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ORIGINAL RESEARCH PAPER

Polycyclic aromatic hydrocarbons species in soil and its probabilistic cancer risk to residents near municipal solid waste landfill site

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ABSTRACT

Present study was undertaken to examine the extent of Polycyclic Aromatic Hydrocarbons (PAHs) contamination in neighbourhood lithospheric environment of landfill site situated in eastern outer edge of Kolkata metropolitan city in West Bengal, India, along with its sources identification, spatial distribution and probabilistic cancer risks to residents. The collection and analytical tests were performed for all prevailing seasons in local geographical condition. The concentration of sum of 16PAHs (Σ_{16}PAHs) in soil ranged from 8561µg/kg to 20268µg/kg and the average concentration is 14459µg/kg. On the basis of experimental information, the likelihood of cancer manifestation through contact to place-linked PAHs was quantitatively estimated. benzo(a)pyrene, Benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a) anthracene, indeno (1,2,3-c,d) pyrene and chrysene, among 16PAHs are ascertained to provoke cancer in the residents. Carcinogenic risk due to oral intake and dermal contact is computed as 1.21E-05 and 4.02E-06 respectively. Progressive lifetime cancer risk to resident is set up as 1.61E-05. Source identification of PAHs indicates that it mainly originated from incomplete combustion of solid waste. Atmospheric diffusion and deposition led to PAHs input to soil all around waste disposal site, resulting in a consistent pyrogenic supply pattern in soil. This risk appraisal grants a realistic tool for resolution at corporation level to take up risk management policy at contaminated location.

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) in environmental descriptor have noticeably picked up interest in current years due to its carcinogenic characteristics (Alshaarawy *et al*., 2016; White *et al*., 2016; Kim *et al*., 2013) and persistence in nature due to lipophilic and hydrophobic quality. Lithospheric environment is prone to PAHs enrichment owing to above fact and hence it is considered as a principal reserve for PAHs (Man *et al*., 2013; Wang *et al*., 2011). As stated by Wilcke, 2000, PAHs possess stumpy vapour pressure and elevated octanol to air partition coefficients of log K_{ow} 3–6 thus, it have the affinity to adhere vigorously onto the soil particles and retain for extended period of time. The consequences of PAHs, including particle or gaseous structure, can promote elevated concentration of PAHs in soil and negatively influence the quality of soil, concurrently acting as a source of pollutant which depreciates ecosystems and human health (Argiriadis

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et al., 2014). Due to their potential carcinogenic, teratogenic (induces a congenital malformation) and mutagenic property (Bostrom *et al*., 2002), 16 PAHs, varying from 2-6 compressed aromatic hydrocarbon rings, are categorized as precedence pollutants by USEPA (2003). Benzo(a)anthracene (BaA), benzo(a) pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(k) fluoranthene (BkF), chrysene (Chr), dibenzo(a) anthracene (DBA), and indeno(1,2,3-c,d)pyrene (InP), are potential carcinogens. Whereas, acenaphthene (Ace), acenaphthylene (Acy), anthracene (Ant), benzo(g,h,i)perylene (BghiP), fluoranthene (Flu), fluorine (Fl), naphthalene (Nap), phenanthrene (Phe), and pyrene (Pyr), are considered non-carcinogens. Along with anthropogenic origin, the petrogenic supply of PAHs comprises unburned petroleum and its merchandise (diesel, fuels, liquefied petroleum gas and fuel oil), while the pyrogenic supply consist of elevated-temperature ignition goods such as partial combustion of organic substance and burning of solid waste. Crops that uptake PAH from contaminated soil can subsequently be transferred to human in the course of food-chain (Wang *et al*., 2012; Chrysikou *et al*., 2008; Gao *et al*., 2008; Tang *et al*., 2005). In view of the human health risks, it is imperative to focus on soil contamination by PAH compound in the vicinity of waste disposal sites where the pollution potential is considered to be severely high. Since PAHs are emitted as a result of partial burning of organic substance following deposition on soil environment through atmosphere and surface runoff, it enters the food chain by means of root uptake from soil and shoots absorption from the ambience. Subsequently the inhabitants and farmers in the areas with PAHs infected soil experiences possible long term undesirable health result. Consequently, there is an urge to measure the prevalent human health hazard of PAHs in soil in the province neighbouring to impending pollution sources. Use of toxic equivalence factors (TEFs) (Nisbet and LaGoy, 1992) facilitates risk assessment more accurately. These allow the toxicity of a mixture of PAHs to be expressed as a single number representing the equivalent concentration of the most toxic or carcinogenic compound. In preceding decade, quite a number of screening studies on PAHs pollution have been performed in different metropolis around the world reporting inconsistency in the overall concentrations of PAHs (Bandowe and Nkansah, 2016; Hussain *et al*., 2015; Liu *et al*., 2015; Melnyk *et al*., 2015; Albanese *et al*., 2014; Nguyenet *et al*., 2014; Yuanet *et al*., 2014; Dong and Lee, 2009; Pies *et al*., 2008), including a few studies reporting soil PAHs contamination in coastal wetland ecosystem of China (Wang *et al*., 2011; Wang *et al*., 2012; Lang *et al*., 2012; Yang *et al*., 2014). These studies mostly stated the results on urban and suburban soil scenario. However, a limited study has been reported regarding spatial allocation of PAH compound in farmland soil neighbouring a waste disposal site. For that reason, Kolkata solid waste disposal site, which spread over 35ha and surrounded by agricultural fields (a part of Ramsar Convention Wetland) in the eastern periphery of the Kolkata city have been identified and selected for the current study in the year 2017-2018. This study was undertaken to examine the intensity of PAHs contamination, identification of source and spatial distributions of the selected PAHs in soil from agricultural fields in the neighbourhood of landfill site; also its probable health risk was assessed by comparing the available relative standards. The study covers three main seasons (winter, summer and monsoon) prevailing in Kolkata. The results of this study will unveil important information to understand the human exposure to such toxic components and its potential health risk.

