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Polycyclic aromatic hydrocarbons (PAHs) in fine fractions of Barapukuria coal in Bangladesh

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Abstract

The existence and distribution of polycyclic aromatic hydrocarbons (PAHs) in fine coal fractions have been determined in order to evaluate their potential carcinogenicity to human beings. Thirteen PAHs of fine coal fractions ($n = 9$) from Barapukuria coal field, situated at the northwestern part of Bangladesh were analyzed by the gas chromatography-mass spectrometry (GC-MS) method in order to examine their distributions and toxicity in the environment. Relative abundances of fluoranthene (Flu), pyrene (Pyr), benzo [*b,j,k*] fluoranthene (Bfla), benzo [*e*] pyrene (BeP) and benzo [*a*] pyrene (BaP) were found to be high, followed by phenanthrene (Phe), indeno [*1,2,3-cd*] pyrene (InP), benzo [*g,h,i*] perylene (BghiP) and coronene (Cor). The average loads of carcinogenic PAHs in the fine coal fractions decreased in the order: Bfla > BeP > BaP > BghiP > InP > Cor. The PAHs ratios of BeP/(BeP + BaP) ranging from 0.61 to 0.85 (average 0.74), reflected the decay of BaP due to ageing in prolonged exposure to the solar radiation. High abundance of land plant markers retene (Ret) and Phe and BaP/BghiP ratio (~0.10 to 6.16, average 1.89) values indicate that organic matters in the studied samples were derived from typical biological sources. Moreover, the existence of more middle- and higher molecular weight (MMW and HMW) PAHs over lower molecular weight (LMW) PAHs in most samples implied the association of high toxicity with negative impacts on human health. The health risk assessment factors (BaP_{eq}) ranging from 0.55 ng g⁻¹ to 6.51 ng g⁻¹ indicates moderate to high health risk related to carcinogenic PAHs in the surrounding atmosphere. The estimated incremental lifetime cancer risk (ILCR) values for adults (9.96×10^{-5} to 1.27×10^{-4}) and children (5.56×10^{-6} to 1.12×10^{-6}) were found to be higher than or equal to the range of 1.0×10^{-6} to 1.0×10^{-4} .

Keywords: Polycyclic aromatic hydrocarbons (PAHs); Coal fractions; Source identification; Health risk assessment; Bangladesh

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are common toxic organic chemicals composed of two or more fused benzene rings arranged in different configurations (Chefetz *et al.*, 2000; Kim *et al.*, 2013; Wu *et al.*, 2014; Hu *et al.*, 2017). PAHs can comprise extra fused rings those are not six-sided. Some representative structures, formula, physicochemical properties and existence in either particle or gas phase are shown in Table 1. The presence of PAHs in natural environment is largely generated during incomplete combustion or pyrolysis of organic materials from both natural and anthropogenic sources (Omar *et al.*, 2006; Ravindra *et al.*, 2008; Li *et al.*, 2016). The natural sources of

PAHs are likely emissions from forest fires and volcanic eruptions (Ravindra *et al.*, 2008; Jamhari *et al.*, 2014), whereas anthropogenic sources of PAHs and their alkyl derivatives are constituents of crude oil, refined petroleum products and industrial chemicals, power plants, waste incineration and coal/biomass burning (Vicente *et al.*, 2015). Several PAHs are also originated from transformation by photolysis, photochemical, thermochemical reactions and oxidation of biological materials (Boström *et al.*, 2002; Bandowe and Nkansah, 2016). However, PAHs are released mostly into the atmosphere, present as gases or in fine particulate matter (e.g. coal dust, street dust etc.) (Wu *et al.*,

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2014; Bandowe and Nkansah, 2016; Lui *et al.*, 2017). In general, PAHs are known to have mutagenic, genotoxic, carcinogenic and estrogenic properties, and their physicochemical properties are highly mobile in the environment via air, soil and water bodies (Boström *et al.*, 2002; Kim *et al.*, 2013; Wincent *et al.*, 2016; Hu *et al.*, 2017; Lui *et al.*, 2017). PAHs in the atmospheric environment behave equal to persistent organic pollutants continue to undergo long-range atmospheric transport (Fang *et al.*, 2004; Mulder *et al.*, 2015; Liu *et al.*, 2017). However, reaction half-lives of persistent organic pollutants in water, soil, and sediments are much higher than in the atmospheric gaseous phase. Recently, atmospheric PAHs have received great attention in air pollution studies globally owing to its high levels of toxicants those are harmful for most city dwellers (Fang *et al.*, 2004; Kim *et al.*, 2013; Jamhari *et al.*, 2014; Hu *et al.*, 2017; Lui *et al.*, 2017).

