracene/phenanthrene	12,181	2,189	584	2,525	5,542	6,768
Methyl anthracene	9,400	1,147	449	1,057	4,965	7,611
Fluoranthene	14,563	2,140	687	733	974	1,051
Pyrene	20,407	3,102	1,084	1,121	979	1,133
Methyl pyrene/fluoranthene	18,580	2,466	1,229	730	1,648	2,453
Benzo[c]phenanthrene	8,845	1,808	468	244	142	175
Chrysene/benz[a]anthracene	20,724	5,220	2,033	581	543	836
Methylchryrene	17,753	1.891	a77	282	1,287	1,559
Benzofluoranthenes	12,835	1,216	818	164	129	241
Benzo[a]pyrene	3,454	555	23%	38	40	97
Benzo[e]pyrene	5,836	1,172	680	61	78	152
Perylene	2,128	198	134	33	24	46
Methylbenzopyrenes	6,582	963	384	65	198	665
Indeno[1,2,3-cd]pyrene	4,202	655	169	—	—	—
Benzo[ghi]perylene	6,181	1,009	419	—	—	—
Total PAH	171,750	25,735	10,249	7,632	16,549	22,787
Total suspended particulate matter (TSP)	21 lb/ton	9 lb/ton	5 lb/ton	20 lb/ton	73 lb/ton	118 lb/ton
Benzene-soluble organics	55%	50%	45%	44%	73%	75%

[a] Moisture content for all fires ranged between 18% and 27%.

reducing atmosphere at elevated temperatures (1,2,5). The more complex PAH (five- or six-ring compounds) require a longer residence time of reactants under these conditions in order to form. Backing fires have a slower moving and more stable pyrolysis/combustion zone than heading fires. The combustible gases being fed into this zone remain longer and are subjected to a time/temperature relationship which should be more conducive to the formation of PAH, especially the five- and six-ring compounds. Data in Tables 1 and 2 support this observation. Backing fires produce a very high ratio of five- and six-ring PAH, whereas heading fires show a high ratio of three- and four-ring compounds. In ‘heading fires, the dependence of PAH formation on a time/temperature relationship is also evident. More PAH is produced during the smoldering phase. Temperatures are lower but residence time of evolved gases is longer than the flaming period which is highly turbulent and of short duration. As shown in Table 5, the high-temperature flaming phase of heading fires lasts 3 to 5 min, whereas the smoldering phase lasts up, to 30 min—depending on loading. In the case of the backing fires, the flaming period ranges from 8 to 13 min, with the PAH values highest for the fires with the longer residence time at elevated temperatures. The temperature profile shown in Table 5 was selected at the point of maximum temperature for each of the fires. Although this table does not show the time rate change of temperature for each thermocouple, it does serve to

TABLE 3. PAH from burning pine needles by fire phases (*ng/g* of fuel burned; dry *weight basis*)[a]

	Heading fires by phases					
	0.1 lb/ft²		0.3 lb/ft²		0.5 lb/ft²	
	Flaming	Smoldering	Flaming	Smoldering	Flaming	Smoldering
Anthracene/phenanthrene	1,621	7,049	865	9,046	2'351	8,791
Methyl anthracene	539	3,072	667	8,193	1,909	11,447
Fluoranthene	445	2,317	244	1,516	622	1,331
Pyrene	750	3,078	342	1,454	888	1,291
Methyl **pyrene/fluoranthene**	455	2,383	494	2,501	1,036	3,396
Benzo[c]phenanthrene	228	397	77	189	179	173
Chrysene/benz[a]anthracene	472	1,324	230	769	628	980
Methylchrysene	263	497	343	1,989	466	2,290
Benzofluoranthenes	178	199	69	174	90	347
Benzo[a]pyrene	33	100	17	55	36	140
Benzo[e]pyrene	56	133	45	102	02	203
Perylene	38	33	14	32	27	61
Methylbenzopyrenes	14	397	52	304	75	1,069
Indeno[1,2,3-cd]pyrene	—		—		—	
Benzo[ghi]perylene	—	—				—
Total PAH	5,097	21,779	3,456	26,324	8,389	31,519
Total suspended particulate matter (TSP)	13 lb/ton	55 lb/ton	11 lb/ton	165 lb/ton	31 lb/ton	222 lb/ton
Benzene-soluble **organics**	39%	48%	54%	76%	69%	76%

[a] Moisture content for all fires ranged between 18% and 27%.