MATERIALS AND METHODS

Study area

Municipal solid waste landfill selected for current study is situated in the eastern outer edge (88°24'N:22°32'E) of Kolkata metropolis (Fig. 1). The environs of landfill cover several near to the ground highlands and succeeding depression as water bodies. The high ground serves as agricultural fields for local farmers while; the water reserves are used for pisciculture. The entire region is a part of large restricted wetland area called the East Kolkata Wetlands (Fig. 2). The city forms a portion of subordinate deltaic alluvial plains of Ganga-Bhagirathi river structure. It is a classic deltaic flat terrain with surface elevation ranging between 3.5m-6.0m above mean sea level (MSL). Kolkata metropolis has a Tropical wet-and-dry type of weather. The yearly mean temperature is 24.8°C (80°F); monthly standard temperatures vary from 15°C-30°C (59°F-86°F). The average annual precipitation (rainfall) is 1600mm.

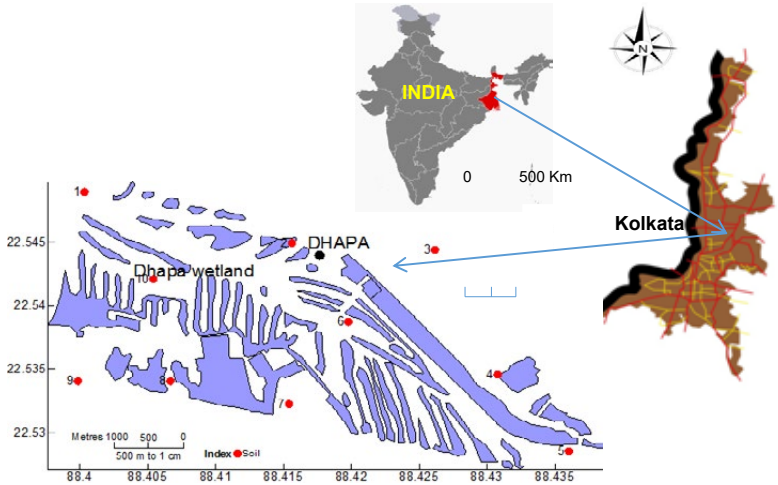

Fig. 1: Location map showing MSW landfill site in Kolkata, West Bengal

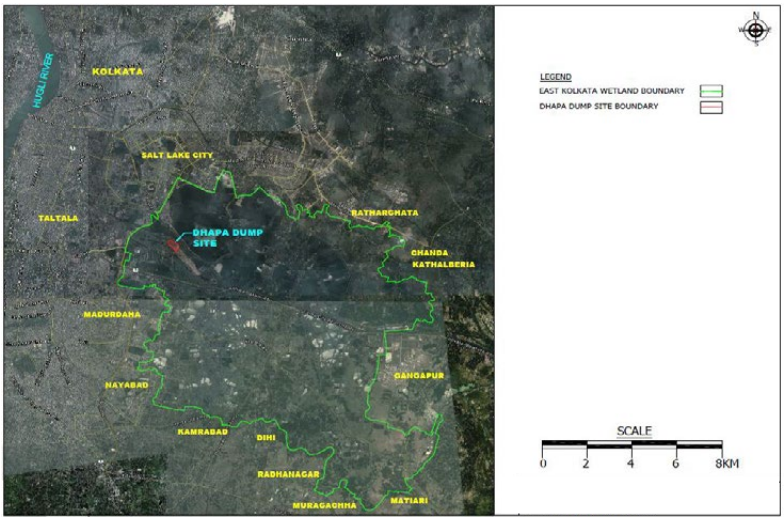

Fig. 2: Airborne view of landfill site as a part of East Kolkata Wetlands

Sample collection and analysis

The soil samples (n=30) were collected for three major prevailing seasons; summer, monsoon, and winter. Surface soil was scooped with the aid of stainless steel trowel up to a depth of 20 cm from the agricultural field located along the landfill site (Fig. 1). Samples were sealed in pre cleaned polythene zipper bags and preserved at 4°C until advance processing. The samples were desiccated in gloomy place and were sieved through 2mm filter after homogenization. The representative sample was acquired by coning-quartering method and PAHs were extracted from soil following EPA 3550C method (adding 4:1, 15.0ml hexane/acetone mixture, 3-5 minutes sonication and repeating this process for minimum three times). The extracted material were combined together and centrifuged at 4000rpm for approximately 5 minutes. The samples were concentrated and swap over to acetonitrile with a rotary evaporator to 5ml total volume and analyzed in high performance liquid chromatography (HPLC). Blank sample and near to the ground spike section were tested directly, while central and elevated spike section were diluted up to 1:10 and

