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Assaying Baseline Status of Particulate Laden Polyaromatic Hydrocarbon for a Grass Root Level Industrial Project

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Abstract A study of particulate laden polyaromatic hydrocarbon was conducted at 13 selected locations in a 10 km radial distance of a proposed site for a grass root level industry. Suspended particulate matter samples were continuously monitored for 24 h over a period of 3 months. The Polyaromatic Hydrocarbons (PAHs) were extracted from the particulate samples and analysed using Gas Chromatograph-Mass Spectrometer. Limit of Quantification was also established for individual PAHs. Coal combustion and traffic emission were the major contributors for PAHs in the region. The relative contribution of 2, 3, 4, 5, and 6 ring PAHs in particulates of different sampling sites was also investigated and it is observed that 4 ring (29.76%) and 5 ring (29.06%) compounds are prominent in the particulates measured in the region.

Keywords PAHs · Biomarkers · Aromatic rings · PAH sources · Industrial Project · GC/MS

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The PAHs were extracted from the SPM samples and analysed using GC-MS. Limit of Quantification (LOQ) was also established for individual PAHs. Coal combustion and traffic emission were the major contributors for PAHs in the region. The relative contribution of 2, 3, 4, 5, and 6 ring PAHs in particulates of different sampling sites was also investigated and it is observed that 4 ring (29.76%) and 5 ring (29.06%) compounds are prominent in the particulates measured in the region.

Baseline monitoring of criteria and specific pollutants is very much required in all environmental impact assessment projects in India (MoEF, India, 2007). One such pollutant envisaged is a group of chemicals known as PAHs. They are complex mixture of hundreds of chemicals, including derivatives of PAH, such as PAH with a NO_2 group (nitro PAH) and oxygenated products, and also heterocyclic aromatic compounds. PAH are frequently found in ambient air. They are formed during incomplete combustion of organic matter. Important PAH sources are transport and electricity and heating generation. Road traffic exhaust provides an increased local contribution of PAH. The lighter PAH (2–3rings) are not carcinogenic, are mostly found in the gas phase while the heavier one are mostly associated with airborne particles. More than 3 ring PAH compounds gets rapidly attached to soot particles, by adsorption or condensation upon cooling of fuel gas (Kamens et al. 1995).

In India very few studies on ambient PAH concentrations have been carried out (Raiyani and Shah 1993; Sahu et al. 2001). However there is no systematic study carried out to know the baseline status of PAH in Environmental Impact Assessment of grass root level Industrial projects. Therefore, a study was carried to generate baseline data to identify the environmental contaminant sources of the PAHs at various locations and develop a PAHs profile for its existence around the project site. The data will be useful in identifying locations with higher concentrations based on the prevailing wind conditions so that care can be taken while preparing environmental management plan for the

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upcoming industries in the region. Some of the PAHs will also be identified as biomarkers in environmental assessment studies.

Materials and Methods

High Volume air samplers (Envirotech Model APM 430 India) were used for collecting airborne suspended particulate matter using Glass Microfibre Filter paper (20.3 × 25.4 cm^2) GF/A, Whatman International Ltd. Maidstone, England. The air was sampled at a flow rate of 1.1 m^3/min. The filter samples were then enclosed in an envelope and carried to laboratory for conditioning prior to analysis.

Sixteen circles of 3.5 cm were punched from the exposed filter samples using a stainless steel punch. These circles were treated with 25 mL cyclohexane and placed in an ultrasonic bath for 30 min extraction. The extracts were then filtered through G-4 sintered crucible. Another 25 mL of cyclohexane was added to the filtrate and the same was agitated in the ultrasonic bath for 15 min. The extract was then reduced in volume in a rotatory evaporator to a volume of about 1 mL and kept in glass stoppered vial for further instrumental analysis. All glasswares, tools, and syringes were rinsed with solvent prior to contacting samples, extracts. No plastic or deformable materials contacted any samples.

A Varian 3800 GC coupled with Varian 2200 ion trap mass spectrometer (Varian, Walnut Creek, USA) was employed for the determination of analytes using electron ionization (EI) mode. Split less injections of 4uL volume were carried out with a split programmable temperature injector (SPI)Type 1079 programmed from 50 to 300°C at the rate of 180°C per min. The Ion trap, manifold and the transfer line were kept at 240, 50, and 310°C, respectively. The GC oven was programmed for 70–150°C at 10°C per min and further to 300°C at 60°C per min with 10 min hold at 300°C. Separations were performed on Varian Chrompack Capillary column WCOT Fused Silica (30 m long, 0.25 mm ID) CP-Sil 8CB. Helium (Ultra pure 99.99%) was employed as a carrier gas. The flow was adjusted to 1.0 mL/min. The detector was programmed to scan over a mass range 40–450 amu. LOQ was also established for each PAH analytes. Table 1 summarizes the PAHs analytes, RT for these analytes, and LOQ, respectively.

A Certified Reference Standard of 16 PAH mix was prepared from individual neat polyaromatic compounds such as obtained from M/S Supelco A multipoint calibration curve was prepared and used for quantitation of PAHs in air samples.