Coal is solid fossil fuels that are omnipresent in sedimentary rock strata. The Permian Gondwana sequence in northwestern Bangladesh contains abundant coals and coaly shales. The coal-bearing Barapukuria basin, covering an area of approximately 6.68 km² (Wardell-Armstrong, 1991; Bakr

et al., 1996; Annual Report, 2017), is located in the Rangpur platform of the Stable Shelf zone in northwestern Bangladesh (Fig. 1). This area lies between the latitudes 25°31'45" to 25°33'50" N and the longitudes 88°57'48" to 88°58'53" E (Tahsin *et al.*, 2016). A total geological coal reserve is estimated to be 390 million tons in the Barapukuria coal basin (Annual Report, 2017). Approximately 4,500 metric tons of coal is extracted every day from coal face no. 1207 within the coal seam VI (Fig. 1b) of the Barapukuria coal mine (Annual Report, 2017), which is mainly used in coal based power plant, brick industry and domestic cooking purposes. Huge amount of fine coal particles are generated during coal extraction from underground coal cutting phase, coal transport and coal storage in an open place in the coal mine area. These fine fractions are often mixed with inside and outside environments via inlet or outlet mine ventilation system to air, soil, and running water that are highly carcinogenic and posing high risk to humans (e.g. pneumoconiosis, lung diseases, chronic obstructive pulmonary disease) from short- and long-time inhaling those fine particles from surrounding atmosphere. Several authors have investigated coal and coal-bearing Gondwana sequence in northwestern Bangladesh from different points of view

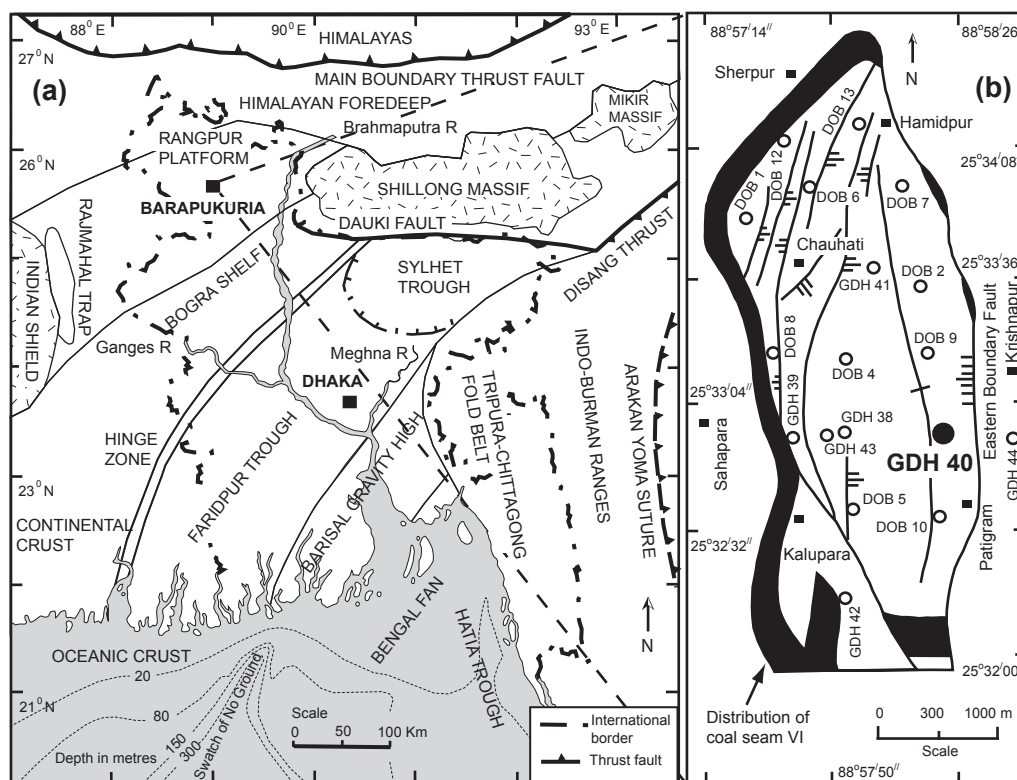


Fig. 1. (a) Location map of the Barapukuria basin and surrounding areas (after Hossain *et al.*, 2013b, 2019) and (b) Distribution of coal seam VI in the Barapukuria basin, northwestern Bangladesh (after Bakr *et al.*, 1996)

such as lithofacies, stratigraphy, sedimentology, geochemistry, petrography and many others (e.g. Wardell-Armstrong, 1991; Uddin and Islam, 1992; Bakr *et al.*, 1996; Islam, 1993, 1994, 2002; Hossain *et al.*, 2002, 2013; Islam *et al.*, 2004; Tahsin *et al.*, 2016). So far no study has been conducted using this fine coal particle to address toxicity and long term cancer risk to humans. So, the present study has been conducted for exploring toxic PAHs in fine coal fractions of Bangladesh, and for assessing the harmful impact into the atmospheric environments.

Materials and methods

Sampling

This study was conducted in Barapukuria coal field area, the only one underground coal mine in Bangladesh which is situated in Dinajpur district, northwestern part of Bangladesh. A total of nine samples of fine coal fractions were collected from the Barapukuria coal mine area during dry season (Fig. 1). The samples were stored in polythene bags (Ziploc) subsequently sealed and transport to the laboratory. All samples were then air dried at room temperature to constant weight and homogenized by grinding in an agate mortar and pestle.

All the fine powdered samples were used for solvent extraction of bitumen. Approximately 5 g powdered samples were extracted using Soxhlet apparatus with a mixture of dichloromethane (DCM) and MeOH solution (9:1) for 72 h. Activated copper granules were added to remove elemental sulfur from the solutions. The extracted solvent was removed using a rotary vacuum evaporator (Hossain *et al.*, 2013a). The *n*-alkanes and PAHs were separated using thin layer chromatography over activated silica gel (Kieselgel 60 PF254, Merck). The extracts were transferred into two ampoule bottles and stored in a refrigerator until analysis in the laboratory.