1:100 correspondingly, before injecting in HPLC device. Standard mixture containing 16 PAHs, EPA 610 PAH Mix in Methanol/Methylene Chloride (1:1) was used for the testing. All solvents (Acetonitrile, Hexane and Acetone) used for sample processing and analysis, were of HPLC grade. The entire procedure was carried out following the application note by Volk and Gratzfeld-Huesgen (2011). Precision and linearity were established by testing a diluted PAH standard mixed in acetonitrile solution varying from 19ngµL^{-1} - 8pgµL^{-1} of Σ_{16}PAH compound in 8 dilution stage (dilution factor 1.0:3.0), this facilitates to analyse a broad intensity sequence. The precision of the retention time is calculated as relative standard deviation (RSD) in %. All RSD values were <0.2 %. Limits of detection and quantification were estimated from the levels of PAHs requisite to give at least a signal-noise ratio of 3 and 10 respectively. Resolution greater than 2 was considered as obligatory for the competent separation of the individual complex (Volk and Gratzfeld-Huesgen, 2011).

Risk assessment

Chronic daily intake (CDI)

For evaluation of CDI; oral intake, dermal contact and inhalation were regarded as the primary exposure routes for PAHs. To assess the exposure intensity accepted by the coverage terminal, the CDI by means of three exposure routes were deliberated using the following Eq. 1, 2, and 3 USEPA (2011).

$$CDI_{(ingestion)} = C_{soil} \times IR \times ED \times EF \times CF / BW \times AT \quad (1)$$

$$CDI_{(inhalation)} = C_{soil} \times ED \times EF \times HR / BW \times AT \times PEF \quad (2)$$

$$CDI_{(dermal)} = C_{soil} \times SA \times AF \times ABS \times ED \times EF \times CF / BW \times AT \quad (3)$$

where, $CDI_{(ingestion)}$, $CDI_{(dermal)}$ and $CDI_{(inhalation)}$, are the chronic daily intake linked with oral intake, dermal exposure and inhalation of soil particle (mg/kg/d), C_{soil} is PAHs levels in soil (µg/kg), IR is ingestion rate (100 mg/d), EF is exposure frequency (350 d/y), ED is exposure duration (20 y), BW is body weight (80 kg), AT is average time (365 d), HR is air inhalation rate (13.04 m^3/d), PEF is particle emission factor (1359344438 m^3/kg), SA is surface area of skin (6032 cm^2/d), AF is relative skin adherence factor (0.07 mg/cm^2), ABS is dermal absorption factor (0.13 unit less) and CF is conversion factor (10^{-6} kg/mg).

Carcinogenic hazard

Carcinogenic risk was deliberated by multiplying the cancer slope factor (CSF) and exposure intensity (Kumar *et al*., 2013; El Morsy *et al*., 2013) as depicted in Eq. 4. CSF for each PAHs was designed on the basis of CSF of BaP and its toxicity equivalency factor (TEF) as referred by Nisbet and LaGoy, (1992). Taking into account, the multi constituent PAHs exposed to the inhabitants, TEF relative to BaP was useful to convert levels of carcinogenic PAHs to an equivalent concentration of BaP (BaPeq), (Wu *et al*., 2011; Xia *et al*., 2010; Yang *et al*., 2014; Kumar *et al*., 2013). Then, the CDI for each carcinogenic PAHs was computed on the basis of BaPeq. (Eq. 4):

$$R_i = CSF_i \times CDI_i \quad (4)$$

where, i refers to oral intake, dermal exposure and air inhalation. CSF is cancer slope factor for BaP through varied pathways (mg/kg/d). Pertaining to estimation of overall likelihood of carcinogenic risks by various pathways, the overall cancer risk concurrent via three exposure routes (Luo *et al*., 2014), was calculated using the following Eq. 5:

$$R = R_{(oral\ ingestion)} + R_{(air\ inhalation)} + R_{(dermal\ exposure)} \quad (5)$$

Normally, cancer risks in the range of 10^{-6}-10^{-4} will cause collective risk, whereas, carcinogenic risks more than 10^{-4} imply high possible health risk, and lesser than 10^{-6} is improbable to cause any carcinogenic consequence (USEPA, 1989).

Seven PAHs, (BaA, Chr, BbF, BkF, BaP, InP, DBA), have carcinogenic threat as classification by International Agency for Research on Cancer, IARC, (2010), whereas, nine PAHs (Nap, Acy, Ace, Fl, Phe, Ant, Flu, Pyr, BP), pose non-carcinogenic hazard. Toxicity parameters of PAHs were tailored from Hazardous Waste Companion Database USEPA, (2011). It is assumed that the apprehensive receptor of PAHs was adult farm man who works out for entire day in agricultural fields and creates their livelihood by farming various crops. As a result the farmers are exposed to PAHs infected soils principally via mentioned pathways: oral ingestion, dermal exposure and inhalation throughout their activities from implant to harvest. Oral ingestion can arise through incidental intake during farming, which is tentative and depends mainly on their daily behaviours (Menzie *et al*., 1992). Exposure via dermal contact is

unavoidable during crop growing. The polluted soil particulates remains to farmer's exposed skin and the nastiest condition prevails during summer, with the major exposure of skin surface area (Brouwer, 1999). In inhalation intake, the fraction of suspended particulate matters received from neighbouring soil depends significantly on properties of soil and local conditions.