TABLE 4. PAH *content* of *total* suspended particulate matter (*TSP*) *from* burning *pine* needler: *μg/g* TSP

Fire type	BaP	Total PAH
Backing		
0.1 lb/ft^2	274	13,982
0.3 lb/ft^{2}t^2	135	6,254
0.5 lb/ft^2	98	4,084
Heading		
0.1 lb/ft^2	3	873
0.3 lb/ft^2	2	399
0.5 lb/ft^2	2	392

illustrate the different temperature profiles for heading and backing fires. The backing fires are characterized by high-bed temperatures in the flaming period relative to gas-phase temperatures, whereas the reverse condition exists for the flaming period in heading fires.

Obviously, many other factors must be examined and correlated to PAH values before causal relationships can be firmly established. Since we have not completed enough investigations to allow rigorous statistical analysis of the data reported, it would be presumptuous to generalize these data to. all types of forest fires. However, it is worth noting that the BaP data reported here with the exception of the lightly loaded (0.1 lb/ft^2) backing fire fall into the general range of values reported elsewhere for the open burning of similar fuels; i.e., landscape refuse 150 ng/g, grass clippings and leaves and

TABLE 5. Weight loss *rate and temperature* profile *of* burning pine needles

Fire type and fuel loading	Fire phase min	Weight loss rate g/min	Temp °C .			
			Fuel bed	3 in	15 in	33 in
Backing^a						
Flaming						
0.1 lb/ft^2	13.3	52	487	97	44	35
0.3 lb/ft^2	0.5	231	620	317	127	62
0.5 lb/ft^2	a.9	347	608	705	155	80
Heading						
Flaming						
0.1 lb/ft^2	2.9	219	469	326	124	75
0.3 lb/ft^2	2.8	464	67	477	207	134
0.5 lb/ft^2	4.0	377	46	511	218	143
Smoldering						
0.1 lb/ft^2	b	b	375	207	103	61
0.3 lb/ft^2			418	128	a6	56
0.5 lb/ft^2			534	126	57	40

[a] The smoldering period for these fires war negligible.

[b] Period of smoldering is highly variable and difficult to quantitate. Time periods range up to 30 min.

branches 346 ng/g (12), and hardwood lea&burning l-00 to 800 ng (BaP, BeP)/g (IO). Benzo[a]pyrene values for the incineration -and open burning of other sources,: have been reported by Hangebrauck et al. (8) and range from 0.2 to 13 ng/g for municipal incinerators to 337 ng/g for the open burning of municipal refuse to 28,600 ng/g for the open burning of automobile components.

Comparison of total PAH values from different studies is difficult because of changing sampling and analysis schemes. However, the leaf incineration study did-employ procedures similar to ours. Total PAH for that study ranged from 12,000 to 78,000 ng/g of fuel ‘burned. Again, this compares, roughly with the data reported here with, the same exception-the lightly loaded (0.1 lb/ft^2 j backing fire which had PAH emission factors several times higher than the other fires. Addition& data for other fuel and fire types are required before we can confidently‘ describe PAH emission factors for all types of forest fires. We are confident that a single value for PAH production will not be appropriate, but that a range of emission factors, as has already been reported for forest fire TSP (15), will be more realistic.

SUMMARY

There are several, different types of forest fires, each with distinct sets of emission characteristics. Emission factors and-rates vary widely with fire behavior and fuel conditions. Wherever* possible, they should be expressed as ranges instead of single average values.

A PAH profile’ has been established for a series of laboratory fires simulating the prescribed burning of pine needle litter. Heading tires (moving with wind) produced substantially more total particulate matter than backing fires (moving against wind). However, the backing fires produced significantly higher amounts “of FAH. Emission factors for benzo[a]pyrene ranged from 238 to 3,454 ng/g in backing fires and from 38 to 97 ng/g in heading fires. Actual amounts formed depend on fuel loading and the residence time of combustible gases in the burning zone.

ACKNOWLEDGMENTS

The authors wish to thank the personnel of ‘the Smoke Management Research and Development Program at the Southern Forest Fire Laboratory for their assistance in this project. A special thanks to Research Foresters Henry McNab and ‘Paul Ryan-McNab for his assistance in fuel bed preparation and Ryan for his assistance with the combustion room facility.

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