

HYDROCARBONS IN SMOKE AEROSOLS FROM CONTROLLED BURNING OF SELECTED TALLGRASS AND LITTERFALL SAMPLES: A PRELIMINARY STUDY

Norhayati Mohd Tahir*¹, Tan Hock Seng¹, Marinah Ariffin¹
Suhaimi Suratman¹

¹Environmental Research Group (ERG),
Department of Chemical Sciences, Faculty of Science and Technology
Kolej Universiti Sains dan Teknologi Malaysia, Mengabang Telipot, 21030 Kuala Terengganu

* Correspondence author email address: hayati@kustem.edu.my

ABSTRAK Satu kajian telah dijalankan bagi mencirikan sebatian hidrokarbon yang dibebaskan daripada pembakaran sampel lalang dan dedaun hutan. Sampel-sampel biojisim ini telah dibakar dibawah keadaan membara dan menyala dan zarah asap yang terhasil disampel menggunakan pensampel berisipadu tinggi diatas penapis gentian kaca. Hidrokarbon diekstrak menggunakan diklorometana sebagai pelarut dan ekstrak yang diperolehi dipisahkan dengan menggunakan turus silika-alumina. Penentuan dan kuantifikasi unsur hidrokarbon alifatik dan PAHs dijalankan dengan menggunakan GC-MS. Sebagai perbandingan, hidrokarbon dari daun lalang segar yang tidak dibakar juga dikaji bagi menentukan perbezaan dalam profil hidrokarbonnya. Keputusan menunjukkan komponen organik utama yang dikelaskan dari zarah asap adalah unsur alifatik rantai lurus dalam julat of C₁₈-C₃₆, dengan lebih banyak karbon nombor ganjil berbanding karbon genap dan 'carbon preference index' (CPI) dalam julat 1.21 - 2.47. Dalam pada itu, hidrokarbon alifatik yang diperolehi dari daun lalang segar yang tidak dibakar adalah sebatian C₂₅ hingga C₃₄, dengan spesies C₃₁ sebagai spesis paling dominan dan nilai CPI sebanyak 10.31. Amnya, CPI > 1 menunjukkan sumbangan *n*-alkana daripada lilin epitukular. Kesimpulannya, walaupun keseluruhan penanda *n*-alkana tidak berubah, pembakaran seakan-akan meningkatkan julat hidrokarbon alifatik yang terhasil dengan penurunan nilai CPI. Keputusan juga menunjukkan pembakaran membentuk lebih banyak unsur PAHs dalam ketiga-tiga sampel asap dengan kepekatan berjulat dari 731 - 3380 µg g⁻¹. Daun lalang segar pula tidak mempunyai unsur PAHs dan ini jelas menunjukkan PAHs hanya terhasil dari proses pembakaran.

ABSTRACT A study has been carried out to characterize hydrocarbons emitted from the burning of selected tall grass and litter fall samples. The biomass samples were burned under smouldering and flaming conditions and their respective smoke particulate emitted was sampled by high volume filtration on a pre-cleaned (solvent extracted) glass fibre filters. Hydrocarbons were extracted from the filters using dichloromethane as solvent and the extracts fractionated on silica-alumina column. Detection and quantification of aliphatic hydrocarbons and PAHs compounds were carried out using GC-MS. For comparison, hydrocarbons in fresh tall grass sample were also characterized to determine differences in hydrocarbon profiles. Result indicated that the major organic component characterized from the smoke particles were straight chain aliphatic compound in the range of C₁₈-C₃₆, with an odd to even carbon number predominance and carbon preference index (CPI) ranging from 1.21- 2.47. On the other hand, hydrocarbons present in the fresh tall grass ranged from C₂₅-C₃₄ with C₃₁ species dominating and CPI value of 10.31. In general, CPI > 1 indicates *n*-alkanes contribution from epitucular waxes. It could be concluded that, even though the overall signature of the source of *n*-alkanes is maintained, burning seems to increase the range of aliphatic hydrocarbon emitted accompanied with a decrease in the CPI values. In addition, results also indicate that burning resulted in the formation of many PAHs compounds in all the three samples with concentration ranging from 731 - 3380 µg g⁻¹. Fresh tall grass on the hand did not exhibit any PAHs compound, which clearly indicated that PAHs were generally generated from combustion process.

