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Monitoring and Assessment of Particulate Matter and Poly Aromatic Hydrocarbons (PAHs) around a Petroleum Refinery

B. Padma S. Rao · M. Faiyaz Ansari · P. Pipalatkar · A. Kumar · P. Nema · S. Devotta

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Abstract Ambient air particulates, both total and respirable fraction collected at number of locations around a petroleum refinery in west coast of India, having crude processing capacity of 12.5 million metric tones per annum, were analyzed and associated PAH concentrations were determined. PAHs in SPM near the refinery varied from 12% to 45% while in urban cities, it varied from 0.45% to 0.65%. The percentage PAHs in RSPM near the refinery varied from 6% to 20% while in urban cities, it varied from 0.5% to 1.45%. The refinery contribution of 11.5%–44.3% PAHs to ambient TSP and 5.5%–18.5% PAHs to ambient RSPM was observed. Non-respirable fraction of ambient TSP near refinery contributed upto 25% PAHs.

Keywords Petroleum refinery · PAH · TSP · SPM · RSPM

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B. P. S. Rao (✉) · M. F. Ansari · P. Pipalatkar · A. Kumar · P. Nema · S. Devotta
Air Pollution Control Division, National Environmental Engineering Research Institute (NEERI), Nehru Marg, Nagpur 440 020, India
e-mail: ps_rao@neeri.res.in

Materials and Methods

Samples of airborne particulate matter were taken from six sites around petroleum refinery. Samples of airborne particulate matter were taken from several other cities in India. The sites were selected originally taking into account representation of the sites near refinery environment with a view to minimizing immediate local emission sources. All filter paper preparation and weighing was carried out. Particulate matter was sampled with high volume air samplers according to the Central Pollution Control Board (CPCB) Delhi Standard for NAAQS, 1998. Glass fibre filters (NUPORE) were weighed prior to use and again afterwards to determine the amount of particulate matter. Approximately 2,000 m^3 of air passed through each filter over 24 h. PAH's were removed from the filter paper using ultrasonic extraction of 10% of the paper in Cyclohexane. Separation and identification of PAH were achieved using GC-FID with packed column. Generally two steps were followed for finding the concentration of PAHs viz, sample processing followed by analytical technique.

PAHs released from combustion processes are primarily adsorbed on fine particulates suspended in air. The suspended dust in air collected on glass fiber filter paper of respirable dust sampler was analyzed. The organic component containing PAHs is extracted by ultrasonic extraction method. Eighteen circle of 1.5 cm diameter were punched from filter paper containing sample. These were treated with cyclohexane for 30 min in ultrasonic bath. The extract was then filtered through sintered glass crucible and

Table 1 Status of SPM, RSPM and various Polyaromatic Hydrocarbon (PAHs) around a petroleum refinery

Location of site (μg/m^3)	SPM	RSPM	FI	Py	B (a) A	B (b)F	B(a)Py	Total PAHs	% PAHs in SPM
Karachia	Direction – NW								
Max	182	90.5	16.46	31.40	18.52	ND	ND	66.38	36
Min	162.4	65	5.187	5.74	–	ND	ND	10.92	6.7
Avg	167.5	77.5	11.40	21.44	18.5	ND	ND	51.34	30
SD	20.50	–	5.72	13.7	–	–	–	19.42	–
Karodia	Direction – S								
Max	152	60	3.182	4.58	47.8	ND	ND	55.56	36.5
Min	135.7	55	1.871	3.15	16.01	ND	ND	21.03	15.4
Avg	143.8	57.5	2.457	3.64	29.93	ND	ND	36.02	25.
SD	11.52	–	0.66	0.81	16.30	–	–	17.77	
Koyali	Direction – W								
Max	330	123	4.184	19.78	89.51	ND	ND	113.47	34.3
Min	110	36.3	3.916	15.45	68.7	ND	ND	08.06	7.3
Avg	220	79.65	4.05	17.62	79.15	ND	ND	100.82	45.4
SD	143.5	46.20	0.18	3.05	14.7	–	–	17.93	–
Bajawa	Direction – SE								
Max	273	98	16.683	14.7	14.84	ND	ND	46.22	16.9
Min	266	84	11.298	11.7	-	ND	ND	22.99	8.6
Avg	269.3	91	13.7683	13.28	14.84	ND	ND	41.8	15.5
SD	3.51	–	2.71	2.11	–	–	–	4.82	–
Undera	Direction – SW								
Max	240	88	32.398	10.4	ND	ND	ND	42.79	17.7
Min	163	75	6.886	7.8	ND	ND	ND	14.68	9.0
Avg	201.5	81.5	16.21	9.1	ND	ND	ND	25.31	12.3
SD	38.8	7	14.07	1.844	–	–	–	15.91	–
Tapti GH	Direction – S								
Max	142	54	5.39	15.41	ND	ND	ND	20.8	14.6
Min	120	36	–	–	ND	ND	ND	–	–
Avg	131	45	5.39	15.41	–	ND	ND	20.8	14.6
SD	–	16.8	–	–	–	–	–	–	–

