HYDROCARBONS IN SMOKE AEROSOLS FROM CONTROLLED BURNING OF *Mangifera foetida* LITTER FALLS AND *Panicum repens*

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Abstract

A study has been carried out to characterize hydrocarbons emitted from the burning of two typical garden wastes, bachang (*Mangifera foetida*) litter falls and grass (*panicum repens*). The biomass samples were burned and their respective smoke particulate emitted was sampled using high volume sampler fitted with pre-cleaned glass fibre filters under smouldering and flaming conditions. Hydrocarbons were extracted using dichloromethane-methanol mixture 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 unburnt bachang litter falls and grass were also analyzed for aliphatic and PAHs content. Result indicated that the major components in the aliphatic fraction for all samples were n-alkane compounds which exhibited a saw-tooth pattern that is characteristic of a biogenic origin. The major components in this aliphatic fraction for smoke particulate matters were n-alkanes in the range of C_{12}-C_{36}, with an odd to even carbon predominance with CPI values ranging from 2.89-4.32 and C_{max} generally at C_{31}; total identified n-alkanes for these samples ranged from 221-939 $\mu g g^{-1}$. On the other hand, hydrocarbons present in the fresh unburnt bachang litter falls and grass ranged from C_{12}-C_{36} with C_{27} and C_{33} species dominating and CPI value of 4.5 and 23.1, respectively; total identified n-alkanes were significantly higher (1530-33000 $\mu g g^{-1}$) than those found in smoke aerosols. In general, CPI > 1 indicates n-alkanes contribution from epicuticular waxes thus it could be concluded that, even though the overall signature of the source of n-alkanes is maintained, burning seems to alter the distribution of aliphatic hydrocarbon emitted accompanied with a decrease in the CPI values and shifting in C_{max}. In addition, results also indicated that burning resulted in the formation of many PAHs compounds in all smoke aerosols samples with total PAHs concentration ranging from 187-296 $\mu g g^{-1}$. Fresh unburnt bachang litter falls and grass on the other hand did not exhibit any PAHs compound, which clearly indicated that PAHs were generally generated from combustion process.

Abstrak

Satu kajian telah dijalankan bagi mencirikan sebatian hidrokarbon yang dibebaskan daripada pembakaran sampel sisa laman iaitu daun bachang (*Mangifera foetida*) dan rumput (*Panicum repens*). Sampel-sampel biojisim ini telah dibakar dalam keadaan membara dan menyala dan zarah asap yang terhasil disampel menggunakan alat pensampelan berisipadu tinggi yang dimuat dengan penapis gentian kaca. Hidrokarbon diekstrak menggunakan campuran diklorometana-methanol (3:1) sebagai pelarut dan hasil ekstrak yang diperolehi dipisahkan dengan menggunakan turus silika-alumina. Penentuan dan kuantifikasi sebatian hidrokarbon alifatik dan PAHs dijalankan dengan menggunakan GC-MS. Sebagai perbandingan, hidrokarbon daripada daun bachang dan rumput segar yang tidak dibakar juga dikaji bagi menentukan perbezaan di antara profil hidrokarbonnya. Keputusan menunjukkan komponen organik utama dalam pecahan alifatik untuk semua sampel adalah bersebatian n-alkana. Taburan n-alkana ini memberi bentuk gerigi yang mencirikan sumber biogenik. Komponen utama dalam pecahan alifatik adalah daripada sebatian n-alkana dalam julat of C_{12}-C_{36}, dengan kehadiran lebih banyak karbon nombor ganjil berbanding karbon nombor genap. 'Carbon preference index' (CPI) adalah dalam julat 2.89-4.32 dan C_{max} pada C_{31}; jumlah n-alkana yang dikenalpasti adalah dalam julat 221-939 $\mu g g^{-1}$. Sebaliknya, hidrokarbon alifatik yang diperolehi daripada daun bachang dan rumput segar yang tidak dibakar adalah terdiri daripada C_{12}-C_{36}, dengan C_{27} dan C_{33} sebagai spesis paling dominan dan nilai CPI masing-masing sebanyak 4.5 dan 23.1; jumlah n-alkana yang dikenalpasti adalah lebih tinggi (1530-33000 $\mu g g^{-1}$) berbanding dalam zarah asap. Amnya, CPI > 1 menunjukkan sumbangan n-alkana daripada lilin epikutikular. Kesimpulannya, walaupun keseluruhan penanda n-alkana tidak berubah, pembakaran didapati mengubah taburan hidrokarbon alifatik yang terhasil dengan penurunan nilai CPI. Keputusan juga menunjukkan pembakaran membentuk lebih banyak sebatian PAHs dalam ketiga-tiga sampel asap dengan kepekatan dalam julat diantara 187-296 $\mu g g^{-1}$. Daun bachang dan rumput segar yang tidak dibakar pula tidak mempunyai sebatian PAHs dan ini jelas menujukkan PAHs hanya terhasil dari proses pembakaran.