Results and Discussion

Atmospheric particulate monitoring at 13 locations was carried out for generation of baseline data for individual 16 PAH compounds. A total of 52 samples were collected The results of individual PAHs such as Naphthalene (NAP), Acenaphthalene (ACY), Acenaphthene (ACE), Fluorene (FLU), Anthracene (ANT), Phenanthrene (PHE), Fluoranthene (FLT), Pyrene (PYR), Benzo (a) anthracene (B(a)A), Chrysene (CHY), Benzo(b)fluoranthene(B(b)F, Benzo(k)fluoranthne(B(k)F), Benzo(a)pyrene(B(a)P, Dibenzo (ah)anthracene(DB(ah)A, Indino(1,2,3 cd)pyrene(In(cd)P,

Table 1 List of PAH analytes with their RT, limits of quantitation

PAHs	MW	No. of Rings	Quan Ions	RT min	LOQ ng	LOQ ng/m^3
Naphthalene	128	2	128	12.17	1.5	0.0028
Acenapthylene	152	3	152	17.55	1.0	0.0019
Acenapthene	154	3	153	18.21	1.5	0.0028
Fluorene	166	3	165	20.13	1.0	0.0019
Phenanthrene	178	3	178	23.92	1.5	0.0028
Anthracene	178	3	178	24.10	1.2	0.0023
Fluoranthene	202	4	202	28.78	1.0	0.0019
Pyrene	202	4	202	29.71	1.5	0.0028
Benz(a)anthracene	228	4	228	34.62	1.5	0.0028
Chrysene	228	4	228	34.81	1.0	0.0019
Benzo(b)fluoranthene	252	5	252	38.20	1.0	0.0019
IBDLeno(1,2,3 cd)pyrene	276	6	276	38.30	2.0	0.0038
Benzo(a)pyrene	252	5	252	40.60	1.0	0.0019
Benzo(k)fluoranthene	252	5	252	40.75	1.2	0.0023
Benzo(ghi)perylene	276	6	276	41.20	3.0	0.0057
Dibenz(ah)anthracene	278	5	278	42.98	2.5	0.0048

Benzo(ghi)perylene(B(ghi)P), at different locations are summarized in Table 2.

Total PAH concentration at each sampling location was obtained by summing up the individual concentration of PAH compounds at each locations. The minimum, maximum, average and standard deviation of the TPAHs at each locations are summarized in Table 3.

The minimum concentration ranged between 0.2 to 142.3, maximum in the range of 0.5 to 176.5 ng/m^3. The mean concentration of TPAHs for all the sites together was 106.6 ng/m^3. The site-1 had the highest total PAH concentration followed by sites 6 and 3. High concentration at this site is due to its proximity to nearby highway. About 7,000 vehicles ply daily on this road. Site-6 was very near to an exploratory site of coal bed methanation plant. A continuous flare burning at the site was observed. The average concentrations in the range of 0.3 to 56.1 ng/m^3 at the other sites may be due to continuous use of Diesel Pump sets, in the agricultural fields in the rural areas. Diesel generators are used to generate electricity due to erratic supply of electricity in the residential areas. It is also observed that high background levels in the region can be attributed to atmospheric transport of aromatic hydrocarbons from nearby coal mining areas. These results also indicate that PAH concentrations are strongly linked to anthropogenic activities in the region.

Ratios of some isomer pairs of PAHs such as phenanthrene/anthracene (PHE/ANT) and fluoranthene/pyrene (FLT/PYR) have been used by many investigators (Budzinski et al.1997; Gschwend and Hites 1981, Neff et al. 2005) to differentiate between pyrogenic and petrogenic sources of PAHs. The ratios of these compounds are useful because of differences in thermodynamic stability between parent PAH compounds. The ratios of PHE/ANT observed for sampling sites 3 and 6 are 0.93 and 0.90, respectively. The ratio of FLT/PYR for sampling site 6 is 1.28. It has been reported (Neff et al. 2005) that PHE/ANT ratios less

Table 3 Mean concentration with Standard Deviation of Total PAHs at different locations around the project site (ng/m^3)

Site No.	Minimum	Maximum	Mean ± Std. Dev.
1	142.3	176.5	156.4 ± 17.9
2	0.2	0.5	0.3 ± 0.15
3	97.5	112.5	104.6 ± 7.5
4	0.7	2.1	1.3 ± 0.7
5	7.6	14.9	10.4 ± 3.9
6	137.1	162.5	150.5 ± 12.7
7	8.7	17.4	12.2 ± 4.6
8	31.4	49.7	43.4 ± 9.2
9	1.4	3.8	2.5 ± 1.2
10	50.2	63.4	56.1 ± 6.7
11	7.5	15.4	11.3 ± 3.9
12	0.3	0.8	0.5 ± 0.3
13	0.7	1.6	1.1 ± 0.5
Mean TPAH for all sites			106.6

Table 2 Concentrations of individual PAHs in Ambient air at different sites (ng/m^3)