ND not detectable, *FI* Fluoranthene, *Py* Pyrene, *B(a)A* Benzo (a) Anthracene, *B(b)F* Benzo (b) Fluoranthene, *B(a)Py* Benzo (a) Pyrene

cleaned by passing through activated alumina column. Final volume was reduced to known minimum quantity by rotary evaporator technique. The samples were persevered in refrigerator at 4°C for analysis.

Perkin Elmer Autosystem XL Chromatograph with Flame ionization detector was used. The packed column-400 was used for the separation of PAHs compounds. The samples were injected after making required dilutions. First the typical chromatogram of standard and sample was obtained and then sample peak were confirmed by spiking the sample with known standards. The following reference standards were used for calibration and quality control exercises.

Fluoranthene Fluka A9, Bnchs S9
Benzo (a) Anthracene Fluka A9, Bnchs S9
Pyrene Fluka A9, Bnchs S9
Benzo (a) Pyrene Aldrich
Benzo (b) Fluoranthene Fluka A9, Bnchs S9

Before using gas chromatograph the column was conditioned by operating the following condition for 2 h before injecting sample.

Oven temperature –270°C
Injector temperature –300°C
Detector temperature –300°C

After that solvent was run for cleaning the column then standard mixture followed by samples were run and spectra were recorded.

Results and Discussion

The study was based on particulate phase Polyaromatic hydrocarbon PAHs around the petroleum refinery and

Table 2 Status of SPM, RSPM and various polyaromatic hydrocarbon (PAHs) in various cities of India

Location of site (ng/m^3)	SPM	RSPM	FI	Py	B(a)A	B(b)F	B(a)Py	Total PAHs	% PAHs in SPM
Mumbai (industry and vehicular sources) – coastal area									
Max	270	148	138.3	814.8	567.1	469	129.2	1481.3	0.54
Min	44	43	2.5	6.2	4.6	10.1	15.4	243.8	0.55
Avg	105.3	70.8	60.17	259.88	121.08	189.13	48.75	679.01	0.64
SD	113.09	49.94	45.41	234.02	185.82	137.62	39.53	415.82	–
Delhi (industry and vehicular sources) – central, semi arid area									
Max	508	176	144.9	752.5	262.9	398.1	214.8	1597.3	0.31
Min	47	47	6.3	35.7	21.7	70.5	51.2	186.9	0.39
Avg	349.5	107.3	67.79	381.92	97.56	207.98	94.96	850.20	0.24
SD	121.96	50.10	46.49	273.42	65.50	101.96	52.59	477.40	–
Kolkata (industry and vehicular sources) – coastal area									
Max	346	225	368.2	1315.3	513.2	572.5	399.1	2113.6	0.61
Min	33	30	17.9	40.4	21.4	44.6	16.2	283.9	0.85
Avg	187.3	116.8	131.26	385.31	134.40	198.37	119.92	969.25	0.51
SD	129.73	83.79	116.00	386.3	132.9	166	99.6	597.3	–
Chennai (industry and vehicular sources) – coastal area									
Max	132.4	104	138.3	814.8	567.1	469	129.2	1481.3	1.12
Min	41.2	43.6	2.5	6.2	4.6	10.1	15.4	243.8	0.59
Avg	74.2	59.3	60.17	259.88	121.08	189.13	48.75	679.01	0.91
SD	39.34	27.60	45.41	234.02	185.82	137.62	39.53	415.82	–
Kanpur (industry)									
Max	358	191	141.3	1185.9	961.6	189.1	143.8	2397.2	0.92
Min	44	43	1.8	27.3	4	56	26.7	197.4	0.44
Avg	141.7	111.2	42.5	304.9	138.9	114.8	59.7	660.8	0.46
SD	146.46	62.17	40.2	322.4	262.5	44.6	33.2	594.8	–