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]. It occurs on a large scale in industrialised, developing and remote areas caused by both anthropogenic and natural initiation (wild fires). In Malaysia, until the year of 2000, agricultural sector had accounted for 11 percent of the gross domestic product (GDP), in which six percent of Malaysia land is under cultivation for field crops and 18 percent is used for plantation agriculture [5]. The practice of burning for clearing vegetated areas and also agricultural wastes has significantly increased the input of organic aerosols to the atmosphere. For instance, the haze episodes that occurred in Malaysia in September-October, 1991, August-October, 1994 and September-October, 1997 have been attributed to suspended smoke particulate matter from biomass burning in southern Sumatra and Kalimantan, Indonesia. Abas *et al.* [6] have reported a study on atmospheric particulate during these haze episodes and their result indicated high concentration of levoglucosan and palmatic acid which were biomarker compounds associated with biomass burning. In addition, Fang *et al.* [7] studied the solvent-extractable organic compounds in the Indonesia biomass burning aerosols and the main PAHs detected were ranged from 3-6 rings with total PAHs concentration ranged from 7-46 ngm^{-3}. These result were similar to study done by Abas *et al.* [8] reported the main PAHs compound detected were 4-6 rings PAH with total PAHs concentration of 48 ngm^{-3}. The knowledge on the chemical composition of these aerosols is important for the understanding of the role of agricultural biomass waste 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 [2,9]. 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 two agriculture biomass waste species which was species of grass (*Panicum repens*) and litterfall of bachang tree (*Mangifera foetida*).

Experimental Methods

Sampling

The fresh leaves of grass were taken at a site located a few kilometers away from roadside at Kg. Wakaf Tembusu, Gong Badak, Kuala Terengganu. This site is also located a couple of kilometers away from KUSTEM campus. Litter falls samples of bachang tree were taken from a resident house located at Tasek Gelugor, Seberang Prai. The grass samples were separated into three portions (fresh unburnt, fresh burnt and dried burnt) while leaves samples were separated into two portions (fresh unburnt and dried burnt). The fresh unburnt portion were dipped into 200 mL of dichloromethane (DCM) for 30 seconds for quantification of fresh wax; another portion was burnt fresh and the other portion was kept in an aluminium lined box and were allowed to dry for a period of two weeks. The fresh and dried leaves samples were burnt completely to ember under flaming and smouldering condition. The smoke emitted during these period were collected using a high-volume air sampler (HVS) fitted with a pre-cleaned glass fibre filter, placed 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 filter using ultrasonic agitation with DCM/Methanol (3:1 v/v) as solvent. Before extraction, two internal standards consist of *n*-teracosane (n-C_{24}) for aliphatic fraction (fraction 1) and predeuterated perylene-d12 for aromatic fraction (fraction 2) were spiked into the filter paper for recovery assessment. The extracts were concentrated to about 1 mL using rotary evaporator. The concentrated extracts were then fractionated into subfractions on 5% deactivated silica (230-400 mesh) and 2% deactivated alumina (70-230 mesh) columns. 20 ml of n-hexane was the used to elute the *n*-alkanes and PAHs compounds were eluted using a combination of 30ml of 10% DCM in hexane followed by 20ml of 50% DCM in hexane.

