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

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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 C_{18}-C_{36}, 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 C_{25}-C_{34} with C_{31} species dominating and CPI value of 10.31. Amnya, CPI > 1 menunjukkan sumber 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.

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 ‘lalang’ (*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’ (*Scorodocarpus 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-C_{32}) 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 (C\textsubscript{12}), n-tetradecane (C\textsubscript{14}), n-hexadecane (C\textsubscript{16}), n-octadecane (C\textsubscript{18}), n-eicosane (C\textsubscript{20}), docosane (C\textsubscript{22}), n-tetracosane (C\textsubscript{24}), n-hexacosane (C\textsubscript{26}), n-octacosane (C\textsubscript{28}), n-triacontane (C\textsubscript{30}), dotriacontane (C\textsubscript{32}), n-tetratriacontane (C\textsubscript{34}), and n-hexatriacontane (C\textsubscript{36}) and the PAHs compound were as follows: naphthalene (NAP), acenaphthylene (ACY), acenaphtene (ACE), fluorene (FLU), phenanthrene (PHEN), anthracene (ANT), fluoranthene (FTH), pyrene (PYR), 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 (BghiP) 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 follows: hold at 50°C for 1 min; 50-140 at 5 °Cmin\textsuperscript{-1}; 140-300°C at 4 °Cmin\textsuperscript{-1} and maintained at 300°C for 15 min. Helium was used as the carrier gas with flow rate at 2.0 mL min\textsuperscript{-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 C\textsubscript{18}-C\textsubscript{36}. Fresh tall grass exhibits aliphatics ranging from C\textsubscript{25} to C\textsubscript{36} with carbon maximum (C\textsubscript{max}) at C\textsubscript{31} whilst the tall grass smoke aerosols exhibit aliphatics ranging from C\textsubscript{18} to C\textsubscript{36} with C\textsubscript{max} at C\textsubscript{29}. It appears that burning of tall grass emitted a wider range of aliphatic compounds with a slight shift in C\textsubscript{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 C\textsubscript{22}-C\textsubscript{34} and C\textsubscript{20}-C\textsubscript{34}, respectively. Both samples exhibit C\textsubscript{max} at C\textsubscript{31}. Carbon Preference Index (CPI) and Carbon maximum (C\textsubscript{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\textsubscript{max} found in the present vegetation smokes and fresh sample are also consistent with earlier reports [1,2,7,9] and the higher C\textsubscript{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 C\textsubscript{18}-C\textsubscript{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 C\textsubscript{25} to C\textsubscript{33} range with C\textsubscript{29} or C\textsubscript{31} 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 C\textsubscript{25} to C\textsubscript{36} range with C\textsubscript{max} at C\textsubscript{31} and a CPI value of 10.31.
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 $C_{\text{max}}$. 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 ($4650 \mu g g^{-1}$), followed by tall grass smoke ($2230 \mu g g^{-1}$), fresh tall grass ($1470 \mu g g^{-1}$) and litterfall 1 smoke ($773 \mu g g^{-1}$).

**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 µg g⁻¹), followed by litterfall 1 smoke (S. multiflora) and litterfall 2 smoke (H. pubescens Ridl) with a value of 355 µg g⁻¹ and 254 µg 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°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 µg g⁻¹) followed by litter fall 1 and litter fall 2 with TIP concentration of 1080 and 731 µg g⁻¹, respectively.

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Litterfall 1 (S. multiflora)</th>
<th>Litterfall 2 (H. pubescens Ridl)</th>
<th>Tall Grass Smoke (I. cylindrica)</th>
<th>Fresh Tall Grass Smoke (unburnt) (I. cylindrica)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total identified aliphatic HC's (TIRAH), (µg g⁻¹)</td>
<td>773</td>
<td>4650</td>
<td>2230</td>
<td>1470</td>
</tr>
<tr>
<td>CPI (18-36)</td>
<td>1.79</td>
<td>2.47</td>
<td>1.21</td>
<td>10.31</td>
</tr>
<tr>
<td>Cmax</td>
<td>31</td>
<td>31</td>
<td>29</td>
<td>31</td>
</tr>
</tbody>
</table>

CPI = 0.5 [ΣC₂₅ – C₃₃/ΣC₂₆ – C₃₄ + ΣC₂₅ – C₃₃/ΣC₂₄ – C₁₂]

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Litterfall 1 (S. multiflora)</th>
<th>Litterfall 2 (H. pubescens Ridl)</th>
<th>Tall Grass Smoke (I. cylindrica)</th>
<th>Fresh Tall Grass Smoke (unburnt) (I. cylindrica)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total PAH, µg g⁻¹</td>
<td>1080</td>
<td>731</td>
<td>3380</td>
<td>0.00</td>
</tr>
</tbody>
</table>

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.
Table 3. Identities of other PAHs compound

<table>
<thead>
<tr>
<th>Compound</th>
<th>Composition</th>
<th>Molecular Weight</th>
<th>Identification or reference basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-methylphenanthrene</td>
<td>C₁₅H₁₂</td>
<td>192</td>
<td>S,1</td>
</tr>
<tr>
<td>2-methylphenanthrene</td>
<td>C₁₅H₁₂</td>
<td>192</td>
<td>S,1</td>
</tr>
<tr>
<td>9-methylphenanthrene</td>
<td>C₁₅H₁₂</td>
<td>192</td>
<td>S,1</td>
</tr>
<tr>
<td>1-methylphenanthrene</td>
<td>C₁₅H₁₂</td>
<td>192</td>
<td>S,1</td>
</tr>
<tr>
<td>Acenaphthantylene</td>
<td>C₁₆H₁₀</td>
<td>202</td>
<td>S,1</td>
</tr>
<tr>
<td>Benzo[c]phenanthrene</td>
<td>C₁₆H₁₂</td>
<td>228</td>
<td>S,1</td>
</tr>
<tr>
<td>1-methyl-chrysene</td>
<td>C₁₀H₁₄</td>
<td>242</td>
<td>V</td>
</tr>
<tr>
<td>Benzo[ghi]flouranthene</td>
<td>C₁₈H₁₀</td>
<td>226</td>
<td>S,1</td>
</tr>
<tr>
<td>Cyclopenta[c,d]pyrene</td>
<td>C₁₈H₁₀</td>
<td>226</td>
<td>S,1</td>
</tr>
<tr>
<td>Dibenzo[b,j]flourene</td>
<td>C₂₀H₁₂</td>
<td>252</td>
<td>S,1</td>
</tr>
<tr>
<td>Benzo[e]pyrene</td>
<td>C₂₀H₁₂</td>
<td>252</td>
<td>S,1</td>
</tr>
<tr>
<td>Perylene</td>
<td>C₂₀H₁₂</td>
<td>252</td>
<td>S,1</td>
</tr>
<tr>
<td>Dibenzo[def,mno]chrysene</td>
<td>C₂₂H₁₂</td>
<td>276</td>
<td>S,1</td>
</tr>
</tbody>
</table>

* 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 C₃₁ 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 C₃₁ 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 C₃₁ 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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