

CONCENTRATION AND DISTRIBUTION OF PAHS IN SOILS AFFECTED BY GRASSLAND FIRE

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ABSTRAK Satu kajian telah dijalankan bagi menentukan kesan pembakaran kawasan tanah rumput ke atas taburan hidrokarbon aromatik polisiklik (PAHs) dalam tanah berhampiran jalanraya di daerah Marang. Sebanyak 15 sampel tanah permukaan telah diambil dari Kuala Tengah di Pulau Kerengga hingga Kg. Baharu di Merchang yang kerap dilanda kebakaran kawasan tanah rumput. Sampel tanah (< 500 μm) di 'ultrasonic' menggunakan diklorometana sebagai pelarut dan ekstrak yang diperolehi dipisahkan dengan menggunakan turus silika-alumina. Penentuan dan kuantifikasi 16 PAHs utama dijalankan dengan menggunakan GC-MS. Hasil menunjukkan kepekatan PAHs dalam tanah dikaji berada dalam julat 30 hingga 450 $\mu\text{g kg}^{-1}$ (jisim kering) dengan hampir kesemua stesen menunjukkan kehadiran benzo[a]pyrene (BaP), satu sebatian penunjuk PAH yang dikaitkan dengan pembakaran biojisim. Benzo[g,h,i] perylene (BgP), sebatian yang biasa dikaitkan dengan asap kenderaan juga didapati dalam sesetengah sampel tanah. Keputusan ini menunjukkan pembakaran tanah rumput dan pelepasan asap kenderaan menyumbang kepada kehadiran PAHs dalam tanah yang dikaji. Namun, korelasi yang lebih tinggi diantara kepekatan BaP dengan jumlah PAHs berbanding BgP dengan jumlah PAHs menunjukkan pembakaran tanah rumput yang baru terjadi di kawasan ini turut mempengaruhi taburan PAHs dalam tanah yang dikaji.

ABSTRACT A study has been carried out to determine the affect of grassland fire on the distribution of polycyclic aromatic hydrocarbons (PAHs) in roadside soils of Marang district. 15 surfacial soil samples were collected from Kuala Tengah in Pulau Kerengga to Kg. Baharu in Merchang, a stretch of area bordering to the national trunk road, which frequently suffered from grassland fires. Soil samples (< 500 μm) were ultrasonicated using dichloromethane as solvent and the extracts fractionated on silica-alumina column. Detection and quantification of 16 priority PAHs compounds were carried out using GC-MS. Results indicated that concentration of PAHs in soils ranged from 30 to 450 $\mu\text{g kg}^{-1}$ (dry weight) with almost all stations showing the presence of benzo[a]pyrene (BaP), a signature PAH compound associated with biomass burning. Benzo[g,h,i] perylene (BgP), a compound generally associated with vehicular emission was also observed in some of the soil samples. These results indicate that both biomass burning and vehicular emission contributed to the presence of PAHs in these soils, however, a higher correlation observed for BaP and total PAHs compared to between BgP and total PAHs suggest that recent grassland fires in the area has an impact on the distribution of PAHs in the soils studied.

Keywords: PAHs, soils, grassland fire, biomass burning, GC-MS detection

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the global environment and soil remains as one of the most important sinks for these compounds. PAHs are known as priority pollutants [1] and due to their mutagenic and carcinogenic potentials; their presence in the environment has received much attention worldwide [2-8]. Main sources of PAHs in soils include incomplete combustion of fossil fuels, vehicular emissions, biomass burning, municipal incinerators and through the atmospheric deposition as a result of long-range atmospheric transport and also formed through natural events like bush fires and volcanic eruptions. These ubiquitous organic pollutants exhibit strong carcinogenic and toxic properties. It is estimated that at least 90% of the environmental burden of PAHs in Great Britain resides in the surface soils [9]; this estimate excludes contaminated sites such as gas-work sites, petroleum refineries, or wood preservation plants. The typical level of endogenous total PAHs in soils is reported to range between 1-10