GC/MS analysis

Identification and quantification of aliphatic hydrocarbons and the 16 priority PAHs compounds were carried out using Shimadzu-QP2010 GC-MS. The compounds detail for aliphatic hydrocarbons were the *n*-alkanes ranging from n-dodecane (C_{12}) to *n*-hexatriacontane (C_{36}), whilst the 16 priority PAHs compounds were as follows: naphthalene (NAP), acenaphtylene (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 (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 0.32 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 mLmin^{-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 blanks

The recovery of the multi-step procedure for the internal standard ranged from 43.6-80.4% (mean = 68.7%, stdev = 14.3) for aliphatic fraction and 80.6-101% (mean = 87.4, stdev = 10.7) for aromatic fraction. 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 and aliphatic compounds of interest 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. These results are preliminary because only one burning test was conducted for each sample included in this study. It must be conceded that distributions and abundances of the bachang litter falls and 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. Thus, the values reported in this study should not be used as absolute value but as a relative chemical fingerprints for each vegetation sample.

Aliphatic alkanes (n-alkanes)

The distribution of individual compounds present in the aliphatic fraction of the smoke aerosols samples collected from burning of bachang litter falls and grass are shown in Figure 1. In addition, distribution of individual aliphatic compounds present in fresh unburnt grass sample is also shown in