Uncertainty factor

A variety of uncertainty factors arise in risk evaluation. Uncertainty is an essential part in the course even while using the specific data and application of sophisticated model. Uncertainties come across are primarily due to fate and transport of contaminant in a miscellaneous and unpredictable environment, which are often inadequately understood. Exposure frequency has the maximum susceptibility to carcinogenic threat uncertainty, following exposure dosage and exposure interval (USEPA, 2000). Consequently, a meticulous compound of relevance may not be the grounds for cancer even if deliberated risk is positive (>0). Ambiguities in exposure appraisal also supply to the uncertainty in risk assessment. Risk investigation of soil in the vicinity of landfill signify that exposure parameters robustly manipulate the results of evaluation. Further, the risk appraisal is based on the route of oral intake, particulate inhalation and dermal contact. Nevertheless, other potential disclosure pathways (food-chain) also required to be measured.

RESULTS AND DISCUSSION

PAH concentration, classification and source

The concentrations of 16USEPA priority PAHs (Σ_{16}PAHs) inclusive of seven carcinogenic PAHs ($\Sigma_7$carPAHs) (BaA, Chr, BbF, BkF, BaP, InP, and DBA) in the soil from surrounding agricultural fields of study area (Fig. 1) during three main seasons are shown in Table 1, which depicts concentrations of Σ_{16}PAHs in winter ranging from 8561-20268.3µg/kg with a mean value of 14459.75µg/kg. The mass concentrations of $\Sigma_7$carPAHs range are 2292.2- 8566.2µg/kg with a mean of 4550.21µg/kg. During summer the levels of Σ_{16}PAHs range is 9038.6- 21184.1µg/kg and average is 15259.7µg/kg, the concentrations of $\Sigma_7$carPAHs range from 2624.5-8802.4µg/kg with mean value of 5028.68µg/kg. The concentration range of Σ_{16}PAHs during monsoon is 6737.2-16003.9µg/kg with an average value of 11129.9µg/kg. $\Sigma_7$carPAHs during monsoon ranges from 1873.5-7812.5µg/kg, with an average concentration of 3458.1µg/kg. The sum minimum, maximum and average concentrations of 16 PAHs including 7 carcinogenic PAHs in soil

Table 1: PAHs concentration (µg/kg) in soil n=10 each for three different seasons

	Winter			Summer			Monsoon		
PAHs	Min	Max	Average±SD	Min	Max	Average±SD	Min	Max	Average±SD
Nap	140.8	584.8	333.35±158.41	240.4	671.3	393.75±142.68	88.9	511	294.82±124.02
Acy	112.8	130.5	123.12±5.99	132.2	307.1	180.82±58.51	54.4	147.4	105.14±32.22
Ace	171.9	312.4	245.26±56.12	202.8	342.1	260.75±58.70	164.6	256.4	197±42.28
Fl	113.9	218.9	162.03±46.10	128.4	305.4	207.63±61.05	61.2	256.2	141.45±79.45
Phe	1210.4	5339.3	2771.47±1207.67	1241.3	5425.8	2906.87±1283.57	1007.5	3576.6	1827.94±820.28
Ant	120.8	2745.9	996.01±950.87	153.1	2775.6	1049.21±947.32	59.2	1325.9	494.3±455.84
Flu	106.9	2121.7	729.08±805.07	129.1	2203.4	782.56±819.25	51.3	2121.7	725.9±808.95
Pyr	2984.6	7914.3	5165.75±1402.66	3024.4	7981.6	5211.15±1411.11	2131.1	6647.7	4442.22±1550.86
BaA*	234.3	2732.2	954±768.45	265.2	2763.5	1079.4±821.63	275.1	1464.9	774.81±428.86
Chr*	113.8	665.5	235.38±197.01	128.5	732.4	302.06±218.17	141.5	692.6	310.17±259.10
BbF*	229.1	882.9	427.48±208.09	260	964.6	472.88±223.67	226.2	882.9	428.85±246.03
BkF*	348.4	2616.2	770.76±672.33	453.5	2645.9	915.16±673.40	334.3	2560.2	716.23±665.10
BaP*	371.6	4450.1	1187.17±1485.20	408.5	4493.7	1233.17±1481.20	362.9	3431.5	964.03±1213.70
InP*	314.9	907.9	541.2±233.53	352.2	989.6	586.6±243.11	258.3	907.9	517.67±245.24
DBA*	392.3	800.5	504.83±145.64	425.4	831.8	560.23±147.44	331.5	755.4	481.3±153.12
BP	116.7	524.3	208.55±161.05	138	278.2	195.02±54.77	65.9	220.5	149.27±64.15
Σ_{16}PAHs	8561	20268.3	14459.75±3998.64	9038.6	21184.1	15259.7±4100.29	6737.2	16003.9	11129.9±2741.52
$\Sigma_7$carPAHs	2292.2	8566.2	4550.21±2186.87	2624.5	8802.4	5028.68±2365.55	1873.5	7812.5	3458.1±1837.08

*carcinogenic PAHs

during winter, summer and monsoon are >1000µg/kg, consequently, the agricultural soil in the area can be classified as 'heavily contaminated' as per Maliszewska-Kordybach, (1996) classification: (not contaminated <200µg/kg, weakly contaminated 200-600µg/kg, contaminated 600-1000µg/kg, heavily contaminated >1000µg/kg).

