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Pyrolytic Deposition of Polynuclear Aromatic Hydrocarbons Due to Slash Burning on Clear-cut Sites

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Polynuclear aromatic hydrocarbons (PNAH) constitute a large group of nonpolar, lipophilic compounds composed of fused aromatic rings. They are produced during incomplete combustion of organic material; quantities of individual PNAH formed are dependent upon both the nature of the starting hydrocarbons and the conditions of combustion (CRITTENDEN and LONG 1976). The most important conditions of combustion which govern PNAH production appear to be burn temperature and oxygen supply.

Release of PNAH into the environment as a result of anthropogenic activities is a cause of growing concern, primarily because many PNAH are procarcinogens (VAN DUUREN 1976). PNAH were the first chemical compounds shown to be carcinogenic; some are classified among the most potent procarcinogens known (SANTODONATO et al. 1981). Knowledge about the occurrence of environmental carcinogens is incomplete and additional data on their production, distribution and fate in the environment is required for a fuller understanding.

A significant potential PNAH source in Oregon is slash burning, the burning of residual materials that remain after logging operations (MIX 1979). Slash is burned on clear-cut sites prior to reforestation in an effort to reduce brush competition with conifer seedlings and to facilitate planting operations. The extent to which slash burning has contributed to environmental PNAH loads has not been investigated. The objectives of this research were to identify qualitatively and quantitatively the deposition, persistence and fate of selected unsubstituted PNAH compounds on burned clear-cut sites in Oregon. The present paper presents data on the initial deposition of PNAH after slash burning. A subsequent paper will consider the fate and persistence of the PNAH produced.

MATERIALS AND METHODS

Study areas. Four clear-cut sites scheduled for slash burning during the summer of 1981 were selected for study. The size and characteristics of these sites are listed in Table 1. The Green Mountain sites are located in the Cascade Mountains in Lane County, approximately 13 km SE of Blue River, Oregon. Benner Wilkinson and Camp Chilcote are located in the Coast Range in Benton County, approximately 15 km SW of Alsea, Oregon. Forests were dominated by Douglas fir *(Pseudotsuga menziesii)* and western hemlock *(Tsuga heterophylla)*.

Table 1. Characteristics and specifications of sites studied.

Site	Size (ha)	Pre-burn fuel loading (t/ha)[a]		Litter moisture (%)	Ignition method	Fuel consumption during burn (t/ha)[b]
		>15 cm	>7.7 cm			
Green Mountain #2	6	30.67	37.71	39	drip torch	8.23
Green Mountain #3	7	2.51	9.12	51	drip torch	5.36
Benner Wilkinson #2	27	NA[c]	NA	52	drip torch	NA
Camp Chilcote #2	20	NA	NA	38	helicopter	NA

[a] Data on fuel loading and fuel consumption from LITTLE et al.(1982).
[b] Fuel consumption for material less than 7.6 cm in diameter.
[c] NA signifies comparable data not available.

Field sampling. A sampling plot approximately 50 m X 50 m was established in a representative portion of each slash burn. A forest litter sample was collected from each site once before burning and on three occasions during the first ten days after burning. Each litter sample consisted of a pooled composite of 50 subsamples, obtained randomly throughout the sample plot. Each subsample contained all the litter within a 5 cm X 5 cm area of the forest floor. Soil samples were taken with a clean spade from site Green Mountain #2 before and after burning in order to evaluate potential PNAH deposition within the soil profile. Each soil sample consisted of a pooled composite of 25 subsamples, collected at depth increments of 0-2 cm and 2-5 cm. In order to convert soil PNAH concentrations (ng/g) into units of g/ha within the various soil depth classes, it was necessary to determine soil bulk density. This was accomplished using a sand cone (BLAKE 1965). All samples were placed in a dark cooler, transported to the laboratory, and stored in a dark freezer until the time of analysis.

Chemicals. The following solvents were purchased from J. T. Baker Chemical Co. and used as received: Photrex grade dimethyl sulfoxide ($\mathrm{ME_2SO}$), HPLC grade acetonitrile, HPLC grade methanol, and reagent grade toluene. Ethanol, trimethyl pentane and benzene were redistilled in glass. Water for use as an HPLC solvent was pre-filtered in a milli-Q system (Millipore Corp.). Other materials included anhydrous sodium sulfate (J. T. Baker); Sephadex LH-20 (Pharmacia Inc.), bed size 1.7 X 35 cm packed in toluene-ethanol (1:1); and florasil (60-100 mesh) (J. T. Baker) which was washed in distilled water and methanol, oven dried, baked at 250° C for 6 hr, and deactivated with 4% water. PNAH standards were obtained for 18 compounds from Ultra Scientific Corp., Hope, RI; Analabs, North Haven, CT; and J. E. Meeker, EPA, Research Triangle Park, NC.

