

AN ABSTRACT OF THE THESIS OF

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Title: Deposition and Persistence of Polynuclear Aromatic Hydro-

carbons after Slash Burning Clear-cut Sites in Oregon

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Michael C. Mix

Research has been completed which identifies qualitatively and quantitatively the deposition, persistence and fate of polynuclear aromatic hydrocarbons (PNAH) on burned clear-cut sites in Oregon. Eight PNAH were identified and quantified in post-burn litter samples taken from four slash-burned sites. Deposition of lower molecular weight, 3-4 ring compounds was considerably higher than deposition of 5-7 ring compounds on all sites, with mean deposition values ranging from 480 g/ha for phenanthrene to 5 g/ha for coronene. PNAH levels were not appreciably higher in soil immediately after burning, indicating that the bulk of PNAH production took place within the litter, rather than the soil layer. Persistence studies indicated that phenanthrene and fluoranthene, three and four ring compounds, were gradually lost from litter, reaching concentrations below detection limits (approximately 2 g/ha) less than two years after burning. Higher molecular weight PNAH were considerably more

persistent in the litter, decreasing after five years approximately to 19-23% of initial deposition. Movement into the top 2 cm of the soil profile was more pronounced for the lower weight PNAH, but all compounds appeared to equilibrate between litter and soil on the basis of organic content within one year after burning. Differential persistence and fate of PNAH on slash burn sites is explained by the physical chemical characteristics of the compounds, such as solubility, vapor pressure, and octanol-water partition coefficient.

Deposition and Persistence of Polynuclear Aromatic
Hydrocarbons after Slash Burning Clear-cut
Sites in Oregon

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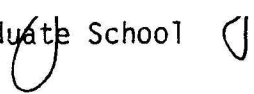
Redacted for Privacy

Professor of Biology in charge of major

Redacted for Privacy

Chairman of Department of General Science

Redacted for Privacy

Dean of Graduate School 

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DEPOSITION AND PERSISTENCE OF POLYNUCLEAR AROMATIC HYDROCARBONS AFTER SLASH BURNING CLEAR-CUT SITES IN OREGON

INTRODUCTION

Current interest in chemical carcinogenesis suggests an important need for additional information concerning the production, fate and persistence of carcinogenic agents in the environment. Polynuclear aromatic hydrocarbons (PNAH) include some of the most potent pro-carcinogens known. Their release into the environment as a result of man's activities constitutes a growing environmental concern. PNAH comprise a large group of nonpolar, lipophilic compounds composed of fused aromatic rings, which are produced during incomplete combustion of organic material. Quantities produced depend upon the nature of the starting hydrocarbons and the conditions of combustion (1).

Research in recent years has demonstrated the ubiquitous environmental distribution of PNAH in soils, sediments, aquatic organisms, and atmospheric samples. The major source of these compounds has been a point of some contention. Since marine and estuarine sediments act as repositories of PNAH, as well as many other pollutants, they have become the focus of numerous investigations concerned with environmental PNAH distributions (2-6). Several possible sources have been suggested for these marine PNAH assemblages, including forest and grassland fires (2), burning of fossil fuels (7,8), and petroleum inputs (3,9). Route of entry into the marine environment from these sources would include such processes as runoff, fuel

spillage, and deposition of air-bourne particulates.

There now seems to be a concensus that most, but not all, PNAH in the sedimentary environment are attributable to combustion processes (10,11). This conclusion is based upon the distribution of alkyl-substituted PNAH measured relative to the parent compounds. Assigning sedimentary PNAH to either natural (forest fire) or anthropogenic sources is difficult and is the crux of much controversy (5). Morales et al. (12) found greatly increased levels of benzo(a)pyrene (BaP) in air samples taken in downtown Caracas, Venezuela at the start of the dry season. This increase is coincident with the recurrence of forest fires in the surrounding mountains. Seasonal difference in BaP concentrations in mussels (*Mytilus edulis*) inhabiting Yaquina Bay, Oregon have reflected a general trend of increasing concentrations in winter followed by a decrease in summer (13,14). Increasing winter BaP concentrations correlate well with increased runoff from the watershed due to heavy winter rains. A significant potential source of PNAH within these watersheds, and throughout western Oregon, is slash burning, the burning of residual materials that remain after logging operations (15). Slash is burned on clear-cut sites in order to reduce competition with conifer seedlings and to facilitate planting (16). The extent to which slash burning has contributed to environmental PNAH loads is not known. This research was undertaken to identify qualitatively and quantitatively the deposition, persistence and fate of PNAH compounds on burned clear-cut sites in the Cascade Mountains and Coast Range of Oregon. The first research paper in this dissertation presents data on the initial

deposition of PNAH as a result of slash burning. The second paper considers the persistence and fate of the PNAH produced.

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PYROLYTIC DEPOSITION OF POLYNUCLEAR AROMATIC HYDROCARBONS DUE TO
SLASH BURNING ON CLEAR-CUT SITES

Timothy J. Sullivan and Michael C. Mix

Department of General Science, Oregon State University,
Corvallis, OR 97331

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 (1). 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 (2). PNAH were the first chemical compounds shown to be carcinogenic; some are classified among the most potent procarcinogens known (3). 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 (4). 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 I.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*).

