Polycyclic Aromatic Hydrocarbons in Sediment Following Forest Fires

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Introduction

The warm and dry winter conditions in the Boreal Plain ecozone of western Canada following El Niño in 1997-1998, and the high occurrence of older, more fire-susceptible forest stands in this region, were important factors behind the above-average fire activity in north-central Alberta during the summer of 1998. These fast moving fires were among the most extensive ever recorded in North America. In Alberta alone, over 350 000 hectares of forest were burnt in over 50 separate fire. The largest and most extensively burned one was in the Virginia Hill area, Northern Alberta. In the fall of 1998, a pilot study was conducted to examine persistent organic pollutants following forest fires. The purpose of this study is to use relevant marker compounds and PCA technique to establish the characteristic of natural influence (e.g. forest fire) and trace specific sources of natural and anthropogenic inputs in the Virginia Hill area.

Materials and Methods

Sampling

Field collection was carried out at three selected sites in September 1998. Site A (54° 26.989 N, 116° 07.590 W) was located on a reach of the Sakwatamau River which ran through the forest fire area. This site was in a partially burned area on the edge of the forest fire zone. Site B (54° 35.659 N, 115° 39.694 W) was a completely burned area near the middle of the forest fire zone on the Freeman River. Site C (54° 15.536 N, 117° 06.458 W) was on the Little Smoke River in an area that had not experienced forest fires during the year. Three streams had similar sediment properties (64%-70% of sand, 17%-20% of silt and 14%-19% of clay). Six representative sampling locations with a sediment deposition zone in only 1-2 feet of water were selected from each river site. The top 1 cm of sediment was collected and placed in a clean glass jar. At Site B, some sediment samples contained abundant burned pine needles. All samples were kept frozen at -20 ^{o}C prior to laboratory analysis.

Chemical Analysis

Analysis was performed by Axys Analytical Services Ltd. in Sidney, British Columbia, Canada. A total of 18 parent and 30 alkyl PAH series of some parent PAHs were analyzed in all samples from all sites. A total of 62 non-routine PAHs were analyzed in one sample from each site. The sample (approximately 6 to 7 grams dry weight) is spiked with a suite of deuterium labeled PAH surrogate standards, ground with anhydrous sodium sulfate, packed into a column and eluted with methanol followed by dichloromethane. The extract was fractionated and transferred onto a silica gel column. The elute was extracted by column chromatograph on silica

gel into a polar PAH and a non-polar (alkane) fractions. The polar fraction was analyzed by gas chromatograph/mass spectrometry (GC/MS). Extract was analyzed using Finnigan MAT INCOS 50 Mass Spectrometers, each equipped with a Varian 3400 gas chromatograph, a CTC A200S autosampler and a Prolab data system. The sample detection limits (the lowest quality of each compound can be measured in each sample) were used. Quality assurance and quality control were monitored on a batch basis by analysis of method blank, a spiked blank and sample duplicate every batch of 8 samples.

Results and Discussion

Summary of concentrations of the parent PAHs and alkyl PAH homologous series are presented in Table 1. Distribution of alkyl PAH homologous series is shown in Figure 1A. Concentrations of the parent PAH totals and alkyl PAH homologous totals, before adjusting total carbon content for each sample, were higher in location order Site C > Site B > Site A. A predominance of alkyl PAH homologues over parent PAHs was observed in all locations. Perylene dominated in the parent PAHs, accounting for 60% to 70% of the parent PAH total. Phenanthrenes and anthracenes (P/A) homologues were the most prevailing in the alkyl PAH totals. Particularly, retene (1-methyl-7-isopropylphenanthrene) and C4 P/A were the most dominating P/A homologues at Site B and C. In contrast, sulphur compounds- dibenzothiophenes and its homologues were the least abundant. In non-routine PAH analysis, the most predominating compounds were dehydroabietin (410 ng/g) and tetrahydroretene (1400 ng/g) at Site B, and simonellite (160 ng/g) and 2,2,9-tetrahydropicene (120 ng/g) at Site C. Sulphur compounds such as 2-methyl and 2,4-dimethyl dibenzothiophenes, benzo[b]naphtho[1,2-d]thiophene, benzo[b]naphtho[2,3-d]thiophene were the least abundant.