Figure 1 for comparison. It can be observed that all samples exhibit the presence of straight chain *n*-alkanes in the range of C_{12}-C_{36}. The *n*-alkanes exhibit a strong odd-to-even carbon number predominance with the dominant *n*-alkanes being C_{29}, C_{31} and C_{33} [10-13]. This is also evident in our study where the *n*-alkanes identified ranged from C_{12}-C_{36}, having the odd-carbon *n*-alkanes exceeding their even-carbon neighbours, thus exhibiting a saw-tooth pattern which is characteristics of biogenic *n*-alkanes. Fresh unburnt bachang litter falls exhibit total *n*-alkanes concentration of 1532 µgg^{-1} with C_{max} at C_{29} whilst dry burnt bachang litter falls smoke samples exhibit total *n*-alkanes concentration of 221 µgg^{-1}; with C_{max} at C_{27}. In addition, fresh unburnt grass samples exhibit total *n*-alkanes concentration of 33015 µgg^{-1}; with C_{max} at C_{33} whilst dry burnt grass and fresh burnt grass smoke exhibiting *n*-alkanes concentration of 939 µgg^{-1} and 708 µgg^{-1}, respectively with both samples exhibit C_{max} at C_{31}. It appears that burning samples resulted in emitting of lower *n*-alkanes concentrations, with a slight shift in C_{max} and differences in *n*-alkanes distribution. The Carbon Preference Index (CPI) calculated for carbon in the chain length between C_{18-36} gave values ranging from 0.77 to 27.3 with CPI average of 7.42 and showing an odd over even C number predominance (Table 1).
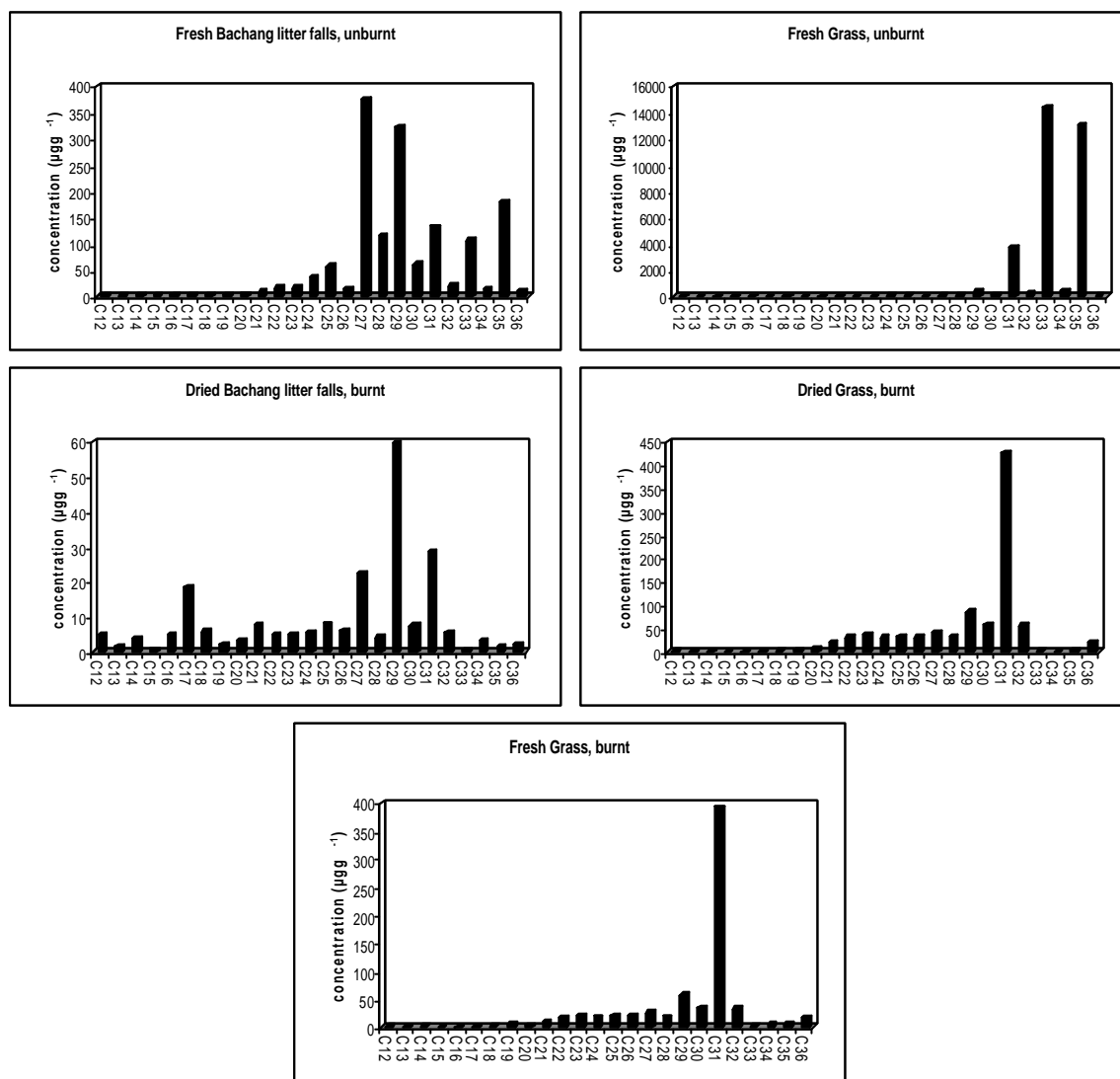
Figure 1: Distribution of individual aliphatic hydrocarbons in smoke and fresh unburnt samples.

Table 1: Concentration of aliphatic hydrocarbon compounds in smoke and fresh unburnt samples.