$\mu\text{g kg}^{-1}$ resulting from plant synthesis and natural fires [10] but actual levels and distribution patterns of PAHs in tropical soils are thought to differ significantly from those of temperate soils owing to the enhanced microbial degradation, photo-oxidation and volatilization of PAHs in tropical soils [6, 11]. Despite of the work reported by Nasr *et al.* in 2002 [2] and Mohd Tahir *et al.* [12], published literatures on the study of PAHs content in soils in Malaysia is still scarce. In view of this, beginning in the year of 2002, a comprehensive study has been initiated to measure the PAHs concentrations in soils in the east coast of Peninsular Malaysia. Main potential sources of PAHs in soils in most parts of the east coast would originate from vehicular emission and biomass burning, through the burning of garden refuse or burning of wood for cooking which are still prevalent in this part of the country, and also natural fires. This paper presents the results of a study carried out on roadside soils located in the Marang district, Terengganu. The area studied was from Kuala Tengah in Pulau Kerengga and Kg. Baharu in Merchang, which forms part of the national trunk road linking Kuala Terengganu and Kuantan. This particular stretch of roadside was chosen because the surrounding areas were prone to natural grassland fires, which might have an affect on the distribution of PAHs in these soils.

EXPERIMENTAL METHODS

Sampling

In this study, soil sampling was done during the months of June-August 2002 and sampling sites were chosen from areas, which have visible traces of charred tree barks, and those not directly affected but adjacent to the affected area. Figure 1 shows the sampling stations of soils taken in this study. Sampling involved the collection of 15 surfacial soil samples (0-10 cm) using metal spades and kept in a small aluminium bag. All samples were then transported to laboratory in icebox to minimize sample degradation. Generally, where possible soil samples were collected ca. one metre from the roadside. Once in the laboratory, soil samples were homogenized and sieved through a 500 μm sieve.