Keywords: smoke aerosols, biomass, controlled burning, hydrocarbons, polycyclic aromatic hydrocarbons.

INTRODUCTION

Biomass burning is an important primary source of soot and organic particulate matter, which influence atmospheric chemical, optical and radiative properties through direct and indirect mechanisms [1-4]. The soot produced during this burning can remain for a long time as suspended matters in the air and have been considered as one of the causes of respiratory diseases [5-6]. It occurs on a large scale in industrialised, developing and remote areas caused by both anthropogenic and natural initiation (wild fires). The practice of burning for clearing vegetated areas and also agricultural wastes has significantly increased the input of organic aerosols to the atmosphere. Biomass burning introduced several compound into the atmosphere, including carcinogenic and mutagenic compound, like polycyclic aromatic hydrocarbons (PAHs). PAHs resulting from incomplete combustion of organic materials are ubiquitous in our environment and sixteen compounds of these PAHs have been listed as priority pollutants by US Environmental Protection Agency (EPA). The knowledge on the chemical composition of these aerosols is important for the understanding of the role of biomass burning emissions to the chemical processes in the atmosphere. In general, each individual plant species emits 'chemical fingerprint' of natural (unaltered) and thermally altered (pyrolysis) organic constituents upon burning which is source specific and unique in composition, thus, they can be utilised as specific indicators for identifying fuel source inputs, transport mechanisms and receptor fate in samples of atmospheric fine particulate matter [2,7]. In this country, biomass burning is mainly practice through clearing of agricultural wastes and garden refuse and in rural areas, through domestic cooking. The widespread practice of biomass burning in Terengganu as well as limited information on the subject in the literature from the tropical region prompted the initiation of this study. This paper presents result of a study carried out to characterize the hydrocarbons, viz. aliphatic and polycyclic aromatic hydrocarbons (PAHs), in the aerosols emitted from the burning of a common tall grass species, commonly known in Malay as 'alang' (*Imperata cylindrica*) and two types of litter fall samples viz. litter fall 1 sample consisting of a mixture of predominantly 'meranti damar hitam' (*Shorea multiflora*) leaves and some 'merawan' (*Hopea spp.*), 'kulim' (*Scoradocarpus spp.*) and 'keruing' (*Dipterocarpus spp.*) leaves and litter fall 2 sample consisting of predominantly 'merawan bunga' (*Hopea pubescens Ridl.*) leaves with some 'meranti' (*Shorea spp.*) and 'keruing' leaves.

EXPERIMENTAL METHOD

Sampling

Tall grass samples were collected from at Gong Pak Jin, a couple of kilometres from KUSTEM campus while litter fall samples were collected from two separate locations within the Agro Setiu Resort. With the exception of some tall grass leaves, the remaining tall grass samples and litter fall samples were placed in aluminium lined boxed and allowed to dry over a two week period. A known amount of fresh tall grass leaves were dipped into 150ml dichloromethane (DCM) for 30 sec, the extract was then fractionated as described below. Each dried vegetation sample was burnt completely to ember under both flaming and smouldering condition. The smoke emitted during these period were collected on a single pre-cleaned (solvent extracted) glass fibre filter using a high-volume air sampler (HVS); to sample the smoke, the sampler was placed at approx. 1m diagonally above and to the side of the flames in the smoke plume.