	Fresh burnt Grass (*Panicum repens*) **smoke**[a]	Dry burnt Grass (*Panicum repens*) **smoke**[b]	Dry burnt Bachang (*Mangifera foetida*) **leaves smoke**	Fresh unburnt Grass (*Panicum repens*)	Fresh unburnt Bachang (*Mangifera foetida*) **leaves**
TIRAH, µgg^{-1}	708	939	221	33015	1532
CPI$_{(C18-C36)}$	0.77	2.14	2.84	27.3	4.04
CPI$_{(C24-C34)}$	3.99	2.89	4.32	23.1	4.15
C$_{max}$	C31	C31	C29	C33	C27

[a] with 52.9$\pm$1.23% of moisture content
[b] with 33.0$\pm$0.84% of moisture content
CPI $_{(C24-C34)}$ = 0.5[?C25 – C33 / ?C26 – C34 + ?C25 – C33 / ? C24 – C32]
CPI $_{(C18-C36)}$ = 0.5[?C19 – C35 / ?C20 – C36 + ?C19 – C35 / ? C18 – C34]

Vascular plants synthesise epicuticular waxes containing odd C number n-alkanes usually in the C$_{25}$ to C$_{33}$ range with C$_{29}$ or C$_{31}$ 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 [14-15]. This is evident in *n*-alkanes distribution isolated from the fresh unburnt grass and bachang litter fall samples, which show a carbon distribution in the C_{12} to C_{36} range with C_{max} at C_{33} and C_{29} and a CPI value of 27.3 and 4.04, respectively. Similarly, the aliphatic distributions found in the present vegetation smokes were also consistent with earlier reports [1,2,9] and confirm an input from epicuticular wax source. It is interesting to note that, whilst retaining the characteristics of biogenic/plant waxes signature; burning of this vegetation seems to reduce *n*-alkanes concentration emitted accompanied by a decrease in the CPI values and in the case of the fresh samples, 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 fresh unburnt grass (33015 µg/g), followed by fresh unburnt bachang litter fall (1532 µgg^{-1}), dry burnt grass smoke (939 µgg^{-1}), fresh burnt grass smoke (708 µgg^{-1}) and dry burnt bachang litter fall smoke (221 µgg^{-1}).

PAHs

Figure 2 shows the distribution of individual priority PAHs present in the aromatic fraction in the smoke aerosols of samples studied. The figure reveals that all smoke samples exhibited PAH compounds. 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 phenanthrene is the most dominant component in dry burnt bachang litter fall smoke and dry burnt grass smoke, whilst benzo[g,h,i]perylene was found to be the most dominant component in fresh burnt grass smoke sample. Highest concentration of phenanthrene was found in the dry burnt bachang smoke with 65.8 µgg^{-1} and followed by dry burnt grass smoke with 59.4 µgg^{-1}. Fresh burnt grass smoke on the other hand gave benzo[g,h,i]perylene as highest PAH component with value of 54.4 µgg^{-1}. 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). In addition, another interesting feature observed from the result obtained in the dry and fresh burnt grass samples where sample's moisture content tend to reduce the PAHs content emitted in the smoke particles.
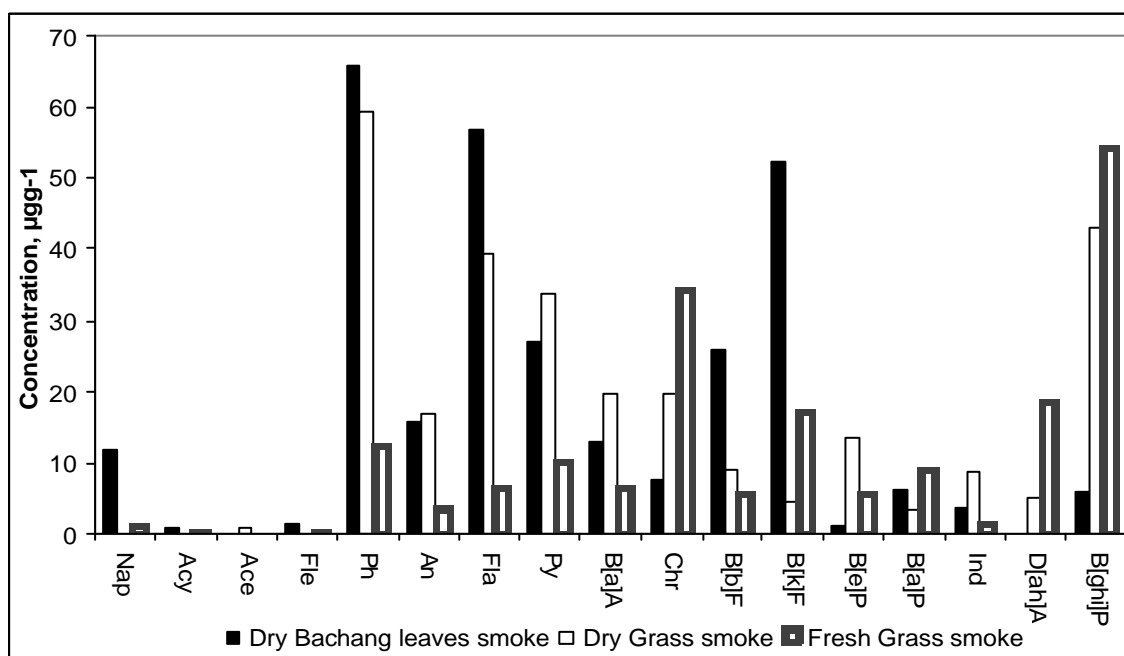
Abbreviations: Nap (naphthalene), Acy (acenaphthylene), Ace (acenaphthene), Fle (fluorene), Ph (phenanthrene), An (anthracene), Fla (fluoranthene), Py (pyrene), B[a]A (benz[a]anthracene), Chr (chrysene), B[b]F (benzo[b]fluoranthene), B[k]F (benzo[k]fluoranthene), B[a]P (benzo[a]pyrene), B[e]P (benzo[e]pyrene), Ind (indeno[1,2,3-cd]pyrene), D[ah]A (dibenz[a,h]anthracene), B[ghi]P (benzo[g,h,i]perylene).