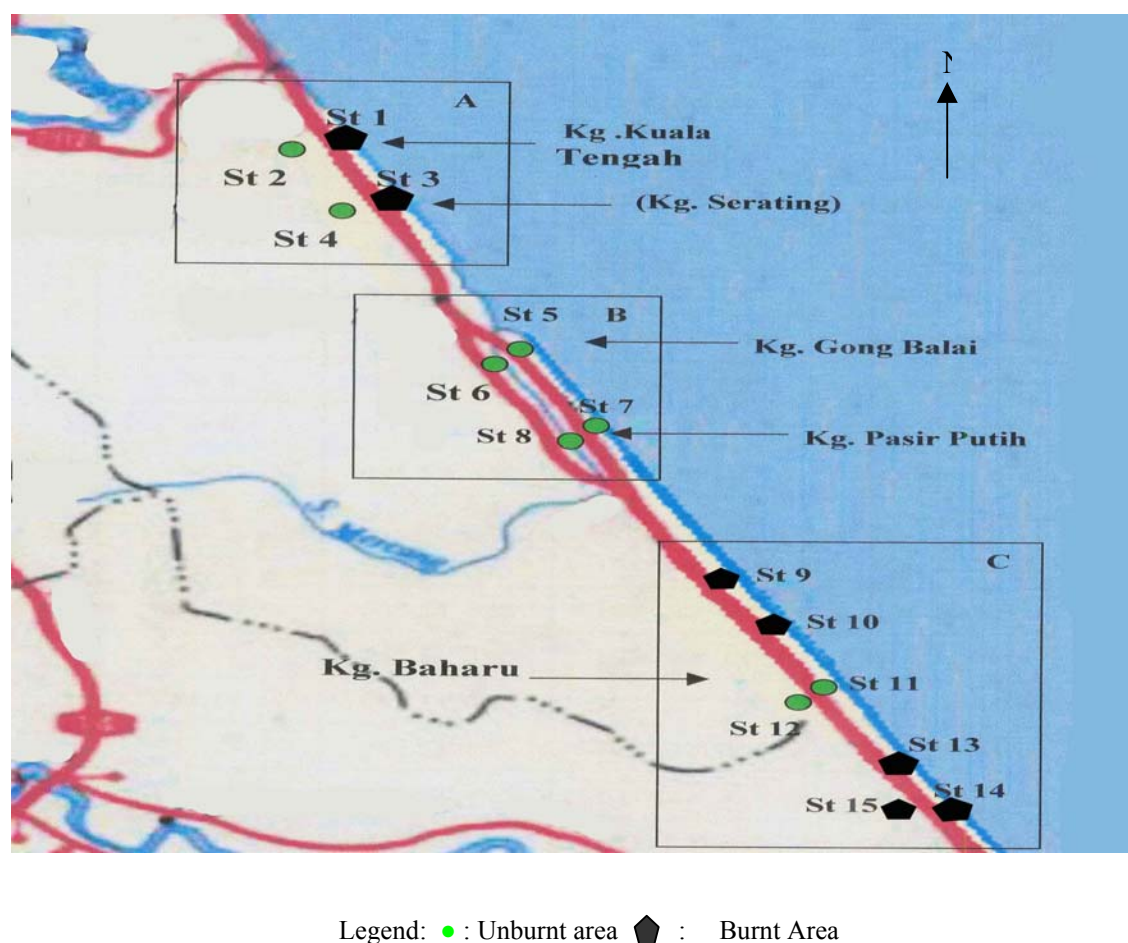


Figure 1. Location of sampling stations

Extraction and Fractionation

The soils (< 500 µm) were ultrasonicated using dichloromethane (DCM) as the extracting solvent. Before extraction, an internal standard (9,10-dihydroanthracene) for PAHs fraction (fraction 2) was spiked into the soils 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; PAHs compounds were eluted using a combination of 20 ml of 10% DCM in hexane followed by 20 ml of 50% DCM in hexane [13].

GC-MS analysis

Identification and quantification of 16 priority PAHs compounds were carried out using GC-MS. The compounds were as follows: naphthalene (NAP), acenaphthylene (ACY), acenaphthene (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 0.25 mm i.d; 0.25 µm film 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°C min⁻¹; 140-290°C at 4°C min⁻¹ and maintained at 290°C for 13 min. Helium was used as the carrier gas with flow rate at 1.0 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 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

Total Organic Carbon

Figure 2 shows the distribution of total organic carbon (TOC) in soil samples; in this study TOC in soils were analysed using Walkley and Black's rapid titration method [14]. Surface soils in the study area contained relatively low organic carbon, with values ranging from 0.12% to 0.99%. In general soils taken from areas affected by the fire exhibited relatively higher percentage of TOC (0.42 – 0.99%) compared to those not affected by the fire (0.12-0.42%). It has been suggested that burning of biomass could lead to an increase in TOC in the affected soils owing to the addition of ash and partially combusted materials or to the accumulation of charcoal [15 and references cited therein]; the trend observed in this study is consistent with this report.

Polycyclic Aromatic Hydrocarbon (PAHs)

The distribution of total identified PAHs (TIP) obtained in this study is shown in Figure 3. Results indicated that the soils studied contained TIP values significantly above the range reported for endogenous total PAHs concentration in soils [10]; values found in this study ranged from 30 to 450 µg kg⁻¹ (dry weight) with a mean concentration of 190 µg kg⁻¹ ± 141 (dry weight). The mean value of TIP obtained in this study is consistent with the value reported for Kuala Lumpur (224 ± 108 µg kg⁻¹) [2]. Interestingly, results obtained in this study showed that no significant differences in concentration range were observed for samples taken from an area directly affected compared to those taken from areas not affected by the fire. This observation could be an indication of the role played by wind in dispersing the PAHs to nearby area. Similarly, there is no clear trend observed in the distribution of PAHs compounds between sites affected directly by the grassland fire and those not affected by the fire; of the 16 priority PAHs compound monitored, their distribution at each sampling site were found to differ with stations, with station 11 showing the presence of all compounds except for naphthalene and acenaphthene and station 10 exhibiting the presence of only the higher molecular weight PAHs viz. BkF, BaP and DA. BgP, another heavy

molecular weight PAHs compound, was found to be present in quite a number of stations. The other feature observed is that almost all stations exhibited the presence of BaP and ANT.