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.

Table I.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

^aData on fuel loading and fuel consumption from Little et al. (11).

^bFuel consumption for material less than 7.6 cm in diameter.

^cNA signifies comparable data not available.

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 (5). 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 (ME₂SO), 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. (6). Recoveries were calculated by adding a known spike of ^3H -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 (7). 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 GC-MS computer system.

RESULTS AND DISCUSSION

Eight PNAH were identified and quantified in post-burn litter

samples taken from four clear-cut sites. Table I.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 (8,9) and from burning grass clippings, leaves and branches (10). 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 I.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 I.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 (11). Site Green Mountain #2, which contained higher fuel loading and lower litter moisture, also exhibited significantly greater duff reduction (11), and substantially higher PNAH

Table I.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		

^aEPA classification: PP-priority pollutant; TP-toxic pollutant (21).

^bNCI classification: C-recognized carcinogen; S-suspected carcinogen; P/Co-tumor promoters or cocarcinogens; M-Ames test mutagens (22).

deposition (Table I.3). Camp Chilcote had the lowest pre-burn litter moisture of the sites analyzed (Table I.1), and also the greatest PNAH deposition (Table I.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.

To minimize the effects of sampling variability, PNAH deposition can best be described by taking the mean value of 3 samples (Table I.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 (12) 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 (12). 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 to slash burning. Based on an average of 43,700 ha of slash (7 yr

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

Site	Days Since Burn	PNAH Concentration ^a							
		Phen	Fluor	Trib ^b	BkF	BaP	BGHIP	IP	Cor
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)

^aAll 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.

^bValues reported for triphenylene are approximations only, due to chromatographic interference.

average. 1975-81) burned per year in western Oregon (13), estimated annual deposition in t/yr were calculated and are presented in Table I.4.

Utilizing fuel consumption data from Little et al. (11), 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 I.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 (14), which were 0.002, 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 (12) 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

Table I.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

Table I.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.

to its potency as a procarcinogen. Estimated BaP deposition on slash burn sites in western Oregon is 2.9 t/yr (Table I.4). Based on the analysis presented above, it is assumed that aerosol emissions of BaP from slash burn sites in western Oregon are equal to, or greater than, 2.9 t/yr. McMahon and Tsoukalas (12) 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 (15), and later revised to 9.5 t/yr (16). In view of the high BaP deposition on slash burns, suspected comparable aerosol emissions, and Cooper's (8) 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.

PNAH levels found in the top 2 cm of soil on site Green Mountain #2 before and after burning are presented in Table I.6. Pre-burn background levels of PNAH in the soil fell within the range reported elsewhere for pristine sites (3,17). There is considerable evidence that PNAH in soils are due primarily to atmospheric deposition of combustion-generated PNAH from anthropogenic activities (18). 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 (19). PNAH levels in soil did not increase appreciably after burning (Table I.6), indicating that the bulk of PNAH

Table I.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)

production took place within the litter, rather than the soil layer.

The practice of slash burning prior to reforestation is a convenient tool which reduces brush competition with conifer seedlings, increases initial availability 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 (20). 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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PERSISTENCE AND FATE OF POLYNUCLEAR AROMATIC HYDROCARBONS DEPOSITED
ON SLASH BURN SITES IN THE CASCADE MOUNTAINS AND COAST RANGE OF
OREGON

Timothy J. Sullivan and Michael C. Mix

Department of General Science, Oregon State University,
Corvallis, OR 97331

Abstract. The persistence of polynuclear aromatic hydrocarbons (PNAH) on slash burn sites and movement of these compounds between compartments of the sites has been investigated in the Cascade Mountains and Coast Range of Oregon. Phenanthrene and fluoranthene were gradually lost from the litter, reaching concentrations below detection limits (approximately 2 g/ha) less than two years after burning. Higher molecular weight PNAH were considerably more persistent in the litter, decreasing after five years approximately to 19-23% of initial deposition. Movement into the top 2 cm of the soil profile was more pronounced for the lower molecular weight PNAH, but all compounds appeared to equilibrate between litter and soil on the basis of organic content within one year after burning. Differential persistence and fate of PNAH on slash burn sites is explained by physical chemical characteristics of the compounds, such as solubility, vapor pressure and octanol-water partition coefficient.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PNAH) comprise a diverse group of nonpolar, lipophilic compounds produced during incomplete

combustion processes. Due to the procarcinogenic activity of several PNAH (1), this group of compounds is of considerable environmental concern. It is therefore essential to develop a better understanding of the sites of PNAH production, quantities produced, transport between environmental compartments, and persistence of these compounds (2). In a previous paper (3) we identified qualitatively and quantitatively PNAH deposition on clear-cut sites as a result of slash burning. A total of eight PNAH were quantified on four slash burn areas in western Oregon. In the present paper we describe PNAH persistence over time on the areas and their movement from charred litter into soil and an adjacent stream.