Figure 2: Distribution of individual PAHs in smoke samples.

These PAHs profiles emitted from the comparison between the dry and fresh burnt grass smoke revealed that sample's moisture content has an influence on the PAHs content emitted in the smoke particle; the TIP emitted from the fresh burnt grass aerosols was significantly lower (187 μgg^{-1}) than the dry burnt grass samples (277 μgg^{-1}) (Table 2). The amount of TIP emitted from dry burnt bachang litter fall (Table 2) was found to be similar to that of dry burnt grass sample (296 μgg^{-1}). No PAHs was detected from the fresh unburnt grass and bachang wax which provide further evidence that PAHs are generally generated from the thermal decomposition of organic matter.

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

	Fresh burnt Grass (*Panicum repens*) smoke[a]	Dry burnt Grass (*Panicum repens*) smoke[b]	Dry burnt Bachang (*Mangifera foetida*) litter falls smoke	Fresh unburnt Grass (*Panicum repens*)	Fresh unburnt Bachang (*Mangifera foetida*) litter falls
Total PAHs (μgg^{-1})	187	277	296	N.D.	N.D.

N.D. = not detected

[a] with $52.9 \pm 1.23\%$ of moisture content

[b] with $33.0 \pm 0.84\%$ of moisture content

Conclusion

Results obtained in this study showed that fresh unburnt bachang litter fall and grass samples exhibit carbon distribution in the C_{12} to C_{36} range with C_{max} at C_{29} and C_{33}; with CPI value of 4.15 and 27.3 respectively. *n*-alkane distribution from the smoke samples showed carbon distribution ranging from C_{12} to C_{36} with odd carbon predominance and C_{max} at C_{29} or C_{31} and CPI values >1 indicating that combustion process retained the epicuticular waxes and terrigenous plant input signature. It was also found that although burning of the biomass samples retains the molecular signature of epicuticular waxes, the process seems to result in an increase of the range of aliphatic hydrocarbon emitted accompanied by a decrease in the CPI values and in the case of the fresh burnt smoke samples and 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 lesser amount of light and higher molecular weight PAHs.

Acknowledgements

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