Classifying and differentiating sources of PAHs contamination is important in controlling its emanation in diversified environmental stratum as they are omnipresent, lethal and amid different sources (point, non-point). This might specifically hypothesize potential processes that produce the origin that add to PAHs contamination load in study region (Emoyan *et al*., 2015). Pearson correlation coefficient (PCC) is statistical evaluations that measure the extent that two quantitative variable are linearly interrelated in a section (Higgins, 2005). This evaluation also supplies an ordinance for upcoming environmental contamination monitoring, strategy formulation and implementation concerning sources of environmental PAHs and other associated toxins. The statistical assessment was performed in SPSS 20 software for the current study. PCC of carcinogenic PAHs (Table 2) show a high positive correlation between BaA vs BaP, BaA vs InP, BaA vs DBA, Chr vs BbF, Chr vs BkF, BbF vs BkF, BaP vs InP, BaP vs DBA, InP vs DBA. However the remaining PAHs pair shows a high negative correlation excluding BkF vs InP. Since all the soil samples were collected from the farm land within 500m radius of dumpsite, the strong positive or negative correlation coefficient demonstrates a common source originating from landfill site. Almost all non carcinogenic PAHs show a high positive correlation coefficient with each other indicating the common source of input except Flu vs BP (0.346714) showing considerably low correlation coefficient (Table 3).

To support the above discussion, PAH isomer diagnostic ratio is calculated. The ratio of particular PAHs was determined to identify potential pollution input. It is the concentration fraction of less stable kinetic isomer against its stable thermodynamic isomer (Yunker *et al*., 2002), which is commonly used to classify the prevailing combustion or petroleum sources (Tobiszewski and Namiesnik, 2012; Yunker *et al*., 2002; Doong and Lin, 2004). The proportion of Ant/ (Ant+Phe) <0.1 is considered as a sign of petroleum input whereas, a ratio >0.1 specify a dominance of burning/combustion input. As recommended by Yunker, (2002), Fla/ (Fla+Pyr) <0.4 designates petroleum contribution, proportion

Table 2: Pearson correlation coefficient of carcinogenic PAHs

	BaA	Chr	BbF	BkF	BaP	InP	DBA
BaA	1						
Chr	-0.87823	1					
BbF	-0.95556	0.980185	1				
BkF	-0.57835	0.898065	0.79314	1			
BaP	0.995486	-0.91966	-0.97923	-0.65317	1		
InP	0.957743	-0.70357	-0.83039	-0.31927	0.926121	1	
DBA	0.999609	-0.89127	-0.96343	-0.60095	0.997751	0.949321	1

Table 3: Pearson correlation coefficient of non-carcinogenic PAHs

	Nap	Acy	Ace	Fl	Phe	Ant	Flu	Pyr	BP
Nap	1								
Acy	0.986052	1							
Ace	0.914891	0.83494	1						
Fl	0.996138	0.996858	0.875911	1					
Phe	0.860216	0.763346	0.992863	0.81212	1				
Ant	0.84536	0.744658	0.989068	0.79519	0.999595	1			
Flu	0.94052	0.983947	0.723321	0.966718	0.635808	0.613591	1		
Pyr	0.826517	0.721299	0.983421	0.773898	0.998029	0.99941	0.586113	1	
BP	0.644756	0.50854	0.898465	0.575148	0.944414	0.953385	0.346714	0.963185	1

between 0.4–0.5 signify liquefied fossil fuel (motor vehicle and crude petroleum) ignition and fraction >0.5 stipulate charcoal, firewood or pasture combustion inputs. BaA/ (BaA+Chr) proportion <0.2 generally implies a petroleum input of PAHs, fraction between 0.2-0.35 specify either a gasoline or an ignition input, and fraction >0.35 refer to combustion as PAHs source. The ratio of Ind/ (Ind+BghiP) >0.5 stipulates pasture/petroleum/timber combustion as sources, fraction between 0.20–0.50 indicates petroleum combustion sources (motor vehicle, crude petroleum oil), whereas, fraction <0.20 specify petrogenic derivation. BaP/BghiP >0.6 signify traffic input of PAHs and BaP/(BaP+Chr) <0.2 signify a petroleum input, fraction between 0.2–0.35 indicates petroleum, timber or pasture burning as PAHs inputs, and proportion >0.35 signify vehicular combustion input. Phe/Ant <10 and Fla/Pyr >1 indicate that PAHs is derived from pyrogenic source, Fla/Pyr <1 and Phe/Ant >15 indicate petrogenic genesis of PAHs. A LMW PAHs/HMW PAHs >1 indicates a petroleum input and <1 indicates a combustion input (Yuan *et al.*, 2001). In present MSW landfill site, the ratios of Ant/(Ant+Phe) is 0.25 indicating combustion source and Fla/(Fla+Pyr) is 0.13 demonstrating petroleum origin, BaA/(BaA+Chr) is 0.76 representative of combustion and Phe/Ant (2.95) is indicative of pyrogenic source, Ind/(Ind+BghiP) is 0.74 indicating Grass/coal/wood combustion as a source of origin whereas BaP/(BaP+Chr) with 0.79 indicates vehicular combustion as a source. Fla/Pyr (0.15) and BaP/BghiP (6.12) is indicative of petrogenic source. The isomer ratio of HMWPAHs/LMWPAHs is 0.4 representative of pyrogenic source. Cross plots for diagnostic ratios (Fig. 3) BaA/(BaA+Chr) vs Ant/(Ant+Phe), Fla/(Fla+Pyr) vs Ant/(Ant+Phe), BaP/(BaP+Chr) vs Ind/(Ind+BghiP), Phe/Ant vs BaA/(BaA+Chr), Ind/(Ind+BghiP) vs Fla/(Fla+Pyr), and HMW/LMW PAHs