Principle component analysis (PCA) was performed to distinguish compound patterns and locations. The preliminary analysis indicated that retene and C4 P/A were associated with Site B. Perylene, C2 and C5 P/A, C1 and C2 fluoranthenes/pyrenes (F/P), cadalene (1,6-dimethly-4-isopropylnaphthalene) and alkyl naphthalene homologues were associated with Site C.

Sediment is a sink of PAHs. Higher abundance of the low molecular weigh alkyl PAH homologues may suggest that a major source of PAHs at these sites is attributed to petrogenic material.[1-4] Perylene in sediment can be formed by diagenetic process (e.g. bacterial degradation).[4] Abundance of perylene may indicate that *in situ* generation of perylene by transformation of some terrestrially-derived precursors occurred at these sites. Sulphur compounds are characteristic of uncombusted fossil fuel origin and other pyrolytic processes.[5] The low proportion of this group of compounds observed in all locations reflects an insignificant input from pyrolytic processes. The low levels of less stable PAH isomers (e.g. anthracene) and high molecular weight PAHs (e.g. benzofluoranthenes, benzopyrene, indeno[1,2,3,cd]pyrene and benzo[ghi]perylene) reflect a minor contribution from pyrolytic relics in these locations.

Presence of retene and P/A homologues may indicate both petrogenic and terrigenous sources. Retene is one of diagenic product of abietic acid, particularly abundant in the resins of conifer.[6] Retene is often considered as a unique marker for coniferous wood combustion (e.g. forest fires).[7] Cadalene, alkylated naphthalene homologous, C2 and C4 P/A, retene and some retene-related precursors such as simonellite, dehydroabietin, tetrahydroretene, are the major constituents of diagenic origins (higher plant alteration).[6,8-9] The distribution patterns of PAHs

Table 1   Summary of Levels of Parent and Alkyl PAH Homologues (ng/g, dry weight)[a]

Compounds	Site A N=6	Site B N=6	Site C N=6	Compounds	Site A N=6	Site B N=6	Site C N=6
Naphthalene*	1.15	2.03	2.30	Flurorene	0.32	0.40	0.18
Acenaphthylene*	nd	nd	nd	C1-fluorenes**	nd	nd	nd
Acenaphthene*	nd	0.18	nd	C2-fluorenes**	nd	nd	nd
Flurorene*	0.32	0.40	0.18	C3-fluorenes**	nd	27.33	71.50
Phennanthrene*	2.50	4.15	19.0	C4-fluorenes**	nd	19.67	39.17
Anthracene*	0.03	nd	0.32	C5-fluorenes**	nd	26.50	56.17
Fluroanthene*	1.13	3.43	13.70	∑ Flurorenes	0.32	73.90	167
Pyrene*	2.65	8.38	24.17				
Benzo[a]anthracene*	nd	0.60	4.32	Dibenzothiophene*	nd	0.15	nd
Chrysene*	1.92	5.15	14.60	C1-dibenzthiophenes**	0.29	1.28	6.95
Benzofluroranthenes*	4.92	5.72	5.50	C2-dibenzthiophenes**	nd	0.76	0.33
Benzo[e]pyrene*	2.82	5.17	nd	C3-dibenzthiophenes**	nd	3.23	6.60
Benzo[a]pyrene*	2.87	8.25	nd	∑ Dibenzothiophene	0.29	5.42	13.88
Perylene*	40.67	67.67	226.7				
Bibenz[ah]anthraccne*	0.05	0.23	0.63	Phenanthrenes/ anthracenes	2.53	4.15	19.32
Indeno[1,2,3,cd]pyrene*	1.45	3.62	5.37	C1-phenanthrenes/ anthracenes**	15.20	41.17	81.00
Benzo[ghi]perylene*	0.37	nd	1.65	C2-phenanthrenes/ anthracenes**	17.85	543.3	245.0
∑Parent PAHs *	62.8	145	318	C3-phenanthrenes/ anthracenes**	27.33	48.00	129.3
∑Alkyl Homologues**	155	1405	1656	C4-phenanthrenes/ anthracenes**	6.50	15.22	24.50
Naphthalene	1.15	2.03	2.30	Retene**	29.18	590.0	355.0
2-methylnahthalene**	1.46	0.77	6.40	C5-phenanthrenes/ anthracenes**	13.33	20.50	78.67
C1-naphthalenes**	2.67	2.30	16.50	∑ Phenanthrenes/ Anthracenes	112	1262	933
C2-naphthalenes**	5.57	6.15	62.67				
1,2-imenthylnaphthalene**	0.15	nd	1.93	Fluoranthenes/ pyrenes	3.78	11.82	37.87
2,6-dimethylnaphthalene**	0.52	0.42	4.78	C1-fluoranthenes/ pyrenes**	3.23	12.37	39.67
C3-naphthalenes**	3.23	7.60	88.67	C2- fluoranthenes/ pyrenes **	9.02	12.10	45.83
2,3,6- trimethylnaphtalene**	0.88	1.66	1.88	C3- fluoranthenes/ pyrenes **	9.00	10.77	23.33
2,3,5- trimethylnaphtalene**	0.49	1.37	17.83	C4- fluoranthenes/ pyrenes **	7.43	5.92	10.73
C4-naphtalenes**	nd	1.17	97.67	C5- fluoranthenes/ pyrenes **	nd	0.97	4.82
C5- naphtalenes**	nd	2.28	56.50	∑ Fluoranthenes/ pyrenes	32.47	53.93	162
Cadalene**	1.87	2.30	81.83				
∑ Naphthalenes	17.98	28.04	439				