EXPERIMENTAL SECTION

Study areas. Of the four sites on which PNAH deposition was measured (3), three were chosen for an evaluation of PNAH persistence. After burning, PNAH levels were determined in litter samples collected from sites Green Mountain #2 and #3 for a one year period, and from site Benner Wilkinson #2 for a one month period. In order to evaluate potential long-term persistence, litter samples were collected from a three year old slash burn (Chintimini North, V-1) and a five year old burn (Benner #1). The Green Mountain sites are located in the Cascade Mountains in Lane County, Oregon. All other sites are located in the Coast Range in Benton County, Oregon.

Field Sampling. Sampling plots approximately 50 m X 50 m were established in each study area. Forest litter samples were collected as pooled composites of 50 subsamples, scattered randomly throughout the plot. Each subsample contained all the litter covering a 5 cm

X 5 cm area. Soil samples were collected with a clean spade at depth increments of 0-2 and 2-5 cm. Each soil sample was a pooled composite of 25 subsamples. Soil bulk density was determined by the method suggested by Blake (4). This sampling protocol allowed expression of PNAH levels in units of g/ha both within the charred litter and within the various soil depth classes. Litter and soil samples were transported to the laboratory in a cooler and frozen until time of analysis.

During the year after burning, water samples were collected on several occasions from a small stream (Green Creek) which flows through site Green Mountain #3. Samples were collected approximately 25 m above and 25 m below the clear-cut. For each sample, 500 ml of water was drawn in increments into a Schleicher and Schuell (Keene, NH) pneumatic hand pump system, first passing through a SS #25 glass micro fiber filter to trap particulates, and then through a Sep-Pak C₁₈ cartridge (Waters Associates, Inc., Milford, MA) at approximately 20 ml/min. Filters and cartridges were returned to the laboratory for elution of PNAH.

Chemical Analysis. Litter and soil samples were Soxhlet extracted in methanol followed by methanol/benzene (2:3) for a total of 48 hrs. Clean-up of sample extracts involved water washing, florasil chromatography, dimethyl sulfoxide partitioning, and Sephadex chromatography. Mean recoveries, determined by adding a known spike of ³H-benzo(a)pyrene before extraction and counting an aliquot of the cleaned-up extract, were 53% for litter and 57% for soil samples. PNAH were separated on a Spectra-Physics Model 8000 HPLC

with data system (Perkin-Elmer ODS column, acetonitrile-water gradient mobile phase), and detected with a Schoeffel Model 770 variable wavelength UV detector and Schoeffel Model 970 variable wavelength fluorescence detector connected in series. See Sullivan and Mix (3) and Mix and Schaffer (5) for additional details regarding chemicals and analytical methods. Phenanthrene was quantified by UV absorbance and all other PNAH reported in this paper were quantified by their fluorescence. Four replicates were chromatographed for each pooled sample, and reported as a mean value. Identities of all PNAH were verified in one litter sample from site Green Mountain #2 using a Finnigan Model 4023 GC-MS computer system.

Sep-Pak cartridges were eluted with 2 ml of tetra hydrofuran (J.T. Baker), which was then evaporated under nitrogen, brought to 50 ul volume in toluene, and subjected to HPLC analysis. Water filters were Soxhlet extracted for 24 hrs in toluene; the extract was dried by passing through anhydrous sodium sulfate, evaporated to 50 ul volume, and analyzed with HPLC. Recovery rates for PNAH from Sep-Pak cartridges has been reported to be 60-100% (6).

RESULTS AND DISCUSSION

In a previous paper (3) we identified and quantified eight PNAH compounds in post-burn litter samples. Persistence of six of these PNAH on sites Green Mountain #2 and #3, and Benner Wilkinson #2 is presented in Table II.1. Triphenylene was excluded from this analysis due to excessive chromatographic interference, although it appeared that triphenylene followed a pattern similar to phenanthrene and fluoranthene on all sites. Coronene was also excluded

Table II.1. PNAH concentrations in forest litter collected from sites Green Mountain #2 and #3, and Benner Wilkinson #2 before and after slash burning.

Sample Site	Time Since Burn (Wks)	PNAH concentration (g/ha)					
		Phen	Fluor	BkF	BaP	BGHIP	IP
GM #2	Pre-burn	ND	ND	ND	ND	ND	ND
	0.1	ND	ND	13	67	45	55
	0.4	603	245	18	73	82	43
	1.5	427	289	17	145	27	42
	2.5	552	347	20	31	65	35
	3.6	869	250	14	52	34	44
	4.5	ND	ND	11	68	50	54
	14.7	523	177	11	47	59	29
	19.6	558	247	49	150	48	100
	33.3	ND	386	38	66	56	76
	41.4	ND	66	11	24	19	32
	47.9	ND	45	24	72	51	56
52.0	ND	34	13	33	16	22	
GM #3	Pre-burn	ND	ND	ND	ND	ND	ND
	0.2	201	30	3	14	32	10
	0.8	136	106	3	2	11	7
	1.3	ND	116	5	17	16	14
	2.3	ND	230	9	24	7	20
	3.5	76	53	2	5	3	4
	19.4	109	62	3	ND	ND	ND
	41.2	70	87	5	14	12	9
	47.8	68	52	5	12	9	10
51.9	60	16	4	14	20	13	
BW #2	Pre-burn	23	ND	ND	ND	ND	ND
	0.1	773	520	15	44	60	42
	0.3	ND	ND	9	37	61	60
	0.4	111	169	10	23	24	24
	0.7	ND	307	24	68	16	49
	1.0	ND	144	21	91	49	70
	2.3	ND	88	15	50	72	39
	4.3	385	302	19	33	52	32