The fractions containing the PAHs were subjected to analyze by a gas chromatography (GC: Shimadzu QP2010) coupled with a mass spectrometry (MS: Shimadzu GCMS-QP2010) instrument through filtration by 0.45 μm filters. The GC is equipped with a programmable temperature injection system and a fused silica capillary column (30 m \times 0.25 mm ID, DB-5MS, Agilent Technology), with a temperature program of 50–300 $^{\circ}\text{C}$ at a rate of 8 $^{\circ}\text{C}/\text{min}$. Helium with a purity of 99.999% is used as the carrier gas. The MS is operated in electron impact ionization mode with an ion source temperature of 250 $^{\circ}\text{C}$ and the electron impact energy is set at 70 eV. All spectra were recorded over a range of 50 to 850 m/z at a scan rate of 0.5 s. Quantification of PAHs is standardized by the comparison of GC retention times, mass

spectra with published data and with standard PAHs Solution Mix (Accu Standard Inc. Z-013-17).

In this study, thirteen PAHs are identified and estimated, such as phenanthrene (Phe, $m/z = 178$), anthracene (Ant, $m/z = 178$), fluoranthene (Flu, $m/z = 202$), pyrene (Pyr, $m/z = 202$), retene (Ret, $m/z = 219$), benzo[*a*]anthracene (BaA, $m/z = 228$), chrysene (Chry, $m/z = 228$), benzo[*b,j,k*]fluoranthene (Bfla, $m/z = 252$), benzo[*e*]pyrene (BeP, $m/z = 252$), benzo[*a*]pyrene (BaP, $m/z = 252$), indeno[1,2,3-*cd*]pyrene (InP, $m/z = 276$), benzo[*g,h,i*]perylene (BghiP, $m/z = 276$) and coronene (Cor, $m/z = 300$). The PAHs are classified based on the number of aromatic rings present in the individual compound such as 2-ring (Naphthalene), 3-ring (Phe, Ant), 4-ring (Flu, Pyr, BaA, Chry), 5-ring (Bfla, BeP, BaP), 6-ring (InP, BghiP), and 7-ring (Cor). Naphthalene was not identified in this study. On the basis of aromatic rings number, investigated PAHs are also categorized as lower molecular weight PAHs (LMW, containing 2- to 3-rings PAHs), middle molecular weight PAHs (MMW, containing 4-ring PAHs), and higher molecular weight PAHs (HMW, containing 5- to 7-rings PAHs).

Human health risk assessment of PAHs

Health risk assessment model was used to evaluate carcinogenic and non-carcinogenic threat obtained from different exposure pathways (USEPA, 1989). Health risk can be calculated using PAHs exposure in the environment through ingestion, inhalation and/or dermal exposure (Jamhari *et al.*, 2014; Kong *et al.*, 2015; Li *et al.*, 2016; Hu *et al.*, 2017). BaP equivalent concentration (BaP_{eq}) was also adopted to assess the health risk of PAHs (Kong *et al.*, 2015; Li *et al.*, 2016). The BaP_{eq} was estimated by multiplying the mass concentrations of individual PAH species of their corresponding toxic equivalency factors as follows:

$$\text{BaP}_{\text{eq}} = 0.001 (\text{NaP} + \text{Ace} + \text{Flu} + \text{Phe} + \text{Fl} + \text{Pyr}) + 0.01 (\text{Ant} + \text{Chry} + \text{BghiP}) + 0.1 (\text{BaA} + \text{Bfla} + \text{InP}) + \text{BaP} + \text{DBA} \quad (1)$$

NaP (naphthalene), Ace (acenaphthene), Fl (fluorene), and DBA (dibenz[*a,h*]anthracene) were not detected in the present study samples. However, NaP value for coaly shale sample in the Barapukuria basin was taken from Hossain *et al.* (2019). The Ace, Fl and DBA values were adopted from published literature (Jamhari *et al.*, 2014; Wu *et al.*, 2014).

The cancer risk can be assessed from direct inhalation of carcinogenic PAHs in the atmospheric environments (USEPA, 1989; Jamhari *et al.*, 2014; Kong *et al.*, 2015). The incremental lifetime cancer risks (ILCR) for human beings was calculated by the lifetime average daily dose (LADD) of

PAHs based on USEPA guidelines (USEPA 1989, 2013; Wiriyā *et al.*, 2013; Jamhari *et al.*, 2014; Kong *et al.*, 2015; Li *et al.*, 2016) as follows:

$$\text{LADD} = C \times \text{IR} \times \text{ED} \times \text{EF} / (\text{BW} \times \text{ALT}) \quad (2)$$

$$\text{ILCR} = \text{LADD} \times \text{CSF} \quad (3)$$

where C is the mass concentration of PAHs in fine coal particles (ng g^{-1}); IR is the inhalation rate ($\text{m}^3 \text{day}^{-1}$, 20 and 7.6 for adult and children, respectively); ED is the lifetime exposure duration (52 years for adult and 6 years for children); EF is the exposure frequency ($250 \text{ days year}^{-1}$); BW is the average body weight (70 kg and 15 kg for adult and children, respectively); ALT is the average lifetime for carcinogens ($70 \text{ years} \times 365 \text{ days year}^{-1} = 25,550 \text{ days}$); and CSF is the carcinogenic slope factor ($1/(\text{mg kg}^{-1} \text{day}^{-1})$). In the present study, CSF value based on the cancer-causing ability of BaP is set as 3.85 ($1/(\text{mg kg}^{-1} \text{day}^{-1})$) for inhalation

(Hu *et al.*, 2017). The total BaP_{eq} (ng g^{-1}) values are used to calculate LADD instead of C (Jamhari *et al.*, 2014; Li *et al.*, 2016).