a: Values are not adjusted by total organic carbon content. Total organic carbon (TOC) is 0.55% at Site A and 2.2% at Site B and Site C. After adjusting TOC, means of ∑parent PAHs are 11.4 μg/g at Site A, 6.6 μg/g at Site B and 14.5 μg/g at Site C, and means of ∑alkyl homologues PAHs are 28.2 μg/g at Site A, 63.9 μg/g at Site B and 75.2 μg/g at Site C.

observed at Site B and C may be attributed to terrigenous origin. Qualitative differences in P/A homologue distribution is illustrated in Figure 1B. Site B had conspicuously elevated levels of retene from combustion in coniferous forest, although the lower P/A alkyls were similar to for all sites, suggesting these have similar sources.
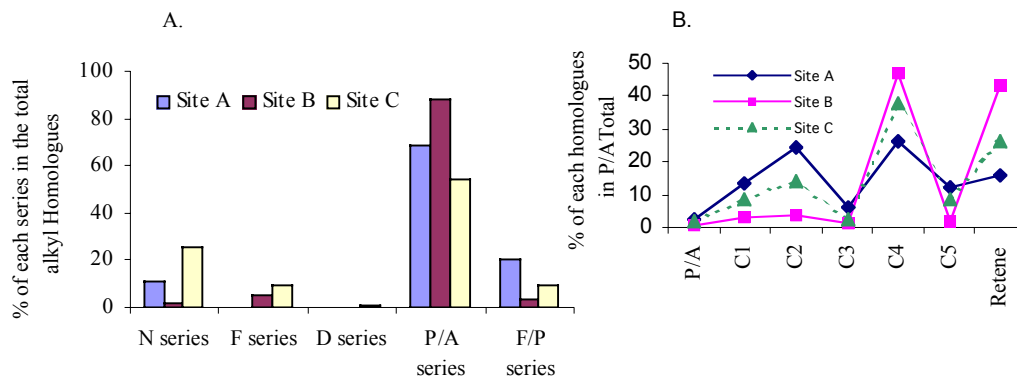
Figure 1 **A**. Distribution Patterns of Sum of Alkyl PAH Homologues in Sediment by Parent PAH Group. **B.** Distribution Patterns of P/A homologues. (N is naphthalenes, F is flurorenes, D is dibenzothiophene, P/A is phenanthrenes/anthracenes, F/P is fluoranthenes/pyrenes)

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