^aND (not determined) due to either excessive chromatographic interference or levels below HPLC detection limits.

due to low concentrations (at the detection limit of HPLC). Phenanthrene and fluoranthene, three and four ring compounds, showed a gradual loss from litter throughout the year. Concentration of these two PNAH were regressed against time for sites Green Mountain #2 and #3. The resulting equations (Table II.2) predicted total loss from litter within two years of burning. In contrast, benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), benzo(ghi)perylene (BGHIP), and indeno(1,2,3-cd)pyrene (IP), five and six ring compounds, exhibited a much more gradual loss from slash burn sites. Regression equations for the five and six ring compounds did not yield significant R^2 values. However, long-term persistence of these compounds may best be evaluated by examining concentrations on clear-cut sites which were burned several years previously (Table II.3). Although it must be recognized that six different sites are included in the data presented in Table II.3, each with a different initial deposition, the patterns are consistent for all five and six ring compounds, indicating a gradual loss over a period in excess of five years. Estimated decreases in concentration after one year were 94% and 90% for phenanthrene and fluoranthene, respectively, while estimates for five and six ring compounds ranged from 50% for BkF to 64% for BaP. Neither phenanthrene nor fluoranthene was present in the litter of the three or five year old burns, while estimated reductions of other PNAH were 67-81% after five years.

When expressed on a g/ha basis, only a small percentage of the PNAH deposited in charred litter by combustion was transported into the soil profile, as indicated in Table II.4. Phenanthrene and

Table II.2. Regression equations of phenanthrene and fluoranthene concentrations in litter as a function of time (wks) since slash burning for sites Green Mountain #2 and #3.

PNAH	Regression Equation		X-intercept ^a	
	Green Mt. #2	Green Mt. #3	GM #2	GM #3
Phen	NA ^b	$Y=141-1.62X$ ($R^2=0.54$)	NA	1.7
Fluor	$Y=301-4.28X$ ($R^2=0.49$)	$Y=127-1.73X$ ($R^2=0.36$) ^c	1.4	1.4

^aPredicted time (yrs) to PNAH concentration = 0.

^bPhenanthrene data at site Green Mountain #2 was not suitable for regression analysis.

^cFluoranthene concentration from the first sampling occasion after burning at site Green Mountain #3 was omitted from analysis due to excessive deviation (>3X) from the observed pattern.

Table II.3. PNAH levels in litter of slash burn sites as a function of time since burning.

Sites Included ^a (mean values)	Time Since Burn (Yrs)	PNAH concentration (g/ha)					
		Phen	Fluor	BkF	BaP	BGHIP	IP
GM#2, GM#3, BW, CC	pre-burn	ND ^b	4	<1	<1	1	1
GM#2, GM#3, BW, CC	deposition ^c	480	241	16	67	49	47
GM#2, GM#3	1	30	25	8	24	18	18
CN	3	ND	ND	4	10	22	12
Ben	5	ND	ND	3	13	16	11

^aSites investigated were Green Mountain #2 (GM#2), Green Mountain #3 (GM#3), Benner Wilkinson #2 (BW), Camp Chilcote #2 (CC), Chintimini North (CN), and Benner #1 (Ben).

^bND indicates PNAH not detected.

^cInitial deposition determined as mean of three samples collected during the ten day period after burning.

Table II.4. PNAH concentration in soil collected from site Green Mountain #2.

Soil Depth Sampled	Time Since Burn (Wks)	PNAH Concentration ^a					
		Phen	Fluor	BkF	BaP	BGHIP	IP
0-2 cm	pre-burn	4.2(0.5)	4.4(0.6)	2.1(0.3)	0.8(0.1)	1.4(0.2)	2.5(0.3)
	1.0	ND	8.7(1.1)	0.9(0.1)	1.6(0.2)	2.1(0.3)	1.3(0.2)
	4.5	ND	6.2(0.8)	0.8(0.1)	0.8(0.1)	3.0(0.4)	3.0(0.4)
	14.7	76.0(9.8)	27.9(3.6)	3.3(0.4)	4.0(0.5)	1.9(0.2)	4.0(0.5)
	41.4	13.0(1.7)	13.0(1.7)	0.5(0.1)	1.5(0.2)	1.7(0.2)	2.3(0.3)
	47.9	9.3(1.2)	3.5(0.4)	0.6(0.1)	1.0(0.1)	3.3(0.4)	1.5(0.2)
	52.0	ND	6.0(0.8)	1.8(0.2)	3.1(0.4)	ND	2.5(0.3)
	2-5 cm	15.0	6.8(1.3)	1.5(0.3)	0.2(<.1)	ND	ND
	52.0	ND	ND	0.3(0.1)	0.7(0.1)	1.1(0.2)	1.2(0.2)