Site PAHs	1	2	3	4	5	6	7	8	9	10	11	12	13	Aromatic rings
NAP	1.05	BDL	BDL	BDL	BDL	5.67	BDL	1.99	0.39	1.55	3.31	BDL	BDL	2
ACY	BDL	BDL	0.28	BDL	0.72	2.58	BDL	0.39	1.09	0.24	BDL	0.15	BDL	3
ACE	BDL	BDL	BDL	BDL	BDL	5.05	1.53	BDL	BDL	BDL	BDL	BDL	BDL	3
FLU	BDL	BDL	0.3	0.73	1.28	11.42	BDL	BDL	BDL	BDL	BDL	BDL	BDL	3
ANT	BDL	BDL	1.69	BDL	BDL	14.22	BDL	BDL	BDL	BDL	BDL	0.21	BDL	3
PHE	0.95	0.3	1.58	BDL	0.22	12.8	BDL	BDL	0.91	BDL	BDL	BDL	BDL	3
FLT	BDL	BDL	3.52	0.33	6.42	25.76	BDL	0.95	BDL	BDL	0.41	BDL	0.64	4
PYR	BDL	BDL	BDL	BDL	BDL	33.24	8.97	BDL	BDL	BDL	BDL	BDL	0.31	4
B(a)A	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	25.35	BDL	BDL	BDL	4
CHY	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	27.66	BDL	BDL	BDL	4
B(b)F	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	5
B(k)F	79.52	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	7.25	BDL	BDL	5
B(a)P	48.72	BDL	BDL	BDL	BDL	BDL	BDL	28.08	BDL	BDL	BDL	BDL	BDL	5
DB(ah)A	20.6	BDL	29.25	BDL	BDL	21.96	BDL	BDL	BDL	BDL	BDL	BDL	BDL	5
In(cd)P	25.7	BDL	67.05	BDL	BDL	19.25	BDL	BDL	BDL	BDL	BDL	BDL	BDL	6
B(ghi)P		BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	6
Total PAHs	176.54		103.67	1.06	8.64	151.95	10.5	31.41	2.39	54.8	10.97	0.36	0.95	

BDL: Below Detectable Level; LOQ: Limit of Quantitation

Table 4 Percentage variation of Ring compounds of PAHs with respect to sampling site

Site No.	2 Ring	3 Ring	4 Ring	5 Ring	6 Ring
1	0.57	0.54	BDL	84.32	14.57
2	BDL	100	BDL	BDL	BDL
3	BDL	3.72	3.39	28.22	64.67
4	BDL	68.87	31.13	BDL	BDL
5	BDL	25.69	74.31	BDL	BDL
6	3.73	30.32	38.83	14.45	12.67
7	BDL	14.57	85.43	BDL	BDL
8	6.34	1.24	3.03	89.39	BDL
9	16.32	83.68	BDL	BDL	BDL
10	2.82	0.45	96.73	BDL	BDL
11	30.18	3.74	66.08	BDL	BDL
12	BDL	100	BDL	BDL	BDL
13	BDL	BDL	100.00	BDL	BDL
Average	10.0	36.06	55.44	54.10	30.64
Average % ring compounds	5.36	19.37	29.76	29.06	16.45

than 5 and FLY/PYR ratio approaching or exceeding 1 indicate the presence of pyrogenic sources at these locations. Thus pyrogenic sources are predominant in the region.

Table 4 shows the relative contribution of 2, 3, 4, 5, and 6 ring PAHs in the particulates of different locations investigated in the present study. The 2 ring compounds were in the range of BDL to 30.18%, 3 ring compounds in the range of BDL to 83.68%, 4 ring compounds in the range of BDL to 96.73%, 5 ring compounds in the range of BDL to 89.39% and 6 ring compounds in the range of BDL to 64.67%. The average percentage of TPAH based on rings were 5.36 (2 ring), 19.37 (3 ring), 29.76 (4 ring), 29.06 (5 ring), 16.45 (6 ring). The higher percentage of 5 and 6 ring compounds in the particulates indicates that petrol engines are widely used in the region.

Some of the PAHs measured such as Naphthalene and Benzo (a) pyrene are well known biomarkers. The most prominent biomarker has been urinary 1-hydroxypyrene (1-HP, a metabolite of pyrene) which is sufficiently sensitive and specific for use in human epidemiology studies (Dor et al. 1999). The precursor of 1-HP is pyrene, a 4 ring PAH which exist in particulate state and measured in the present study. Due to limitations, we could not identify urinary metabolites in conjunction with the air levels of the parent compounds.

From these baseline data, we conclude that samples of SPM yield precise results for levels of particulate bound 3, 4, 5, and 6-ring PAHs in ambient air. It also gives an indication of background levels of such compounds in the ambient air. These are mainly from the fugitive sources in the region. The meteorological data also supports the high concentration of T-PAHs in the downwind direction of the plant site. Care may have to be taken while preparing environmental management plan for the industries coming up in the upwind direction.

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