Extraction and clean-up. Aliquots of approximately 60-80 g of litter or 120 g of soil were Soxhlet extracted for 24 hr in methanol, followed by methanol-benzene (2:3) for an additional 24 hr as suggested by HITES et al. (1980). Recoveries were calculated by adding a known spike of ^{3}H-benzo(a)pyrene (Amersham Corp.) to each sample prior to extraction and counting a known fraction of the cleaned-up extract. Additional aliquots were dried to constant weight at 105° C for percent moisture determination, followed by combustion at 475° C for 16 hr to determine weight loss of organic matter.

PNAH methods employed in this study involved a modification of procedures described by Dunn (DUNN and ARMOUR 1980). Extracts were subjected to rotary evaporation to remove benzene and methanol, and resuspended in trimethyl pentane. Subsequent clean-up involved water washing, florasil chromatography, Me_2SO partitioning, and Sephadex chromatography. Samples were brought to a volume of 2 ml for litter and 1 ml for soil samples and analyzed using HPLC.

HPLC. Individual PNAH were separated on a Spectra-Physics Model 8000 HPLC with data system, Perkin-Elmer HC-ODS column, with acetonitrile-water gradient mobile phase. Eluted compounds were detected with a Schoeffel Model 770 variable wavelength UV detector (296 nm) and a Schoeffel Model 970 variable wavelength fluorescent detector (326 excitation, >412 emission) connected in series. Phenanthrene and triphenylene were quantified using their UV absorbance. All other PNAH were quantified using their fluorescence. Four replicates were chromatographed for each pooled sample and a mean result reported. All PNAH were verified in one sample from site Green Mountain #2 with a Finnigan Model 4023 GS-MS computer system.

RESULTS AND DISCUSSION

Eight PNAH were identified and quantified in post-burn litter samples taken from four clear-cut sites. Table 2 lists the compounds identified, abbreviations used throughout this paper for each, and their current classification. Verification studies with GC-MS also indicated the presence of chrysene, which was not detected with HPLC, presumably due to the presence of interfering compounds with similar retention times. Mean extraction and clean-up recovery for litter samples was 53%. Additional PNAH have been reported to occur in smoke samples from wood stoves and fireplaces (COOPER, 1980, DEANGELIS et al. 1980) and from burning grass clippings, leaves and branches (HANGEBRAUCK et al. 1964). It seems reasonable to assume that these compounds (notably pyrene, benzo(e)pyrene, and benzo(a) anthracene) were also deposited in the present study, but were masked by interfering compounds during HPLC analysis.

Table 3 summarizes the data on PNAH levels before and after slash burning at the four sites. Data from the two Green Mountain sites offer a good opportunity to compare PNAH production between sites, since they differed markedly in fuel loading and pre-burn litter moisture (Table 1). Those two sites were under study by the U.S. Forest Service, Pacific NW Forest and Range Experimental Station, to compare post-harvest fuel loading and consumption resulting from two different levels of wood fiber removal. Unit #2 was yarded according to current practice (i.e. all material larger than 20 cm in diameter by 3 m was removed). Unit #3 was yarded to a closer utilization standard, removing all material larger than 15 cm X 1.8 m or 41 cm X 0.6 m (LITTLE et al. 1982). Site Green Mountain #2, which contained higher fuel loading and lower litter moisture, also exhibited significantly greater duff reduction (LITTLE et al. 1982), and substantially higher PNAH deposition (Table 3). Camp Chilcote had the lowest pre-burn litter moisture of the sites analyzed (Table 1), and also the greatest PNAH deposition (Table 3). However, Camp Chilcote was unusual, in that the burn was ignited by helicopter, which may have influenced burn intensity and PNAH deposition. Although not conclusive, the data suggest that fuel loading and/or fuel moisture may be important factors affecting PNAH deposited during slash burning.

Table 2. PNAH compounds identified and quantified on clear-cut sites after slash burning.

Compound	Abbreviation	Classification	
		EPA[a]	NCI[b]
phenanthrene	Phen	PP	
fluoranthene	Fluor	PP,TP	P/Co,M
triphenylene	Tri		
benzo(k)fluoranthene	BkF	PP,TP	S
benzo(a)pyrene	BaP	PP,TP	C,M
benzo(ghi)perylene	BGHIP	PP	P/Co,M
indeno(1,2,3-cd)pyrene	IP	PP,TP	C,M
coronene	Cor		

[a] EPA classification: PP-priority pollutant; TP-toxic pollutant (KEITH and TELLIARD 1979).

[b] NCI classification: C-recognized carcinogen; S-suspected carcinogen; P/Co-tumor promotors or cocarcinogens; M-Ames test mutagens (NCI et al. 1981).