^aAll concentrations reported as ng/g dry weight and (g/ha). Entries reported as not determined (ND) were due to either excessive chromatographic interference or levels below HPLC detection limits.

fluoranthene were incorporated into the soil to a greater extent than were the higher molecular weight PNAH. The greatest increase in PNAH concentration in soil occurred between weeks 4.5 and 14.7, during which time 25.7 cm of precipitation was recorded at the site. No rainfall was recorded during the first 4.5 weeks after burning. A variety of processes may influence PNAH transport between environmental compartments based on mass transfer principles such as Fick's Law of Diffusion, Henry's Law, and equilibrium partitioning between phases. The suspected influence of these processes on PNAH transport within slash burn sites is illustrated in Figure II.1. The movement and fate of PNAH within the soil profile and the chemical properties which govern soil/PNAH interactions are poorly understood (7). The major pathways by which PNAH could move from litter to soil appear to be via evaporation/precipitation and dissolution/sorption. Due to the abundant rainfall received by the Cascade Mountains and Coast Range of Oregon, the dramatic increase in soil PNAH levels after the first rainfall, and to the low vapor pressure of PNAH, the dissolution/sorption pathway probably predominates in the transfer of PNAH from litter to soil.

It has been well documented that the sorptive behavior of neutral, nonpolar, organophilic molecules, such as PNAH, is dependent primarily upon the organic matter content of the substrate (7,8,9). The utility of expressing PNAH concentrations based on organic matter content of sediments in both marine and freshwater systems has been described by Dunn (10) and Black (11). Chiou et al. (8) have also presented convincing data in support of the hypothesis