Extraction and Fractionation

Hydrocarbon compounds were extracted from the glass fibre filter using ultrasonic agitation with DCM as solvent. Before extraction, two internal standards consist of dotriacontane (n-C₃₂) for aliphatic fraction (fraction 1) and 9, 10-dihydroanthracene for aromatic fraction (fraction 2) were spiked into the glass fiber filter for recovery assessment. The extracts were concentrated to about 1 mL using rotary evaporator. The concentrated extracts were then fractionated into subfractions on 4% deactivated silica (230-400 mesh)-alumina (70-230 mesh) columns. N-hexane (25 ml) was used to elute the *n*-alkanes while PAHs compounds were eluted using a combination of 30ml of 10% DCM in hexane followed by 20ml of 50% DCM in hexane. Sterol fraction was eluted in the third fraction with 40 mL of 10% methanol in DCM as solvent. This paper is concerned primarily on the first and second fraction; the third fraction was kept under -4°C for further analysis.

GC-MS analysis

Identification and quantification of aliphatic hydrocarbons and the 16 priority PAHs compounds were carried out using GC-MS. The compounds for aliphatic hydrocarbons were as follow: *n*-dodecane (C₁₂), *n*-tetradecane (C₁₄), *n*-hexadecane (C₁₆), *n*-octadecane (C₁₈), *n*-eicosane (C₂₀), docosane (C₂₂), *n*-tetracosane (C₂₄), *n*-hexacosane (C₂₆), *n*-octacosane (C₂₈), *n*-triaicosane (C₃₀), dotriacontane (C₃₂), *n*-tetratriacontane (C₃₄) and *n*-hexatriacontane (C₃₆) and the PAHs compound were as follows: naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHEN), anthracene (ANT), fluoranthene (FTH), pyrene (PYP), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DA), benzo(g,h,i)perylene (BgP) and indeno(1,2,3,cd)pyrene (IP). The sum of these 16 priority PAHs compounds is known as total identified PAHs (TIP). The GC-MS operating conditions were as follows: fused silica column (30m x 0.25 mm i.d; 0.25 µm filmed thickness); injection temperature was set at 290°C using splitless mode. The column temperature was programmed as follow: - hold at 50°C for 1 min; 50-140 at 5°Cmin⁻¹; 140-300°C at 4°Cmin⁻¹ and maintained at 300°C for 15 min. Helium was used as the carrier gas with flow rate at 2.0 mL min⁻¹. GCMS interface was set at 300°C. Verification of peaks was carried out based on key fragment ions, retention times compared to those of external aliphatic hydrocarbons and PAHs standards, and/or mass spectra.

Recovery and blanks

The recovery of the multi-step procedure for the internal standard ranged from 65-75%. Appropriate corrections were made to the measured concentrations. Procedural blanks as well as solvent blanks were analysed and quantified to ensure that there were no significant background interferences; no PAHs compounds were detected in these blanks.

RESULTS AND DISCUSSION

The major organic components identified and quantified in the aliphatic and PAH fractions are shown in Figures 1 and 2. It must be conceded that distributions and abundances of the litter falls and tall grass smoke aerosols constituents are strongly dependent on combustion conditions (e.g. smouldering versus flaming, duration) and although attempt has been made in this study to sample aerosols during both flaming and smouldering conditions, uncertainty remains with respect to the duration of each combustion phase.

Aliphatic alkanes (n-alkanes)