Results and discussion

PAHs ring number distributions and sources

The distribution and possible source of PAHs and their influence in atmospheric environments can be found in different concentrations of LMW, MMW, and HMW PAHs existing in the studied environmental samples. Representative TIC (total ion current) chromatograms and average PAHs distributions of the studied samples are shown in Figs. 2 and 3. The relative abundance of 4- (Flu, Pyr) and 5-rings (Bfla, BeP) PAHs are considerably high, followed by 3- (Phe), 6- (InP, BghiP), and 7-rings (Cor) PAHs. The biological origin of Phe and Ret sets them at higher abundances, while combustion derived high molecular

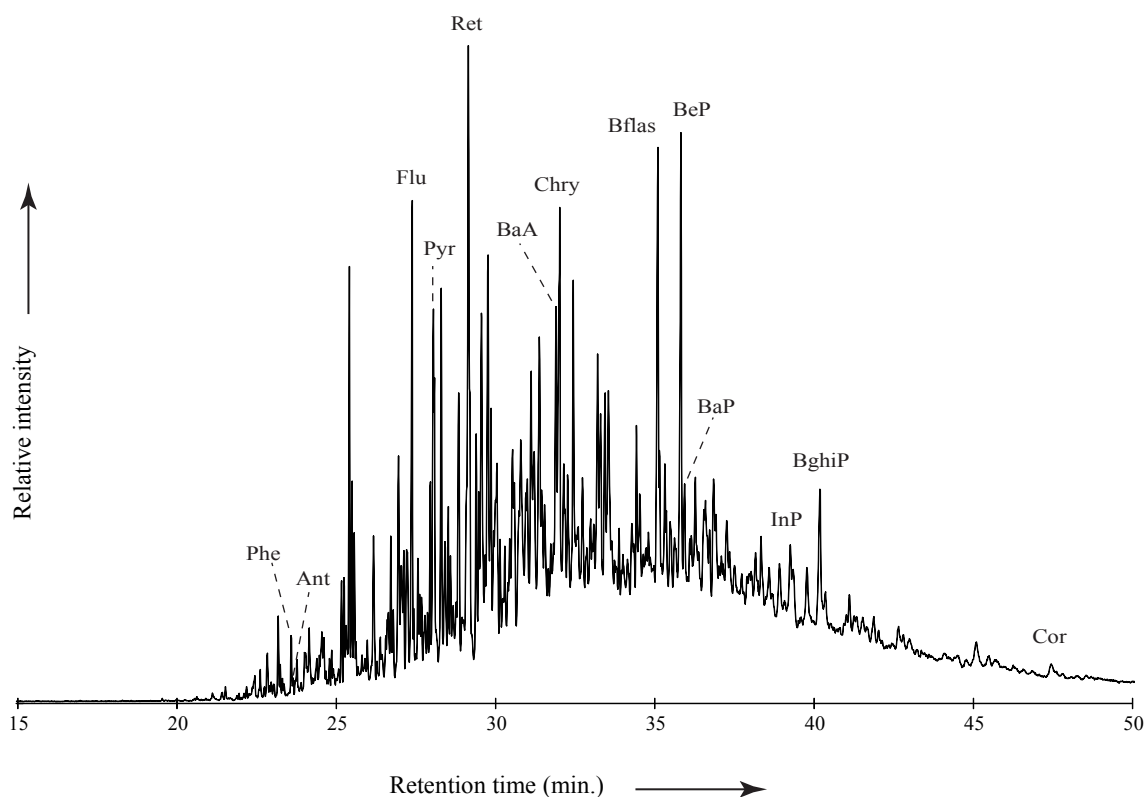


Fig. 2. Representative total ion chromatograms (TICs) of aromatic hydrocarbon fractions (m/z 57) of fine coal samples from the Barapukuria coal field, northwestern Bangladesh. Abbreviations: Phe, phenanthrene; Ant, anthracene; Flu, fluoranthrene; Pyr, pyrene; Ret, retene; BaA, benzo [a] anthracene; Chry, chrysene; Bfla, benzo [b,j,k] fluoranthrene; BeP, benzo [e] pyrene; BaP, benzo [a] pyrene; InP, indeno [1,2,3-cd] pyrene; BghiP, benzo [g,h,i] perylene; Cor, coronene