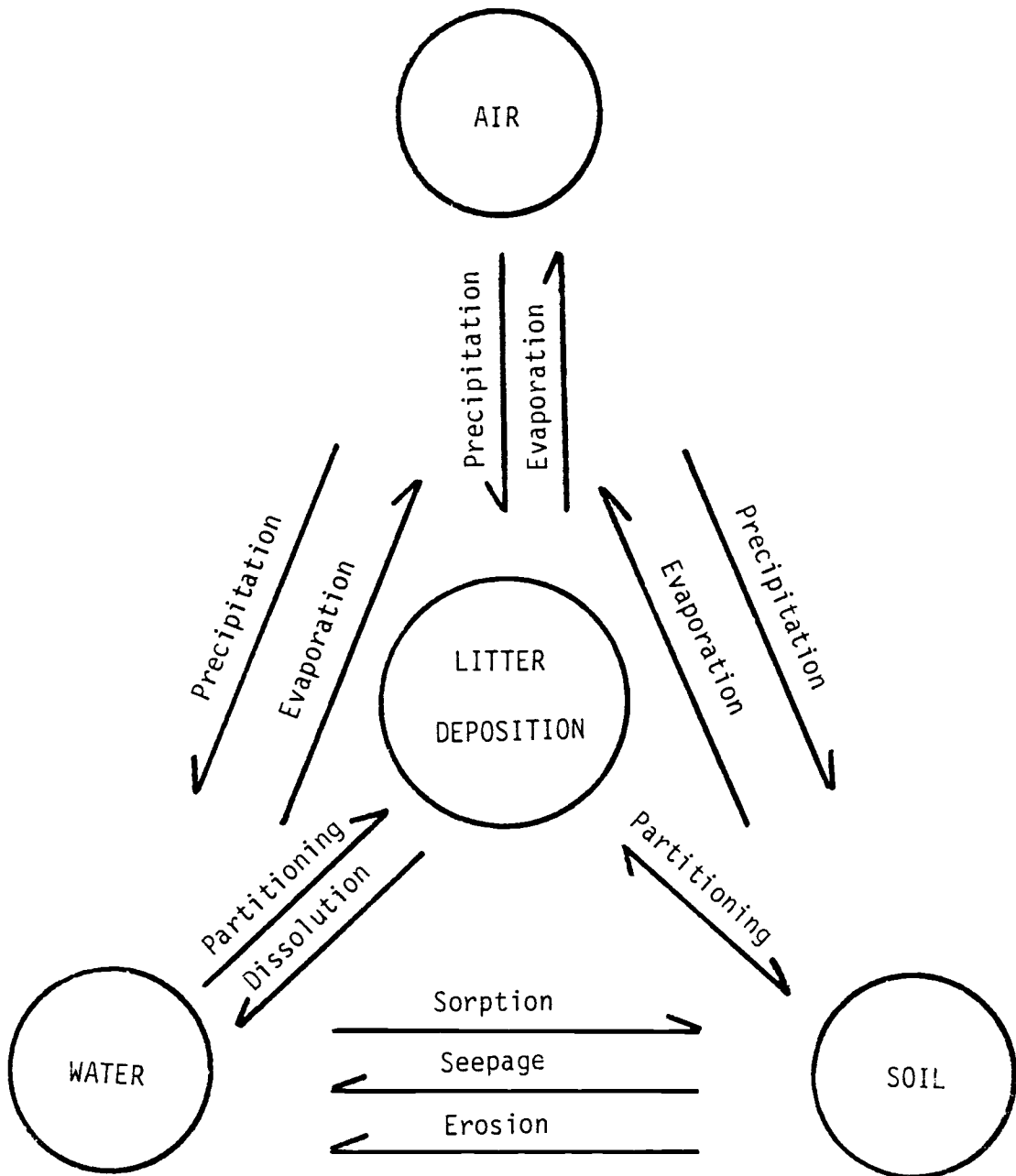


Figure II.1. Transport of PNAH between compartments of slash burn sites, modified from reference #30.

that sorption by soil organic matter in a moist system is primarily a partitioning, rather than an adsorption, process. It would therefore be expected that PNAH concentration in litter would come into equilibrium with that in soil, when expressed on the basis of organic matter content, assuming equal chemical potential or fugacity in each organic phase. PNAH concentration in litter and soil (0-2 cm depth) are compared in Table II.5 for seven sampling occasions at site Green Mountain #2. The data suggest that all PNAH established an equilibrium between litter and soil, on an organic content basis, during the year after burning. It also appears that the lower molecular weight PNAH, phenanthrene and fluoranthene, equilibrated more rapidly, which would be expected based upon their higher water solubility and vapor pressure (Table II.6). This pattern is particularly evident in the data for phenanthrene and BGHIP (Figure II.2). Data from Chintimini North, V-1, a three year old burn, suggest that this equilibrium may be maintained for some time, although additional analyses would be needed for a more conclusive interpretation.

Of the various processes involved in PNAH transfer between compartments of the slash burn site, seepage, erosion, and evaporation all result in an export of PNAH from the site via stream, groundwater, or evaporative loss to the atmosphere. In addition, PNAH may be modified or degraded on site via photolysis or microbial activities. PNAH are prime candidates for photochemical degradation due to their high absorptivities in the environmental UV range (12), although they have been shown to vary considerably in their susceptibility to photodegradation under laboratory conditions (13). BaP is

Table II.5. Comparison of PNAH levels in litter and the top 2 cm of soil when expressed on the basis of organic matter content for sites Green Mountain #2 and Chintimini North.

Site	Time Since Burn (Wks)	PNAH concentration (ng/g organic) ^a											
		Phen		Fluor		BkF		BaP		BGHIP		IP	
		L ^b	S	L	S	L	S	L	S	L	S	L	S
GM #2	pre-burn	ND	13	ND	14	ND	6	ND	2	ND	4	ND	7
	1.0	NA	ND	NA	54	NA	6	NA	10	NA	13	NA	8
	4.5	ND	ND	ND	34	10	5	66	4	48	17	53	16
	14.7	495	422	167	164	10	20	44	23	56	11	27	23
	41.4	ND	76	84	76	13	3	30	9	24	10	40	13
	47.9	ND	58	30	22	16	4	49	6	35	30	38	9
	52.0	ND	ND	27	33	10	10	26	17	13	16	17	14
CN	~150	ND	ND	ND	ND	8	9	23	10	51	26	28	25

^aND indicates PNAH concentration not determined due to either excessive chromatographic interference or levels below HPLC detection limits. NA indicates sample not analyzed.

^bL designates PNAH concentration in litter; S designates soil.

Table II.6. Physical chemical properties of PNAH.

PNAH	Molecular Weight	Solubility ^a (g/m ³)	log K _{ow} ^b	Vapor Pressure ^c (torr)
Phen	178	1.29	4.46	9.06 X 10 ⁻²
Fluor	202	0.26	5.22	NA ^d
BkF	252	NA	NA	1.28 X 10 ⁻⁶
BaP	252	0.0038	6.50	7.32 X 10 ⁻⁷
BGHIP	276	0.00026	7.10	NA
IP	276	NA	NA	NA

^aSolubility from reference #31.

^bLog K_{ow} (octanol/water partition coefficient) from references #26,27.

^cVapor pressures are extrapolations from references #28,29 at 25° C.

^dNA signifies data not available.