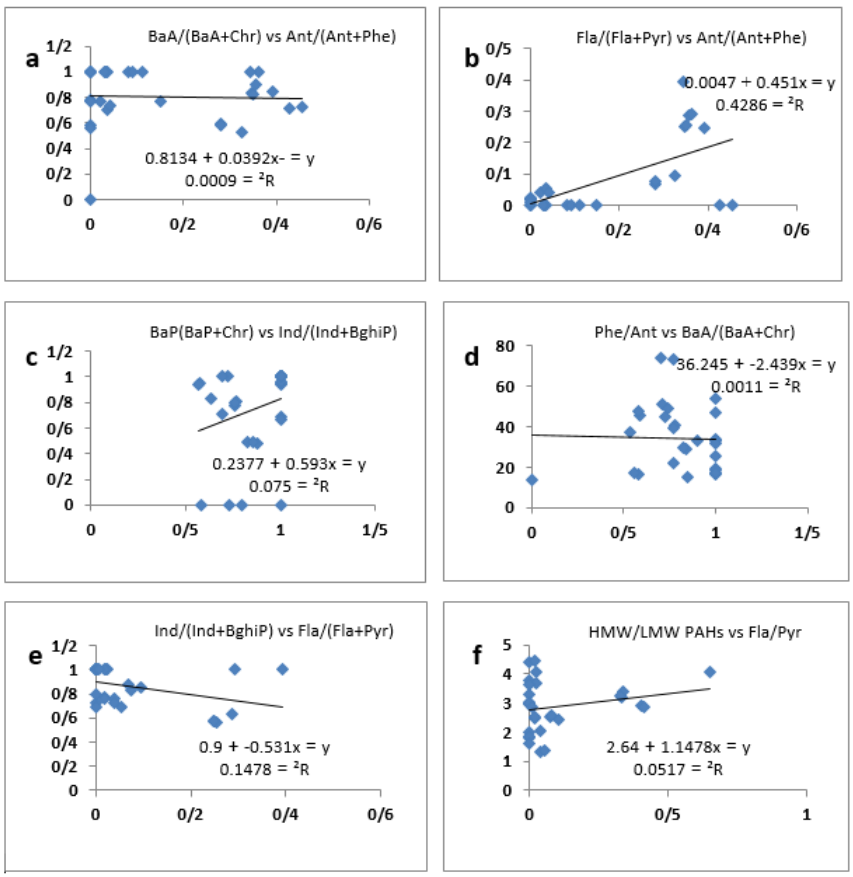

Fig. 3: Cross plot for the diagnostic ratios a. BaA/(BaA+Chr) vs Ant/(Ant+Phe), b. Fla/(Fla+Pyr) vs Ant/(Ant+Phe), c. BaP/(BaP+Chr) vs Ind/(Ind+BghiP), d. Phe/Ant vs BaA/(BaA+Chr), e. Ind/(Ind+BghiP) vs Fla/(Fla+Pyr), f. HMW/LMW PAHs vs Fla/Pyr in soil samples.

vs Fla/Pyr demonstrate that the pyrogenic process and combustion (burning of solid wastes) is the major contributor of PAHs in soil around Kolkata landfill site with the moderate effects of petroleum/petrogenic source.

Carcinogenic risk is articulated as the likelihood of cancer manifestation in the course of exposure to place related chemical compounds. Carcinogenic potency related to exposure of a particular PAHs compound is acquired by calculating its BaP equivalent levels (BaPeq). To calculate the BaPeq of individual group, toxic equivalent factor (TEF) of the given group relative to BaP is used (Table 4). Total BaPeq concentrations were deliberated by following Eq.6:

$$\text{Total BaPeq} = \Sigma_i C_i \times TEF_i \quad (6)$$

where C_i is the intensity of individual PAHs, TEF_i is the subsequent toxic equivalency factor.

Cancer risk of seven compounds

Potency equivalence factors (BaP PEFs) were used to measure the carcinogenic hazard to human from PAHs contaminated soil. CCME, (2010) has declared human health based soil quality guiding principle for direct exposure (SQGDH). Based on tolerable increasing lifetime cancer risk from soil exposure of 10^{-6}, the SQGDH for BaP is 0.006µg/kg, CCME, (2006). The carcinogenic risk of PAHs to the residents via ingestion and dermal contact is 1.21E-05 and 4.02E-06 respectively, while the carcinogenic risk via inhalation (1.34E-08) is almost negligible (within acceptable limits) as compare to other two pathways (Table 4). The cumulative cancer risk encountered in the study area is 1.61E-05. Usually, cancer risks in the array of 10^{-6}–10^{-5} will provoke collective malignancy risk, while, carcinogenic risks >10^{-4} suggests elevated potential health hazard, and <10^{-6} is improbable to cause any cancer (Li *et al*., 2014; USEPA, 1989). This outcome demonstrate the significance of classification of chief exposure routes for health risk appraisal, which is crucial to limit the undesirable health effects as a result of exposure to soil contaminated with PAHs. Canadian soil quality guidelines for the protection of environmental and human health CCME, (2010), have demonstrated the desirable value of BaP (600µg/kg) in soil, (Liu *et al*., 2010). BaPeq values of individual PAHs except BaPeq of BaP in soil during seasons (winter, summer, and monsoon) as shown in Fig. 4 are below the safe value. However toxicity equivalent quotient (TEQ) is exceeding the safe limits during winter, summer, and monsoon, 1985.27µg/kg, 2124.21µg/kg, and 1706.36µg/kg respectively, which is obtained by adding the products of individual PAHs and corresponding TEFs (Table 4).