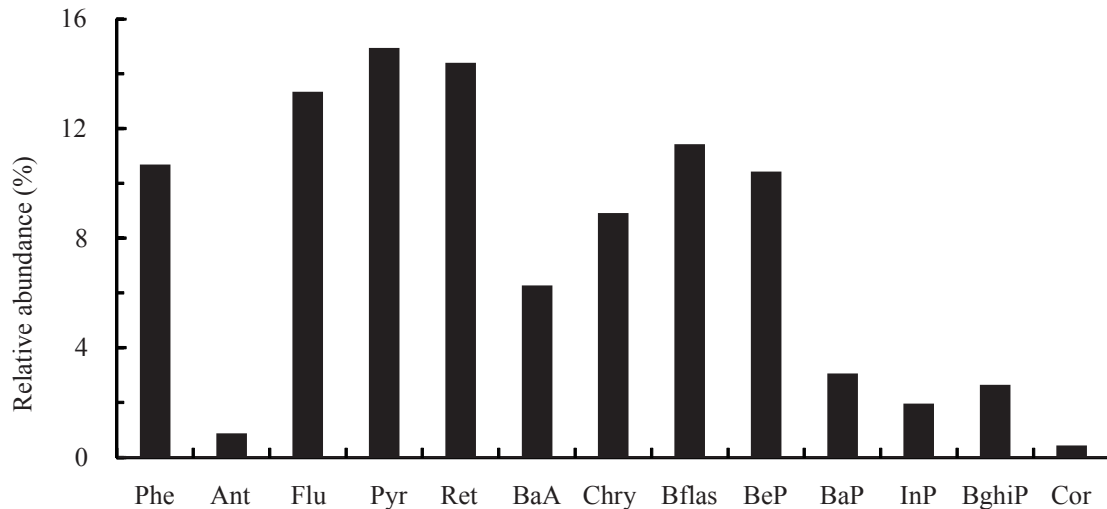


Fig. 3. Average relative abundance of PAHs for the studied fine coal fractions in Barapukuria coal field, northwestern Bangladesh

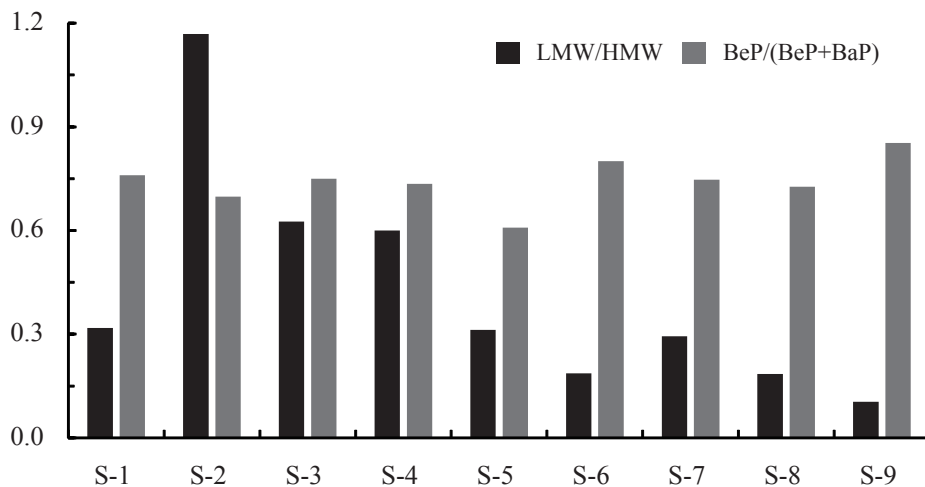


Fig. 4. Comparison of LMW/HMW and BeP/(BeP + BaP) ratios for each sample of the fine coal fractions in Barapukuria coal field, northwestern Bangladesh

weight PAHs (e.g. Cor) are present in low abundances (Fig. 2). However, average Phe loads are nearly identical to Bfla and BeP, whereas Ant alone is two times higher than Cor. Meanwhile, average relative abundance of MMW PAHs is significantly higher than some compound of HMW PAHs in the samples studied (Fig. 3). The ratios of LMW/HMW PAHs in the samples ranged between 0.10 and 1.17, with high values in one sample (S-2, Fig. 4) and two samples contained

>0.5, and others fall below 0.5 (Fig. 4). These features suggest that some contrasts in source materials (diagenetic or combustion) exist between the samples, and their adverse human health effects in short- and long-time inhalation are discussed in sub-section 3.2.

Among the PAHs, LMW or MMW compounds are typically semi-volatile and partition in both the gas and particle phases

(Table 1), while HMW compounds are highly non-volatile and retain commonly in the particle phase (Huang *et al.*, 2006; Wu *et al.*, 2014; Kong *et al.*, 2015; Hu *et al.*, 2017). Thus, LMH PAHs are more volatile than HMW PAHs, and has a larger ability to transport in the air phase systems as Wu *et al.* (2014) and Kong *et al.* (2015) noted that PAHs with LMW are mostly distributing in gas phase in the natural environments. PAHs originated from numerous sources, including combustion (both biomass and diagenetic alteration of natural biolipids), and emissions of non-combustion derived diagenetic processes (Chefetz *et al.*, 2000; Yunker *et al.*, 2011). The contribution of PAHs is mainly controlled by accessibility of biological yield and organic matter particle size, and organic matter stability through oxidative weathering, rock alteration, biodegradation and bioaccumulation, and long-run transport to sedimentary environments (Yunker *et al.*, 2002; Marynowski *et al.*, 2011). On the other hand, biomass burning and fossil fuel combustion of power plants, industries, residential cooking and vehicles are major sources of PAHs in the atmosphere due to their incomplete combustion or pyrosynthesis process (Omar *et al.*, 2006; Ravindra *et al.*, 2008; Jamhari *et al.*, 2014; Kong *et al.*, 2015). Moreover, PAHs with HMW (e.g. Bfla, BeP and Cor)

are less susceptible to environmental transportation, oxidative modification and bacterial degradation (Jiang *et al.*, 1998), while BaA and BaP are frequently degraded during those processes (Sicre *et al.*, 1987; Yunker *et al.*, 2002, 2011; Stout and Emsbo-Mattingly, 2008). Jamhari *et al.* (2014) reported that high concentrations of Flu, Pyr, BaA and Chry in the natural environmental samples are regarded as natural gas and coal combustion. The investigated coal fractions contained high relative abundances of Bfla, BeP, Flu, Pyr, BaA and Chry (Fig. 2), suggesting that these PAHs were originated primarily from combustion sources, leading to probable carcinogenic to humans. The relative abundances of total carcinogenic PAHs in individual samples are shown in Fig. 5. Most samples containing elevated level of carcinogenic PAHs (>30%), indicating higher health risks from long-term PAHs exposure in the environment. Furthermore, large contributions of these PAHs in the Barapukuria coal mine areas may bear a worst health impact to the mine workers as well as nearby populations. Presence of high relative abundances of Phe and Ret in the studied coals suggests biological source materials input to the atmospheric environment.