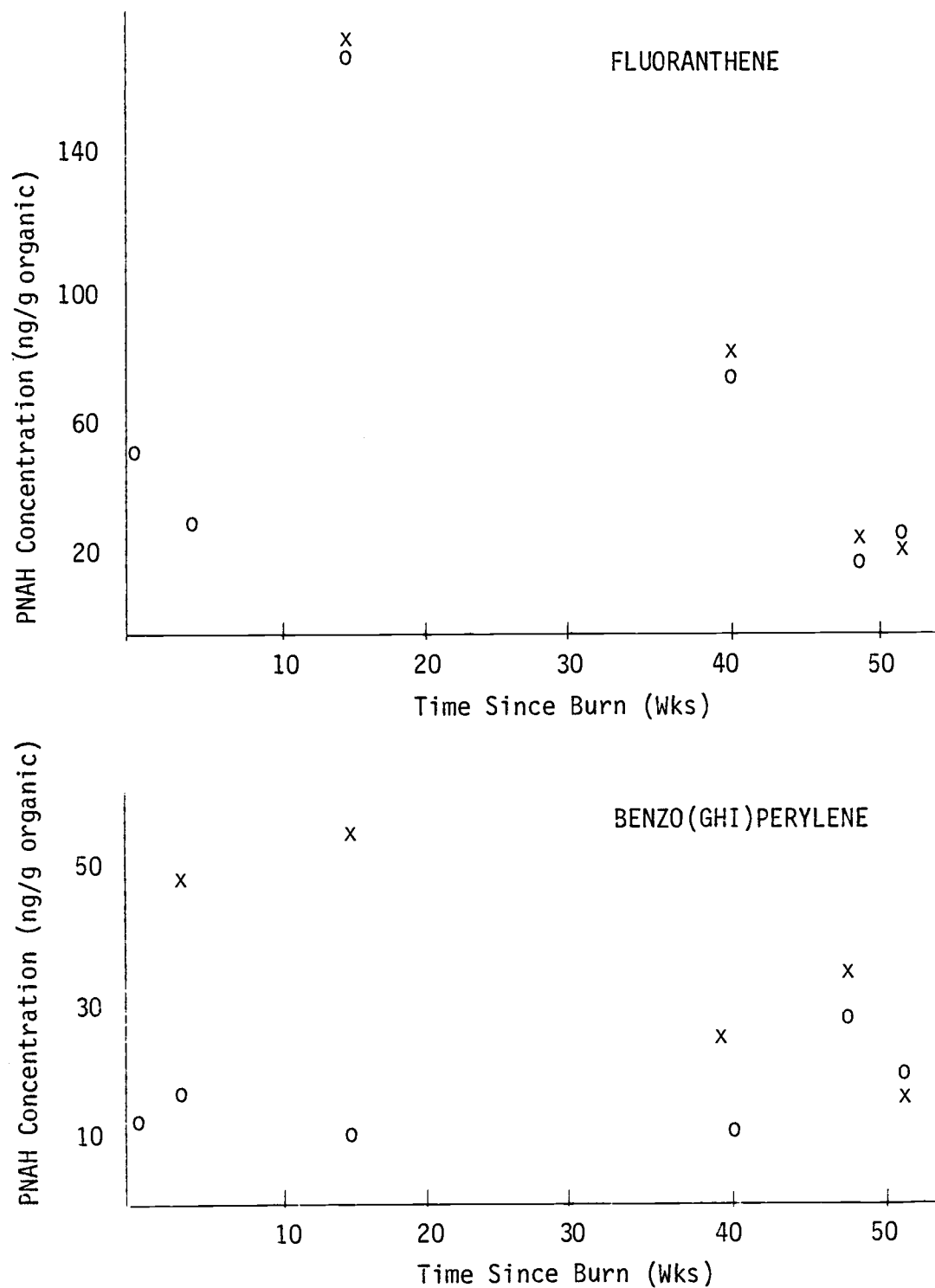


Figure II.2. Concentrations of fluoranthene and benzo(ghi)perylene, on the basis of organic content at site Green Mountain #2. Litter concentrations are designated by x, soil concentrations by o.

particularly susceptible, with a laboratory half-life of less than one hour (14). The significance of photodegradation of PNAH in a field situation is not known. BaP, and presumably other PNAH, is rapidly degraded by some microflora, but the rate of degradation probably varies with the species of microflora present (15). Although seepage was more significant for phenanthrene and fluoranthene, movement of PNAH into the lower soil layer was not appreciable. Concentrations of all PNAH were ≤ 0.23 g/ha within the 2-5 cm soil depth class one year after burning.

Results of the analyses of water samples from Green Creek are presented in Table II.7. Based on this limited data, stream export did not appear to be a significant route of PNAH loss from site Green Mountain #3. It is generally recognized that transport of PNAH in aqueous systems is primarily via adsorption to particulate matter, rather than in dissolved form (2,16,17). However, levels of adsorbed PNAH in particulate samples were generally very close to HPLC detection limits of approximately 1 ng/l or not detected. PNAH were not detected in samples of water filtrate.

Hermann et al. (18) investigated downstream concentration profiles of BaP and fluoranthene introduced into a small stream and found losses of 99% for BaP and 92% for fluoranthene within 449 m of the injection point. This would be expected based upon the rapid photolysis of some PNAH in aerated water (19), and the surprisingly high evaporation rates of low solubility compounds in aqueous solutions (20). Based on the data from Green Creek, slash burns do not appear to be significant point sources of PNAH in the

Table II.7. PNAH levels found in particulates and filtrate of water samples collected from Green Creek 25 m below site Green Mountain #3.