Spatial distribution

Kriging (geostatistical gridding) interpolation analysis recommended by Journel, (1989), was used to construct the spatial distribution of Σ_{16}PAHs and BaPeq in the soil of MSW landfill site by Surfer8

Table 4: Toxic equivalent concentration (BaPeq) and cancer risk

PAH compound	TEFs	BaPeq winter	BaPeq summer	BaPeq monsoon	Ingestion risk	Inhalation risk	Dermal risk	Total risk
Nap	0.001	0.33335	0.39375	0.29482	-	-	-	-
Acy	0.001	0.123129	0.180829	0.105143	-	-	-	-
Ace	0.001	0.245267	0.26075	0.197	-	-	-	-
Fl	0.001	0.162033	0.207633	0.14145	-	-	-	-
Phe	0.001	2.77147	2.90687	1.82794	-	-	-	-
Ant	0.01	9.960143	10.49214	4.943	-	-	-	-
Flu	0.001	0.729083	0.782567	0.7259	-	-	-	-
Pyr	0.001	5.16575	5.21115	4.44222	-	-	-	-
BaA*	0.1	95.4	107.94	77.48111	6.11E-07	1.26E-08	2.04E-07	8.28E-07
Chr*	0.01	2.353857	3.020667	3.10175	1.85E-09	1.23E-13	6.16E-10	2.46E-09
BbF*	0.1	42.748	47.288	42.885	2.89E-07	1.93E-11	9.65E-08	3.86E-07
BkF*	0.1	77.076	91.516	71.623	5.23E-08	3.49E-12	1.74E-08	6.97E-08
BaP*	1	1187.17	1233.17	964.0333	7.36E-06	4.91E-10	2.46E-06	9.80E-06
InP*	0.1	54.12	58.66	51.767	3.58E-07	2.39E-11	1.20E-07	4.78E-07
DBA*	1	504.83	560.23	481.3	3.37E-06	2.25E-10	1.12E-06	4.49E-06
BP	0.01	2.0855	1.9502	1.49275	-	-	-	-
Total TEQ		1985.274	2124.211	1706.361				
Total Risk		-	-	-	1.21E-05	1.34E-08	4.02E-06	1.61E-05

*carcinogenic PAHs

software (Fig. 5). The highest concentration of Σ_{16}PAHs occurred in the northeast, southwest and central part during winter and summer, while the northern area show highest level of PAH during monsoon. High levels of BaPeq occurred in the northeast and southwest during winter and summer whereas the high concentrations occurred in northeast during monsoon. According to categorization principles of