To minimize the effects of sampling variability, PNAH deposition can best be described by taking the mean value of 3 samples (Table 3). Deposition of lower molecular weight, 3-4 ring compounds, was considerably higher than deposition of 5-7 ring compounds on all sites studied. MCMAHON and TSOUKALAS (1978) obtained similar PNAH distributions in aerosol emissions from laboratory fires using slash pine *(Pinus elliottii)* needle litter as fuel. Since PNAH formation requires a complex series of pyrosynthetic steps, formation of the more complex 5-7 ring compounds requires a longer residence time of reactants under suitable pyrolytic conditions (MCMAHON and TSOUKALAS 1978). Lower molecular weight PNAH appear to predominate in both aerosol emission and deposition on slash burn sites.

There is considerable variability in PNAH emission and deposition from forest fires and prescribed burning due to different fuels, fuel moisture, fire types, and fire intensities. Nevertheless, PNAH deposited on the 4 sites in this study generally differed by less than an order of magnitude. PNAH levels (g/ha) were averaged for all 4 sites to obtain a rough estimate of PNAH deposition due

Table 3. PNAH concentrations in litter collected before and after burning on four clear-cut sites.

Site	Days Since Burn	Phen	Fluor	Trib[b]	BkF	BaP	BGHIP	IP	Cor
		PNAH Concentration[a]							
GM 2	Pre-burn	ND	ND	ND	ND	ND	ND	ND	ND
	0.6	ND	ND	395 (422)	12 (13)	63 (67)	42 (45)	52 (55)	ND
	2.0	762 (603)	309 (245)	355 (281)	23 (18)	92 (73)	104 (82)	54 (43)	5 (6)
	10.0	443 (427)	300 (289)	646 (623)	17 (17)	150 (145)	28 (27)	43 (42)	ND
GM 3	Pre-burn	ND	ND	ND	ND	ND	ND	ND	ND
	1.1	215 (201)	33 (30)	111 (103)	3 (3)	15 (14)	35 (32)	11 (10)	ND
	5.5	121 (136)	94 (106)	ND	3 (3)	2 (2)	10 (11)	6 (7)	ND
	9.0	ND	86 (116)	ND	4 (5)	12 (17)	12 (16)	10 (14)	ND
BW	Pre-burn	21 (23)	ND	ND	ND	ND	ND	ND	ND
	0.6	1310 (773)	882 (521)	1297 (765)	26 (15)	74 (44)	102 (60)	72 (42)	ND
	1.9	ND	ND	727 (620)	10 (9)	43 (37)	71 (61)	71 (60)	ND
	2.8	247 (111)	379 (169)	ND	22 (10)	51 (23)	54 (24)	53 (24)	ND
Chil.	Pre-burn	ND	18 (18)	ND	2 (2)	1 (1)	3 (3)	4 (4)	2 (1)
	0.9	1286 (752)	345 (196)	156 (352)	25 (15)	105 (61)	68 (25)	69 (40)	ND
	1.9	1247 (836)	856 (578)	984 (660)	89 (59)	316 (212)	154 (104)	258 (173)	16 (11)
	3.8	ND	26 (27)	ND	29 (30)	108 (111)	96 (99)	56 (57)	15 (16)
		Mean Deposition Values for 3 Sampling Occasions							
GM 2		602 (515)	304 (267)	465 (442)	17 (16)	102 (95)	58 (51)	50 (47)	5 (6)
GM 3		168 (168)	71 (84)	111 (103)	3 (4)	10 (11)	19 (20)	9 (10)	ND
BW		778 (442)	630 (345)	1012 (662)	19 (11)	56 (35)	76 (48)	65 (42)	ND
Chil.		1266 (794)	411 (267)	570 (506)	48 (35)	176 (128)	106 (76)	128 (90)	16 (14)

[a] All concentrations reported as ng/g organic material and (g/ha). Entries reported as not determined (ND) were due to either excessive chromatographic interference or levels below HPLC detection limits.

[b] Values reported for triphenylene are approximations only, due to chromatographic interference.

to slash burning. Based on an average of 43,700 ha of slash (7 yr average, 1975-81) burned per year in western Oregon (OREGON DEPARTMENT of FORESTRY 1981), estimated annual deposition in t/yr were calculated and are presented in Table 4.

Table 4. Concentration of PNAH deposited on slash burn sites (g/ha), reported as a mean of 4 sites, and estimated deposition (t/yr) in western Oregon.