Sample Date	Sample Type	PNAH Concentration (ng/l)			
		BkF	BaP	BGHIP	IP
07/15/81	particulate	-	1.50	-	-
07/19/81	particulate	-	-	-	-
07/23/81	particulate	0.80	0.96	-	-
07/23/81	filtrate	-	-	-	-
09/22/81	particulate	-	-	-	-
10/24/81	particulate	-	0.90	-	15.50
10/24/81	filtrate	-	-	-	-
04/29/82	particulate	-	-	-	-
04/29/82	filtrate	-	-	-	-

aquatic environment, since the low initial concentrations in water are probably lost rapidly from the stream. However, it must be recognized that burning on steep slopes may result in greater erosion and, therefore, greater PNAH input into streams. Bennett (21) found that slash burning significantly increased soil erosion on steep slopes in the Oregon Coast Range, with up to twelve times as much erosion on burned sites.

Evaporative loss may be an important process, particularly for lower molecular weight PNAH. PNAH vapor pressures vary considerably, from 9.06×10^{-2} for phenanthrene to 1.96×10^{-10} for coronene. Evaporation of water from soil and litter may accentuate PNAH evaporation by moving the compounds to the surface by the "wick effect", as explained by Hartley (22). Evaporative loss of trace components in a moist soil or litter system is largely determined by H/K_{om} (23), where H is the Henry's law constant (air/water partition coefficient) which can be expressed as

$$H = P/S \quad (1)$$

where vapor pressure is in dynes/cm² and solubility is in g/cm³ for low water soluble solutes, and K_{om} is the solute partition coefficient between soil (or litter) organic phase and water. Since an essentially linear relationship exists between $\log K_{om}$ and $\log K_{ow}$ (octanol/water partition coefficient) (24), relative rates of PNAH evaporative loss from the system will vary according to H/K_{ow} . On this basis it would be expected that evaporative loss rate would be several orders of magnitude greater for phenanthrene than for BaP.

Thus, physical chemical characteristics of PNAH probably account

for our finding that higher molecular weight PNAH were considerably more persistent on slash burn sites than the lower molecular weight compounds. The 5-7 ring compounds exhibit greater sorption by soil and litter organic matter as reflected by their higher octanol/water partition coefficients (Table II.6). Evaporative loss and leaching are less significant. Field results similar to those obtained in this study were described by Black (11), who found a greater persistence of higher molecular weight PNAH in river sediments downstream from a creosote point source in Michigan. Our finding that PNAH persist in the environment in a field study (slash burning) is significant. The tendency of chemicals to persist within an ecosystem is a function not only of the properties of the chemical, but also of the characteristics of the ecosystem (25). An understanding of ecosystem characteristics and dynamics, and their effects on chemical behavior is still limited.

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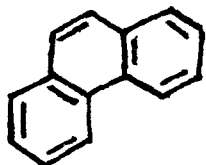
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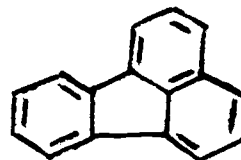
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Appendix A

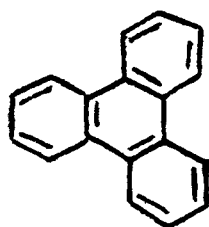
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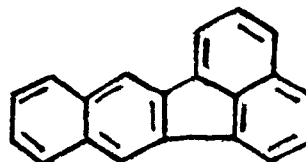
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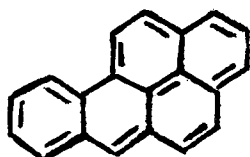
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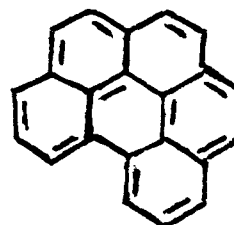
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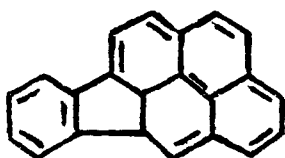
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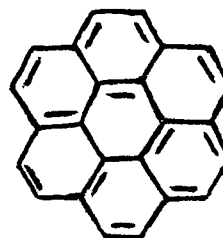
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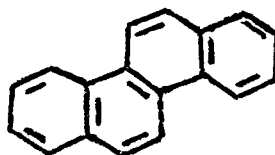
Benzo(ghi)perylene



Indeno(1,2,3-cd)pyrene



Coronene



Chrysene

Appendix B

Abbreviations used:

PNAH - polynuclear aromatic hydrocarbon

Phen - phenanthrene

Fluor - fluoranthene

Tri - triphenylene

BkF - benzo(k)fluoranthene

BaP - benzo(a)pyrene

BGHIP - benzo(ghi)perylene

IP - indeno(1,2,3-cd)pyrene

Cor - coronene

HPLC - high performance liquid chromatography

GC - gas chromatography

MS - mass spectrophotometry

Me₂SO - dimethyl sulfoxide

t - tonne

ha - hectare

ODS - octadecyl silane

H - Henry's law constant (dyne-cm/g)

K_{ow} - octanol/water partition coefficient

K_{om} - soil organic/water partition coefficient