5-ring PAHs such as BaP is more reactive than BeP in the

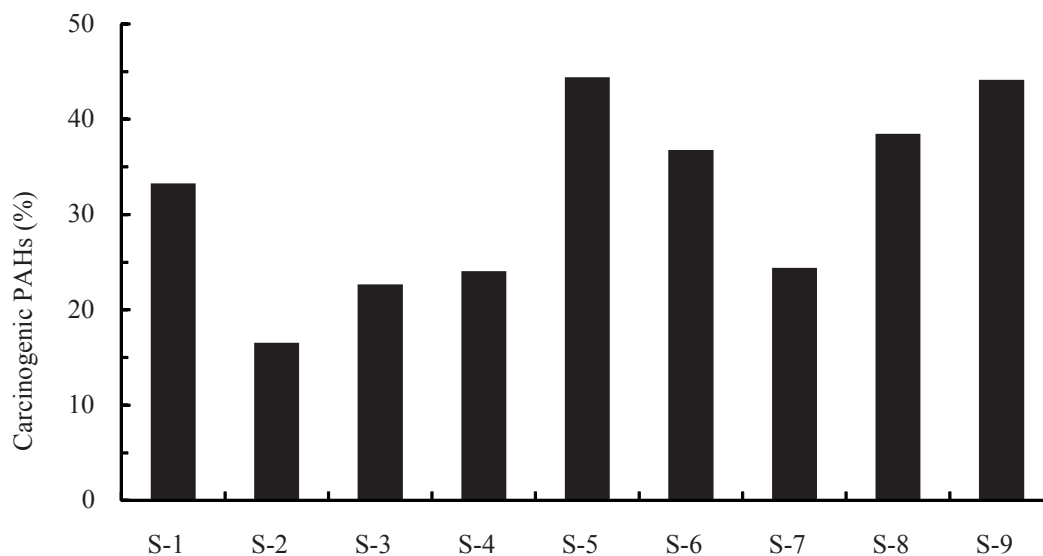


Fig. 5. Relative abundances (percentage) of carcinogenic PAHs for each sample of the fine coal fractions in Barapukuria coal field, northwestern Bangladesh

atmospheric environment (Kong *et al.*, 2015), and BeP/(BeP + BaP) ratio is remarked as an indicator of the aging process of aerosols (Huang *et al.*, 2006; Omar *et al.*, 2006). BaP is readily susceptible to photochemical oxidation in natural environment (Kong *et al.*, 2015). Therefore, photochemical degradation of PAHs in the atmospheric environment might enriched BeP/(BeP + BaP) ratio (Omar *et al.*, 2006; Kong *et al.*, 2015). The BeP/(BeP + BaP) ratios in the investigated samples ranged from 0.61 to 0.85 (Fig. 4), reflecting decay of BaP due to aged and prolonged exposure to solar radiation (Nielsen, 1988; Omar *et al.*, 2006). The significantly higher level of BaP/BghiP ratios (>1.25) in the atmosphere were suggested for residential heating and industrial operation of coal (Ravindra *et al.*, 2008). Thus, the ratios of BaP/BghiP in the coal fractions studied are ranging from ~ 0.70 to 6.16 (average 1.89), and most of the samples have values >1.25 reflecting occurrence of coaly organic matter sources.

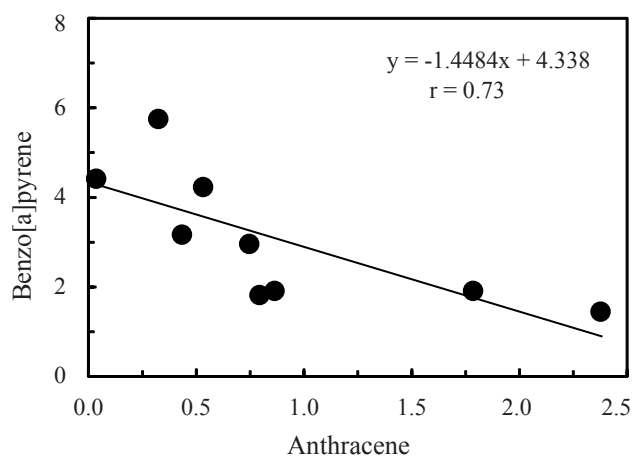


Fig. 6. Relationship between benzo[a]pyrene and anthracene of the studied fine coal fractions in Barapukuria coal field, northwestern Bangladesh

However, correlation between BaP and Ant in the studied samples is negative ($r = 0.73$) (Fig. 6), increasing BaP with decreasing Ant suggests that these PAHs might be originated from different sources.