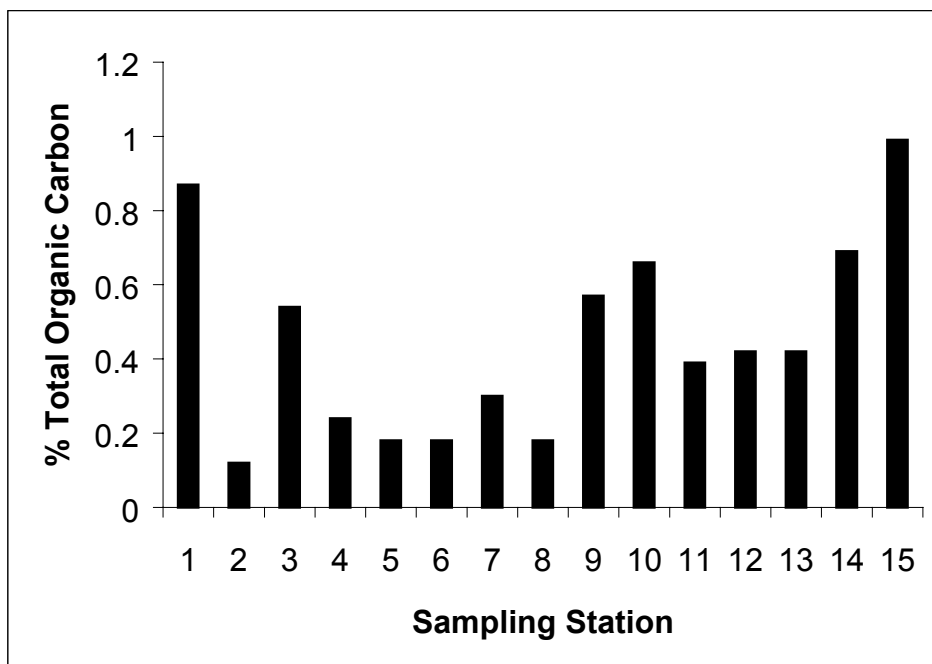


Figure 2. Distribution of total organic carbon with sampling stations

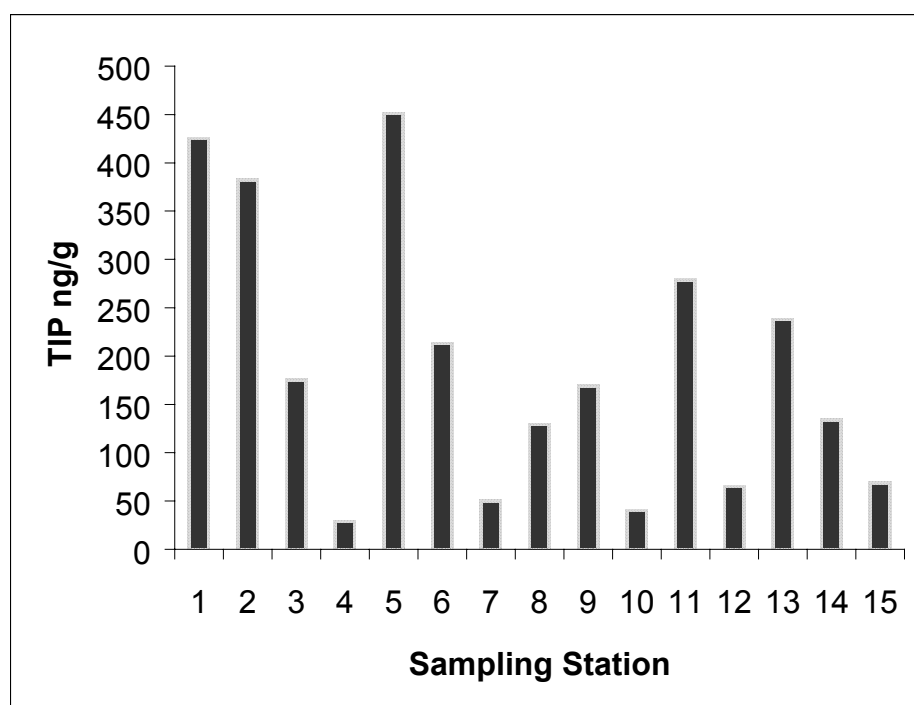


Figure 3. Distribution of total identified PAHs (TIP) with sampling stations

Phenanthrene to anthracene (PHEN/ANT) ratio has often been used to investigate possible source of PAHs in the environment where low ratio (<10) is generally indicative of pyrolytic sources [16]. With the exception of station 14 which exhibited a PHEN/ANT ratio of 12.56, all other stations exhibited PHEN/ANT ratios ranging from 0.03 - 1.54 with an average of $0.33 \pm 0.53_{(stdev)}$. The low ratio values suggest that the PAHs compounds found in the roadside soils were mainly derived from pyrolytic sources.