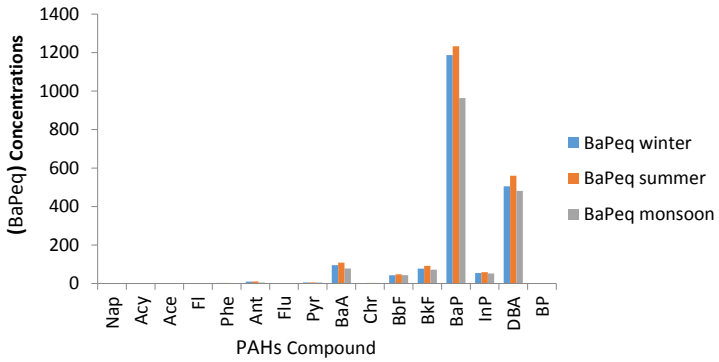

Fig. 4: BaPeq concentrations (µg/kg) of the PAHs in soil

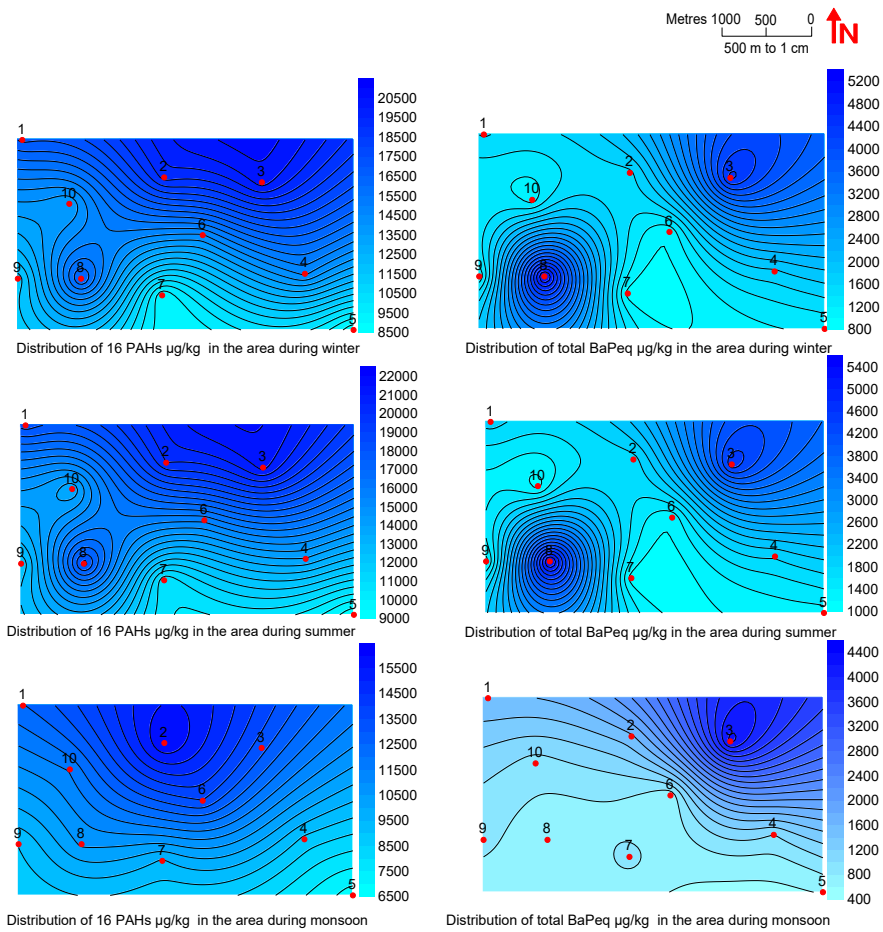

Fig. 5: Spatial distributions of Σ_{16}PAH and BaPeq in soil

Maliszewska-Kordybach, (1996), the entire landfill area is ranked as contaminated with PAHs concentration in soil ranging from 600–1000 µg/kg and remaining half of the deliberated area is heavily contaminated with PAHs concentration in soil >1000 µg/kg.

CONCLUSION

In present work, the extent of pollution of PAHs in soil environment, its sources and spatial distribution along with its likelihood of cancer risk to residents in the vicinity of solid waste disposal site were analyzed. The concentration of sum of 16PAHs (Σ_{16}PAHs) in soil ranged from 8561µg/kg to 20268µg/kg and the average concentration is 14459µg/kg. Source apportionment by means of isomer diagnostic ratio of Ant/(Ant+Phe) is 0.25 indicating combustion as a source and Fla/(Fla+Pyr) = 0.13 demonstrates petroleum origin, the ratio of BaA/(BaA+Chr) = 0.76 is representative of combustion input and Phe/Ant (2.95) is indicative of pyrogenic source, Ind/(Ind+BghiP) = 0.74 indicating pasture/petroleum/timber combustion as a source of origin where as BaP/(BaP+Chr) = 0.79 indicates vehicular combustion as a source. Fla/Pyr (0.15) and BaP/BghiP (6.12) is indicative of petrogenic source. The cross plots of diagnostic ratios of PAHs demonstrate that the pyrogenic process and combustion (burning of solid wastes) is the major contributor of poly aromatic hydrocarbons in soil around Kolkata MSW landfill site with the moderate effects of petroleum/petrogenic sources. The highest concentration of Σ_{16}PAHs occurred in the northeast, southwest and central part during winter and summer, while the northern area show highest level of PAHs during monsoon. High levels of BaPeq can be seen in the northeast and southwest during winter and summer, while high concentrations occurred in northeast during monsoon. The entire landfill area is ranked as 'contaminated' with PAHs concentration in soil ranging from 600–1000 µg/kg and remaining half of the deliberated area is 'heavily contaminated' with PAHs concentration in soil >1000 µg/kg as per classification principles. The carcinogenic risk of PAHs to the residents via ingestion and dermal contact is 1.21E-05 and 4.02E-06 respectively and the cumulative cancer risk encountered is 1.61E-05. Oral intake and dermal contact is the main exposure pathway for carcinogenic risk to occur. In view of the above results, a risk management programme of soil environment that are polluted or assumed of being polluted by PAHs is highly recommended.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript. In addition, the ethical issues; including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy have been completely observed by the authors.

ABBREVIATION

ABS	Dermal Absorption Factor
Ace	Acenaphthene
Acy	Acenaphthylene
AF	Relative skin adherence Factor
Ant	Anthracene
AT	Average Time
BaA	Benzo(a)anthracene
BaP	Benzo(a)pyrene
BbF	Benzo(b)fluoranthene
BghiP	Benzo(g,h,i)perylene
BkF	Benzo(k)fluoranthene
BW	Body Weight
CCME	Canadian Council of Ministers of the Environment
CDI	Chronic Daily Intake
CF	Conversion Factor
Chr	Chrysene
CSF	Cancer Slope Factor
DBA	Dibenzo(a)anthracene
ED	Exposure Duration
EF	Exposure Frequency
Fl	Fluorine
Flu	Fluoranthene
HMW	High Molecular Weight
HPLC	High Performance Liquid Chromatography
HR	Air Inhalation Rate
IARC	International Agency for Research on Cancer
InP	Indeno(1,2,3-c,d)pyrene
IR	Ingestion rate
LMW	Low Molecular Weight
MSL	Mean Sea Level
MSW	Municipal Solid Waste

Nap	Naphthalene
PAH	Polycyclic Aromatic Hydrocarbon
PCC	Pearson correlation coefficient
PEF	Particle Emission Factor
PEF	Potency Equivalence Factors
Phe	Phenanthrene
Pyr	Pyrene
R	Risk
RSD	Relative Standard Deviation
SA	Surface Area of skin
SQGDH	Soil Quality Guiding Principle for Direct Exposure
TEF	Toxic Equivalence Factors
TEQ	Toxicity Equivalent
USEPA	US Environmental Protection Agency

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