The distribution of individual compounds present in the aliphatic fraction of the smoke samples and fresh tall grass sample are shown in Figure 1. It can be observed that all samples exhibit the presence of straight chain aliphatics in the range of C₁₈-C₃₆. Fresh tall grass exhibits aliphatics ranging from C₂₅ to C₃₆ with carbon maximum (C_{max}) at C₃₁ whilst the tall grass smoke aerosols exhibit aliphatics ranging from C₁₈ to C₃₆ with C_{max} at C₂₉. It appears that burning of tall grass emitted a wider range of aliphatic compounds with a slight shift in C_{max}. Litterfall 1 (with predominance of *S. multiflora* leaves) and litterfall 2 (with predominance of *H. pubescens* Ridl. leaves) exhibits aliphatics in the range of C₂₂-C₃₄ and C₂₀-C₃₄, respectively. Both samples exhibit C_{max} at C₃₁. Carbon Preference Index (CPI) and Carbon maximum (C_{max}) can be used as possible indications of the distribution of recent biogenic matter and anthropogenic materials in samples [8] and CPI is useful in making estimates of plant wax contribution versus fossil fuels contamination. The C_{max} found in the present vegetation smokes and fresh sample are also consistent with earlier reports [1,2,7,9] and the higher C_{max} obtained reflects the higher ambient temperature which result in biosynthesis of longer carbon chain lipid which have higher melting points [10]. The CPI calculated for carbon in the chain length between C₁₈₋₃₆ gave values ranging from 1.21 to 10.31 with average CPI of 3.95, showing an odd over even carbon number predominance (Table 1). Vascular plants synthesise epicuticular waxes containing odd carbon number n-alkanes usually in the C₂₅ to C₃₃ range with C₂₉ or C₃₁ as dominant homologues, which often contribute up to 90% of all paraffins found in plant waxes [11]; thus these fingerprints has been widely accepted as a signature of epicuticular wax alkanes from leaf surfaces or sometime referred to as terrigenous plant wax source or higher plant origin [12, 13]. This is evident in *n*-alkane distribution isolated from the fresh tall grass sample, which show a carbon distribution in the C₂₅ to C₃₆ range with C_{max} at C₃₁ and a CPI value of 10.31.