Differentiating between the two major pyrolytic source, viz. biomass or engine combustion require the use of other molecular markers; presence of BaP in the environment is generally indicative of incomplete combustion sources, in particular combustion of organic matter (also known as biomass) whilst the association of BgP with vehicular emission has long been established [17]. A linear correlation analysis between TIP and BaP and between TIP and BgP gave an r-value of 0.55 and 0.42, respectively (Fig.4 and Fig. 5) which suggest that both sources contribute to the presence of PAHs in these soils. The contribution of vehicular emission source is expected, since the soil samples were taken near the national trunk road. It is interesting to note that the correlation between TIP and BaP was relatively stronger than that of TIP and BgP indicating that biomass burning is a relatively more important source of PAHs found in these samples. Thus, it can be concluded that a stronger correlation of TIP vs. BaP compared to TIP vs BgP is consistent with the impact of recent forest fires on the distribution of PAHs compounds present in these samples.

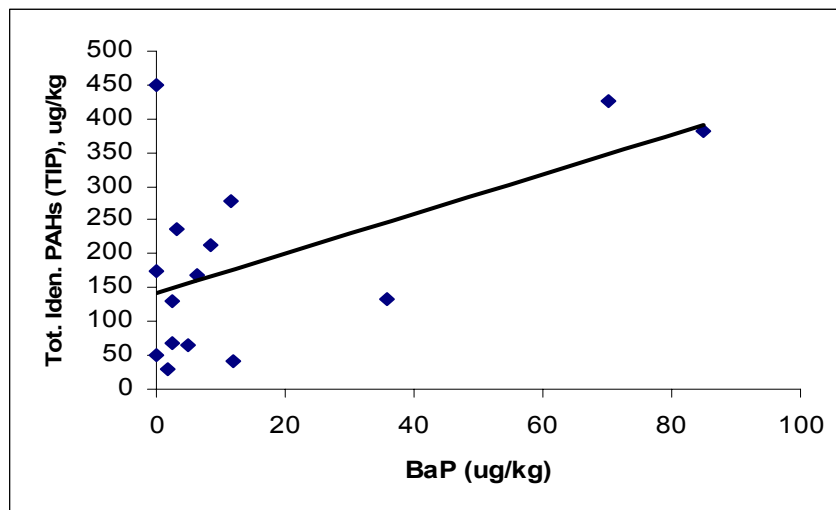


Figure 4. Correlation between total identified PAHs (TIP) and benzo[a]pyrene (BaP)

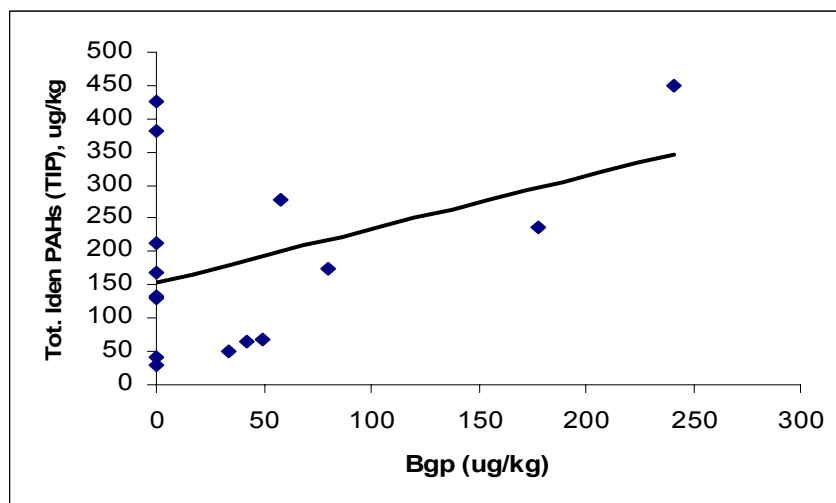


Figure 5. Correlation between total identified PAHs (TIP) and benzo[g,h,i]perylene (BgP)

CONCLUSION

The total concentration of TIP found in this study ranged from from 30 to 450 $\mu\text{g kg}^{-1}$ (dry weight) with a mean concentration of 190 $\mu\text{g kg}^{-1} \pm 141$ (dry weight). Almost all stations showed the presence of BgP, BaP and ANT compounds. The fairly strong correlation between BgP and TIP and between BaP and TIP as well as low values of PHEN/ANT diagnostic ratio indicate that the PAHs compounds were of mixed pyrolytic sources (i.e. biomass and engine combustion). A relatively higher correlation between BaP and

TIP compared to between BgP and TIP suggests that that recent grassland fires in the area has an impact on the distribution of PAHs in the soils studied.

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