Environmental health risk assessment

PAHs have adverse health effects from short- or long-term human exposure through breathing and/or skin contact in atmospheric environment (Omar *et al.*, 2006; Kim *et al.*, 2013). But atmospheric PAHs are partitioned between particulate matter and gas phase (Table I), they are commonly linked principally with particulate matter (Fang *et*

al., 2004; Huang *et al.*, 2006). The coaly particulate matters are widespread inside and outside atmosphere of the Barapukuria coal mine. This particulate material contains toxic PAHs that are being highly carcinogenic. Kim *et al.* (2013) suggested that mixtures of PAHs are extremely carcinogenic to human exposures than individual PAHs. Human exposure to PAHs and associated carcinogenicity has been tabulated in Table II. The probable human carcinogen PAHs includes BaA, BaP, Bfla, Chry, and InP (USEPA, 2008). Average abundances of these carcinogenic PAHs in the samples studied are in decreasing order as follows: Bfla $>$ BeP $>$ BaP $>$ BghiP $>$ InP $>$ Cor (Fig. 3). Ravindra *et al.* (2008) reported that increasing molecular weight with increasing carcinogenicity of the heavier PAHs. Thus, high relative abundance of HMW PAHs (Fig. 2) in some samples indicating high carcinogenic potency. Furthermore, particulate PAHs are considered to be significant hazardous substances to human health through inhaling due to their prolonged residence time in the natural environment. In particular, BaP has been recognized as being highly carcinogenic to people living there on long-run human exposure (Fang *et al.*, 2004), uptake PAHs (e.g. BaP) with inhalation. Ravindra *et al.* (2008) also demonstrated that the first known chemical carcinogen material discovered so far is BaP. The PAHs emission from biomass burning (wood, coal, and peat) is relatively predominant in the study area which is often conducted for diverse skin effects to human beings. The partial combustion of coal makes a significant contribution to the gross PAHs emission to the atmosphere worldwide (Ravindra *et al.*, 2008). Accordingly, Boström *et al.* (2002) estimated that approximately 430 kg BaP has been generated from wood burning in Sweden during 1994, although gasoline and diesel vehicles combinedly contribute much lower BaP (~ 320 kg). In the studied coals, BaP content ranged from 2 to 6% of the total PAHs and is the third highest in abundance among the carcinogenic PAHs (Fig. 3). This high BaP concentration in the particle phase may lead to elevate hazardous PAHs pool in the atmosphere. Additionally, Kumata *et al.* (2006) noted that biomass burning seems to contribute 17 to 45% of PAHs load of fine particles in residential areas of suburban Tokyo.

The potential health risk assessment of PAHs can be evaluated based on the toxic equivalency factors (BaP_{eq}) (Kong *et al.*, 2015; Li *et al.*, 2016). The BaP_{eq} data for this study samples ranged from 0.55 ng g^{-1} to 6.51 ng g^{-1} (average 2.15 ng g^{-1}), suggesting moderate to high health risk associated with exposure to PAHs in the atmospheric environment. The BaP contents in the samples are ranging from 0.04 ng g^{-1} to 3.41 ng g^{-1} (average 0.86 ng g^{-1}), inferring

Table I. Structure, formula, physicochemical properties and phase distribution of the studied PAHs (After ATSDR, 1995; Ravindra *et al.*, 2008; Kim *et al.*, 2013)














Order	Compound name	Formula	Mol. wt. (g mol ⁻¹)	CAS number	Vapor pressure at 25°C (Pa)	Melting point (°C)	Boiling point (°C)	Particle/gas phase distribution	Structure
1	Phenanthrene	C ₁₄ H ₁₀	178	85-01-8	9.07×10 ⁻²	100	339-340	Particle gas phase	
2	Anthracene	C ₁₄ H ₁₀	178	120-12-7	3.4×10 ⁻³	218	340	Particle gas phase	
3	Fluoranthene	C ₁₆ H ₁₀	202	206-44-0	1.08×10 ⁻³	107	375-393	Particle gas phase	
4	Pyrene	C ₁₆ H ₁₀	202	129-00-0	5.67×10 ⁻⁴	149	360-404	Particle gas phase	
5	Retene	C ₁₈ H ₁₈	219	483-65-8	5.34×10 ⁻⁶	98.5	390	-	
6	Benzo[<i>a</i>]anthracene	C ₁₈ H ₁₂	228	56-55-3	6.52×10 ⁻⁷	157	435	Gas phase	
7	Chrysene	C ₁₈ H ₁₂	228	218-01-9	1.04×10 ⁻⁶	254	441-448	Gas phase	
8	Benzo[<i>b,j,k</i>]fluoranthene	C ₂₀ H ₁₂	252	205-99-2	1.07×10 ⁻⁵	165	168	Gas phase	
9	Benzo[<i>e</i>]pyrene	C ₂₀ H ₁₂	252	192-97-2	5.7×10 ⁻⁹	179	495	Gas phase	
10	Benzo[<i>a</i>]pyrene	C ₂₀ H ₁₂	252	50-32-8	6.52×10 ⁻⁷	178	493-496	Gas phase	
11	Indeno[1,2,3- <i>cd</i>]pyrene	C ₂₂ H ₁₂	276	193-39-5	1.3×10 ⁻¹⁰	164	162	Gas phase	
12	Benzo[<i>g,h,i</i>]perylene	C ₂₂ H ₁₂	276	191-24-2	1.33×10 ⁻⁸	278	525	Gas phase	
13	Coronene	C ₂₄ H ₁₂	300	191-07-1	-	438	525	-	

Table II. Carcinogenic classifications of selected PAHs in airborne materials (PAHs data from ATSDR, 1995; USEPA, 2008; IARC, 2010; Kim *et al.*, 2013)