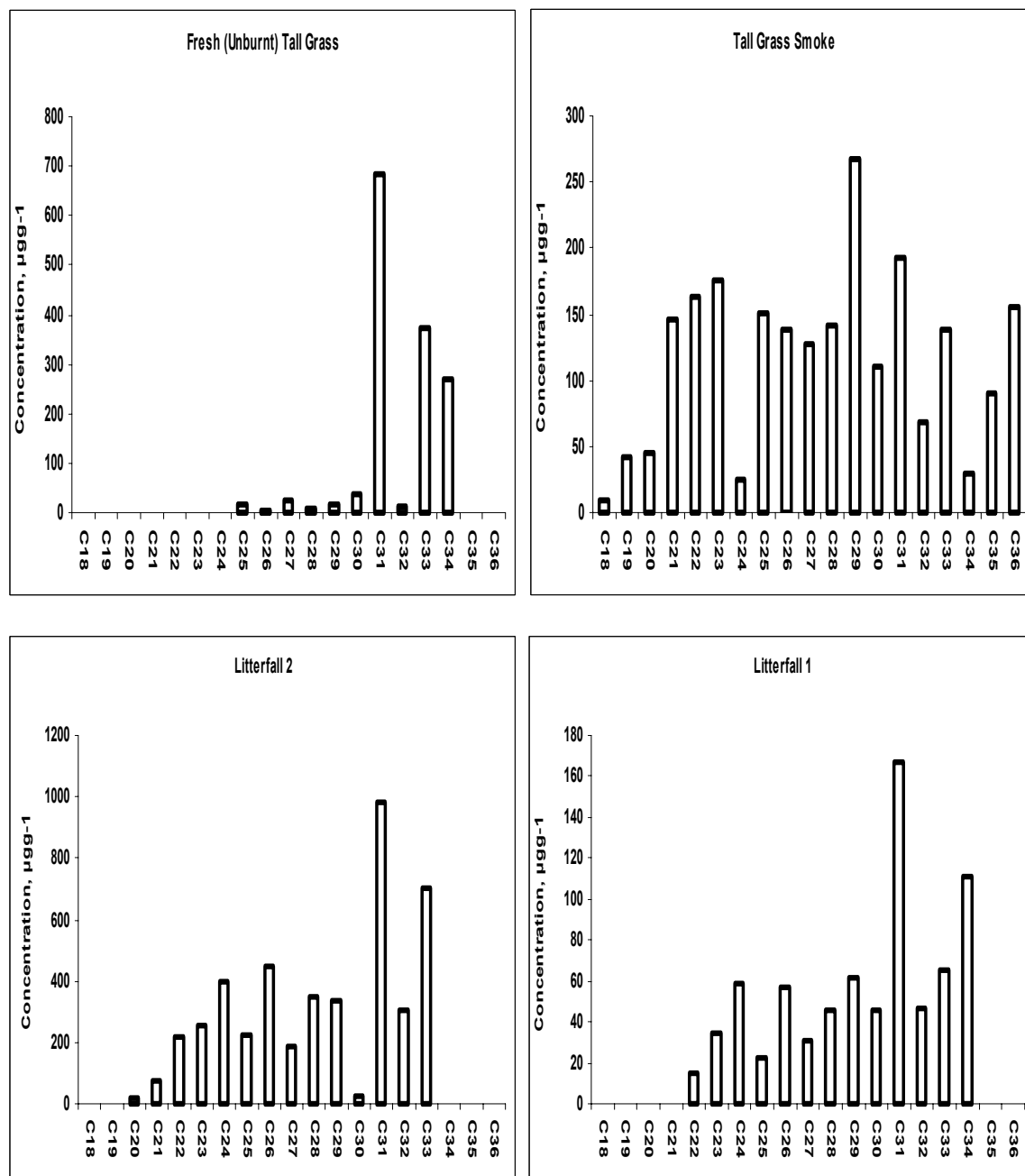


Figure 1. Distribution of individual aliphatic hydrocarbons.

Similarly, the aliphatic distributions found in the present vegetation smokes are also consistent with earlier reports [1,2,7] and confirm an input from epicuticular wax source. It is interesting to note that, whilst retaining the characteristics of the precursor (molecular marker), burning of these vegetation seems to increase the range of aliphatic hydrocarbon emitted accompanied by a decrease in the CPI values and in the case of the tall grass, also resulted in a shift of C_{max} . Table 1 also shows the concentration of total identified resolved aliphatic hydrocarbons (TIRAH) for the samples. Highest concentration of TIRAH was obtained from litter fall 2 smoke ($4650 \mu\text{g g}^{-1}$), followed by tall grass smoke ($2230 \mu\text{g g}^{-1}$), fresh tall grass ($1470 \mu\text{g g}^{-1}$) and litterfall 1 smoke ($773 \mu\text{g g}^{-1}$).

PAHs

Figure 2 shows the distribution of individual priority PAHs present in the aromatic fraction of the smoke samples and fresh tall grass sample. The figure reveals that all smoke samples exhibit PAH compounds. On the contrary, fresh tall grass does not show the presence of any PAHs. PAH compounds are generally formed by thermal decomposition of any organic matter containing C and H atom through either incomplete

combustion (pyrolysis) or carbonisation process. All biomass fires are pyrolysis processes; PAHs are formed from either the process of high temperature thermal alteration of natural product precursors in the source organic matter or process of recombination of molecular fragment in the smoke. Results also showed that pyrene is generally the most dominant component detected in these smoke samples. Highest concentration of pyrene was found in the tall grass smoke (843 $\mu\text{g g}^{-1}$), followed by litterfall 1 smoke (*S. multiflora*) and litterfall 2 smoke (*H. pubescens Ridl*) with a value of 355 $\mu\text{g g}^{-1}$ and 254 $\mu\text{g g}^{-1}$, respectively. Another interesting feature observed is that the low molecular weight (3-4 rings) PAH compounds (e.g. phenanthrene, fluoranthene, pyrene) are more dominant than higher molecular weight (5-6 rings) PAHs (e.g. benz[a]anthracene and benzo[g,h,i] perylene). This could be indicative of the general combustion temperature as the latter tend to be formed in temperatures $> 700^\circ\text{C}$. In addition, only tall grass smoke sample showed a minimal presence of the 2 ring PAHs, viz. fluorene and acenaphthylene. Table 2 shows the concentration of the total identified PAHs (TIP) found in the biomass smoke studied. Smoke emitted from burning of tall grass sample shows the highest TIP (3380 $\mu\text{g g}^{-1}$) followed by litter fall 1 and litter fall 2 with TIP concentration of 1080 and 731 $\mu\text{g g}^{-1}$, respectively.