Source: NAAQM NEERI Report (1997)

FI Fluoranthene, *Py* Pyrene, *B(a)A* Benzo (a) Anthracene, *B(b)F* Benzo (b) Fluoranthene, *B(a)Py* Benzo (a) Pyrene

various urban cities. From the Table 1 it was found that only Fluoranthene, Pyrene and Benzo (a) Anthracene was detectable. Benzo (a) Anthracene is at a higher concentration in all sites around the petroleum refinery and urban cities. This high concentration of Benzo (a) Anthracene was due to higher contribution from refinery sources like distillation, catalytic cracking, storage and handling and fuel combustion units.

From Table 1 it was found that at various sites around petroleum refinery the average concentration of SPM, RSPM and total PAHs ranged from 131 to 269, 45 to 91 and 20.8 to 100.8 μg/m^3, respectively. The highest concentration of PAHs 100.82 μg/m^3 found at site Koyali. The Koyali site was located less than 0.5 km to the north west of petroleum refinery. While highest value of SPM, RSPM found to be at Bajuwa site with 269.63 and 91 μg/m^3, respectively. The Bajuwa site was located less than 0.5 km to the South East of petroleum refinery. SPM RSPM and PAHs were measured at several Indian cities and comparison was made with value measured around petroleum refinery.

From Table 2 it is found that in Mumbai the average concentration of SPM, RSPM and PAHs were 105.0 μg/m^3, 70.8 μg/m^3 and 679.01 ng/m^3, respectively. In Delhi the average concentration of SPM, RSPM and PAHs were 349.5 μg/m^3, 107.3 μg/m^3 and 850.20 ng/m^3 respectively. In Kolkata the average concentration of SPM, RSPM and PAHs were 187.3 μg/m^3, 116.8 μg/m^3 and 969.25 ng/m^3, respectively. In Chennai the average concentration of SPM, RSPM and PAHs were 74.2 μg/m^3, 59.3 μg/m^3 and 679.01 ng/m^3, respectively. In Kanpur the average concentration of SPM, RSPM and PAHs were 141.7 μg/m^3, 111.2 μg/m^3 and 660.8 ng/m^3, respectively. In major Indian cities the SPM and RSPM concentration were about same as around studied refinery. But PAHs concentrations were 969.25–660.8 ng/m^3, which is less than the PAHs concentration around petroleum refinery.

Results from the extensive series of analysis of high volume samples of suspended particulate matters at several sites in the USA indicate that organic matters contain 10% of the total contribution (USEPA 1974). From Fig. 1 it is found that percentage PAHs in SPM near the source around petroleum refinery vary from 12% to 45% while in urban cities vary from 0.45% to 0.65% also the percentage PAHs in RSPM near the source vary from 6% to 20% while in urban cities vary from 0.5% to 1.45%. Near the refinery,