Order	Agency	PAH compounds	Carcinogenic classification	Reference
1	Agency for Toxic Substances and Disease Registry (ATSDR)	Benzo[<i>a</i>]anthracene, Benzo[<i>b</i>]fluoranthene, Benzo[<i>a</i>]pyrene, Dibenz[<i>a,h</i>]anthracene,* and Indeno[1,2,3- <i>cd</i>]pyrene Benzo[<i>a</i>]anthracene and Benzo[<i>a</i>]pyrene	Known animal carcinogens Probably carcinogenic to humans	ATSDR, 1995
2	International Agency for Research on Cancer (IARC)	Benzo[<i>a</i>]fluoranthene,* Benzo[<i>k</i>]fluoranthene, and Indeno[1,2,3- <i>cd</i>]pyrene Anthracene, Benzo[<i>ghi</i>]perylene, Benzo[<i>e</i>]pyrene, Chrysene, Fluoranthene, Fluorene,* Phenanthrene, and Pyrene	Probably carcinogenic to humans Not classifiable as to human carcinogenicity	IARC, 2010
3	U.S. Environmental Protection Agency (EPA)	Benzo[<i>a</i>]anthracene, Benzo[<i>a</i>]pyrene, Benzo[<i>b</i>]fluoranthene, Benzo[<i>k</i>]fluoranthene, Chrysene, Dibenz[<i>a,h</i>]anthracene,* and Indeno[1,2,3- <i>cd</i>]pyrene Acenaphthylene,* Anthracene, Benzo[<i>ghi</i>]perylene, and Fluoranthene	Probably carcinogenic to humans Not classifiable as to human carcinogenicity	USEPA, 2008

* not analyzed in this study

that the cancer risks of coal mine workers and surrounding habitants exposed to PAHs would be paid more attention. The estimated ILCR values for adults and children are ranged from 9.96×10^{-5} to 1.27×10^{-4} (average 8.44×10^{-5}) and 5.56×10^{-6} to 1.12×10^{-6} (average 3.69×10^{-6}), respectively. In general, the ILCR values lower than or equal to 1.0×10^{-6} are consider as negligible health risks, values range from 1.0×10^{-6} to 1.0×10^{-4} means potential health risks, and ILCR values over 1.0×10^{-4} indicates high health risks to human (Bandowe and Nkansah, 2016; Hu *et al.*, 2017). The overall ILCR values obtained in the present study imply that exposure of both adults and children to fine coal fractions from Barapukuria coal field area could lead to potential as well as high cancer risks. Meanwhile, peoples could be exposed to this toxic PAHs in the atmosphere are likely prone to adverse health effects when absorbed into their body over long periods of time. Therefore, it is essential to monitor the level of particulate PAHs in the Barapukuria coal mine area and in addition to the city region.

In the studied coals, carcinogenic PAHs are found in significant abundances (Fig. 3) having average ranged of 17 to 44% (Fig. 5). The result suggests high health risks for human exposed to these PAHs especially for coal mine workers and surrounding dwellers. However, high- or low-temperature coal combustion contributes ~74 to 80% total PAHs burden to the Czech Republic soils (Bosch *et al.*, 2015). A coal-fired power plant also exist nearby the Barapukuria coal mine, releasing toxic PAHs to atmosphere might bear adverse health effect to adults as well as children residing surrounding regions. Kong *et al.* (2015) reported that coal-fired power plant may possibly emitted large amount of BaP/BeP ratios for atmospheric particles. Therefore, extra precaution is urgently needed for controlling PAHs emission in the vicinity of Barapukuria coal mine and associated power station. The influx of PAHs in surrounding environments of the coal field areas should therefore be further investigated in response to ILCR of the coal mine workers and nearby citizens.

Conclusions

The PAHs in fine coal fractions from Barapukuria coal field in northwestern Bangladesh were examined to quantify their occurrence, distribution and possible human health impacts. A total of nine coal samples were analyzed using GC-MS. Among the PAHs, Flu, Pyr, Ret, Bfla, and BeP are significantly high, followed by Phe, InP, BghiP, and Cor representing that the PAHs were originated primarily from combustion sources, leading to probable carcinogenic to

human beings. However, the biological origin of Phe and Ret are predominant their abundances, while combustion origin of Cor present in small amount. The average concentrations of carcinogenic PAHs in the coals are in decreasing order as follows: Bfla > BeP > BaP > BghiP > InP > Cor. The ratios of BeP/(BeP + BaP) ranging from 0.61 to 0.85 (average 0.74), reflecting decay of BaP due to ageing on prolonged exposure to solar radiation. BaP/BghiP ratios ranged between ~0.10 and 6.16 (average 1.89) suggest occurrence of coaly organic matter. Correlation between BaP and Ant in the studied coals is marked negative ($r = 0.73$), increasing BaP with decreasing Ant implies that PAHs probably originated from different organic matter sources. The BaP_{eq} values ranged from 0.55 ng g⁻¹ to 6.51 ng g⁻¹ means the potential health risks of PAHs at the studied sites are perhaps highest. The ILCR values for adults (9.96×10^{-5} to 1.27×10^{-4}) and children (5.56×10^{-6} to 1.12×10^{-6}) are greater than or equal to the range of 1.0×10^{-6} to 1.0×10^{-4} indicates that the potential higher health risks to human living there. Therefore, the possible PAHs pollution in fine coal particles at the Barapukuria coal field area should be paid attention by the local environmental monitoring authority. However, further investigation of these coals with more extensive and comprehensive PAHs datasets will assist in increasing our understanding of the factors controlling carcinogenicity to human beings.

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