Table 1. Concentration of aliphatic hydrocarbon compounds in smoke samples.

Parameter	Samples			
	Litterfall 1 (<i>S. multiflora</i>)	Litterfall 2 (<i>H. pubescens Ridl</i>)	Tall Grass Smoke (<i>I. cylindrica</i>)	Fresh Tall Grass (unburnt) (<i>I. cylindrica</i>)
Total identified aliphatic HC's (TIRAH), ($\mu\text{g g}^{-1}$)	773	4650	2230	1470
CPI ₍₁₈₋₃₆₎	1.79	2.47	1.21	10.31
C _{max}	31	31	29	31

$$\text{CPI} = 0.5 \left[\frac{\sum \text{C}_{25} - \text{C}_{33}}{\sum \text{C}_{26} - \text{C}_{34}} + \frac{\sum \text{C}_{25} - \text{C}_{33}}{\sum \text{C}_{24} - \text{C}_{32}} \right]$$

Table 2. Concentration of the total identified PAHs (TIP) in smoke samples.

	Litterfall 1 (<i>S. multiflora</i>)	Litterfall 2 (<i>H. pubescens Ridl</i>)	Tall Grass Smoke (<i>I. cylindrica</i>)	Fresh Tall Grass (unburnt) (<i>I. cylindrica</i>)
Total PAH, $\mu\text{g g}^{-1}$	1080	731	3380	0.00

In addition to the above PAH compounds, several other PAHs compound were identified based on their mass fragmentogram and by comparison with MS library (NIST & WILEY) as well as by comparison with mass fragmentogram cited by Simoneit *et al.* [14]; these other PAH compounds identified are shown in Table 3. Quantification of these compounds was not carried due to the unavailability external standard in this laboratory.