Estimates	PNAH							
	Phen	Fluor	Tri	BkF	BaP	BGHIP	IP	Cor
Mean concentration (g/ha)	480	241	428	16	67	49	47	5
Estimated deposition (t/yr)	21.0	10.5	18.7	0.7	2.9	2.1	2.1	0.2

Utilizing fuel consumption data from LITTLE et al. (1982), deposition factors (g PNAH deposited/kg fuel combusted) were calculated for the Green Mountain #2 and Green Mountain #3 sites and are included in Table 5. Calculated deposition factors for fluoranthene (0.016-0.032), BaP (0.002-0.012), and BGHIP (0.004-0.006) are similar to aerosol emission factors (g/kg) calculated for wood burning stoves (DEANGELIS et al. 1979), which were 0.022, 0.0025, and 0.0059 respectively. If aerosol emission factors are similar for slash burning and for wood burning stoves, then quantities of PNAH in aerosol emissions from slash burning would be expected to be approximately equivalent to those deposited on the site. Although aerosol emissions of PNAH from slash burning have not been studied in the field, similarities in combustion between slash burning and wood burning stoves are suspected. MCMAHON and TSOUKALAS (1978) calculated aerosol emission factors for slash pine needle combustion in a laboratory situation which were more than an order of magnitude higher than deposition factors calculated in this study. However, those laboratory emission factors are probably unreasonably high in comparison to slash burns in the field due to the low moisture content of the needles (18-20%) and to combustion on an asbestos sheet rather than on a moist duff and soil layer, as in the field. Thus, the evidence suggests aerosol emissions comparable to, or higher than, depositions.

Many studies on PNAH emissions have concentrated on BaP, due to its potency as a procarcinogen. Estimated BaP deposition on slash burn sites in western Oregon is 2.9 t/yr (Table 4). Based on the analysis presented above, it is assumed that aerosol emission of BaP from slash burn sites are equal to, or greater than, 2.9 t/yr. MCMAHON and TSOUKALAS (1978) expressed an uncertainty about many estimates in the literature of BaP emissions from combustion sources. BaP emission from forest and agricultural fires throughout the U.S. was originally estimated to be 127 t/yr (NAS 1972), and later revised to 9.5 t/yr (EPA 1975). In view of the high BaP deposition on slash burns, suspected comparable aerosol emissions, and COOPER's (1980) estimate of 1.27 t/yr of BaP emitted from residential wood combustion in the Portland, Oregon/Vancouver, Washington area alone, the EPA estimate of 9.5 t/yr should be questioned as being too low.

Table 5. Deposition factors (g PNAH deposited/kg fuel combusted) for sites Green Mountain #2 and #3.

Site	Deposition factor (g/kg)							
	Phen	Fluor	Tri	BkF	BaP	BGHIP	IP	Cor
Green Mt.#2	0.063	0.032	0.054	0.002	0.012	0.006	0.006	0.001
Green Mt.#3	0.031	0.016	0.019	0.001	0.002	0.004	0.002	N.D.

PNAH levels found in the top 2 cm of soil on site Green Mountain #2 before and after burning are presented in Table 6. Pre-burn background levels of PNAH in the soil fell within the range reported elsewhere for pristine sites (LAFLAMME and HITES 1978, SANTODONATO et al. 1981). There is considerable evidence that PNAH in soils are due primarily to atmospheric deposition of combustion-generated PNAH from anthropogenic activities (MIX, in press). However, natural forest fires cannot be discounted as a potential source of PNAH in soils of western Oregon. Fire has historically been a normal process in Pacific Northwest ecosystems, occurring every 50-400 years in Douglas fir forests prior to fire control programs (MARTIN et al. 1976). PNAH levels in soil did not increase appreciably after burning (Table 6), indicating that the bulk of PNAH production took place within the litter, rather than the soil layer.

Table 6. PNAH levels in the top 2 cm of soil before and after burning of site Green Mountain #2.

Time since burn (wks)	PNAH concentration as ng/g dry weight (g/ha)						
	Phen	Fluor	Tri	BkF	BaP	BGHIP	IP
Pre-burn	4.2(0.5)	4.4(0.6)	4.4(0.6)	2.1(0.3)	0.8(0.1)	1.4(0.2)	2.5(0.3)
1.0	N.D.	8.7(1.1)	18.6(2.4)	0.9(0.1)	1.6(0.2)	2.1(0.3)	1.3(0.2)

The practice of slash burning prior to reforestation is a convenient tool which reduces brush competition with conifer seedlings, increases initial availibility of certain nutrients, and facilitates planting. However, the effects of fire on the site are not well understood; much of the literature is confusing or seemingly contradictory due to a lack of complete data and burn conditions (BOYER and DELL 1980). Potential long-term effects on site productivity are also not well understood. The production of significant quantities of PNAH constitutes an additional environmental concern which should be taken into consideration in the evaluation of slash burning as a forest management tool.

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