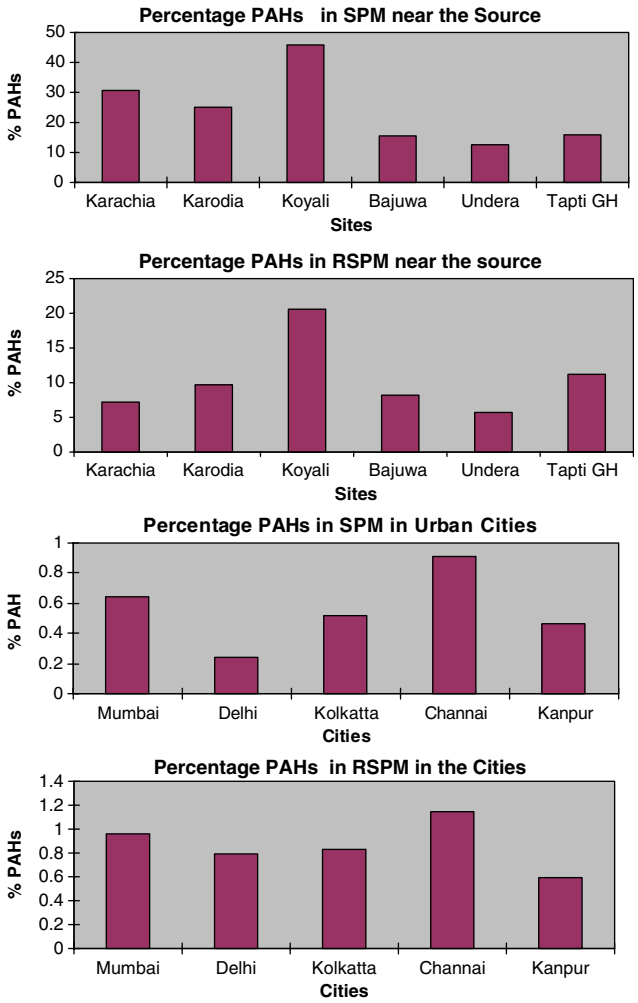

Fig. 1 Contribution of total PAHs near refinery and cities

PAHs concentration in ambient TSP was more than in RSPM. This shows that upto 25% PAHs were associated with non-respirable particulate fraction of ambient TSP near refinery. Most of the direct releases of PAHs to the environment are to the atmosphere from both natural and anthropogenic sources. These are mostly associated with particulate matter in the atmosphere. In general PAHs having two–three rings (naphthalene, acnaphthalene etc) are present in vapour phase and those with four rings Fluoranthene, Pyrene chrysene and Benzo (a) Anthracene exit in both phase while those with five or more rings [Benzo (a) Pyrene, Benzo (g, h, I) perylene etc.] are found predominately in particulate phase (Baek et al. 1991). Since out of these Benzo (a) Anthracene is the most carcinogenic compound and also its ratio in particle to gas phase is 3.15. The monitoring program is based on particulate phase with Benzo (a) Anthracene along with other parameters.

Petroleum manufacturing process is termed as air pollution generating operation because all the activity related to its manufacture viz process, storage, handling, transportation and vehicle transportation etc. generate huge amount of pollution like SO_2, NOx, SPM RSPM, Vocs and Poly aromatic hydrocarbon (PAHs) etc. PAHs are a group of toxic compound that are remotely formed as a result of fugitive emission as well as incomplete combustion of organic materials (Vo Dinh 1989; Wagrowaski and Hites 1997). Suspended particulate matters and Poly aromatic hydrocarbons are widely distributed into the environment from both natural and anthropogenic sources. SPM, RSPM, and PAH's have recently attracted interest because several of these components have shown strong carcinogenic and mutagenic activities active (Baek et al. 1991). Crude oil contains small amounts of naturally occurring aromatics, including some polycyclic organic matters (POM) that may be emitted from some processes and operations at petroleum refineries. Other processes may form POM, which may be emitted at the point of generation or downstream in another operation. Processes at petroleum refineries can be grouped into five types separation processes, conversion processes, treating processes, auxiliary processes and operation, and feedstock/product storage and handling. The first phase in petroleum refining operations is the separation of crude oil into its major constituents using four separation processes: desalting, atmospheric distillation, vacuum distillation, and light ends recovery.

Many different reports concerning the determination of SPM, RSPM and PAH's in urban atmosphere are available in literature. In most studies the concentration of PAH's associated with airborne particulate matter have been determined after collection on glass fiber filter paper by high volume sampler (Miguel et al. 1998; Allen et al. 1997). The determination of concentration of SPM, RSPM and PAH's associated with airborne particulate matter is to evaluate the hazardous nature of these pollutants. The determination of concentration of PAH's in particle phase individually has gained a considerable attention during the last decade (Yamasaki et al. 1982). The Department of Health and Human Services Atlanta, GA: US (DHHS) has determined that some PAHs may reasonably be expected to be carcinogens and people who have breathed or touched mixtures of PAHs and other chemicals for long periods of time have developed cancer. Also some PAHs have caused cancer in laboratory animals when they breathed air containing them (lung cancer), ingested them in food (stomach cancer), or had them applied to their skin (skin cancer). The work described here, has the objective of determining the ambient concentration of SPM, RSPM, and particulate phase polyaromatic hydrocarbon (PAHs) at several sites around the petroleum refinery, and the contribution of PAHs in these particulate fraction as a function of human exposure.

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