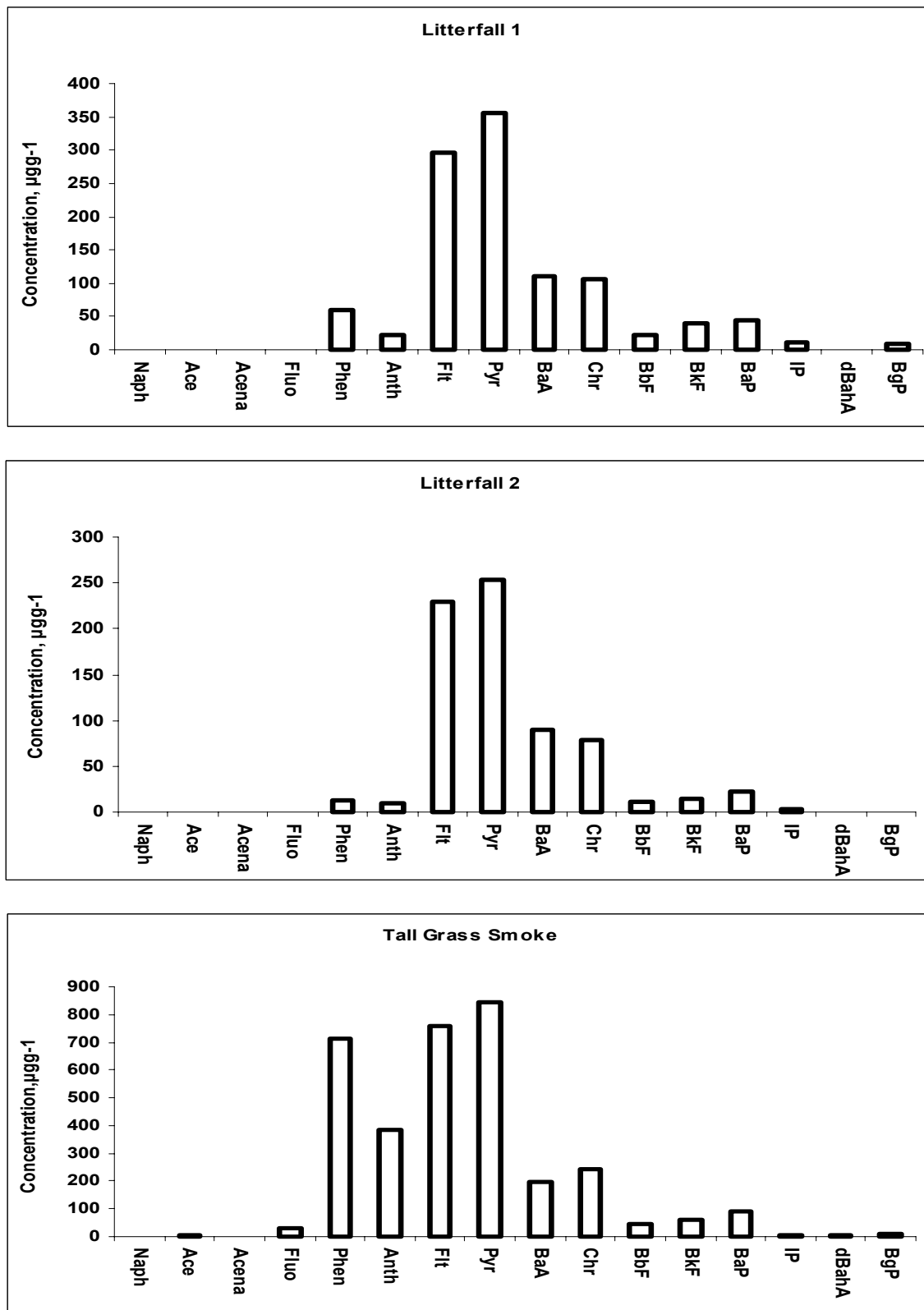


Figure 2. Distribution of individual PAHs in smoke samples.

Table3. Identities of other PAHs compound

Compound	Composition	Molecular Weight	Identification or reference basis ^b
3-methylphenanthrene	C ₁₅ H ₁₂	192	S,1
2-methylphenanthrene	C ₁₅ H ₁₂	192	S,1
9-methylphenanthrene	C ₁₅ H ₁₂	192	S,1
1-methylphenanthrene	C ₁₅ H ₁₂	192	S,1
Acenaphenanthrylene	C ₁₆ H ₁₀	202	S,1
Benzo[c]phenanthrene	C ₁₈ H ₁₂	228	S,1
1-methyl-chrysene	C ₁₉ H ₁₄	242	V
Benzo[ghi]flouranthene	C ₁₈ H ₁₀	226	S,1
Cyclopenta[cd]pyrene	C ₁₈ H ₁₀	226	S,1
Dibenzo[b,jk]flourene	C ₂₀ H ₁₂	252	S,1
Benzo[e]pyrene	C ₂₀ H ₁₂	252	S,1
Perylene	C ₂₀ H ₁₂	252	S,1
Dibenzo[def,mno]chrysene ?	C ₂₂ H ₁₂	276	S,1

^a Compounds arrangement are based on elution (retention time) order.

^b Identification criteria: S = interpolated from homologous series fragmentation pattern, V = interpreted from mass spectrum fragmentation pattern .

? Completely based on comparison with mass-spec library, not cited in literature

CONCLUSION

Results obtained in this study showed that fresh tall grass exhibit carbon distribution in the C₂₅ to C₃₆ range with C_{max} at C₃₁ and a CPI value of 10.31. *n*-alkane distribution from the smoke samples showed carbon distribution ranging from C₁₈ to C₃₆ with odd carbon predominance and C_{max} at C₂₉ or C₃₁ and CPI values >1 indicative of epicuticular waxes and terrigenous plant input. It was also found that although burning of the biomass samples still retains the molecular signature of epicuticular waxes, the process seems to result in an increase the range of aliphatic hydrocarbon emitted accompanied by a decrease in the CPI values and in the case of the tall grass, also resulted in a shift of C_{max}. Most of the dominant PAH compounds found in the smoke samples were of medium weight molecular compounds with pyrene being the most dominant constituent.

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