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STUDY ON POLYCYCLIC AROMATIC HYDROCARBONS AND POLY CHLORINATED BIPHENYLS YEARLY BASED CONCENTRATION IN WASTE OIL-SLUDGE AT MATHURA-AGRA REGION

MITALI SHARMA* and M. K. RAWAT

Department of Chemistry, Agra College, AGRA – 282010 (U.P.) INDIA

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ABSTRACT

A study of Polycyclic Aromatic Hydrocarbons (PAHs) and Poly Chlorinated Biphenyl (PCBs) in waste oil-sludge was conducted at selected locations in Mathura-Agra region for a span of two year in order to ascertain the contamination levels. The concentration of PAHs and PCBs were measured at two locations in the city of Mathura-Agra, which covers industrial, roadside areas. The samples were extracted with n-hexane by ultrasonic agitation and analysis by GC. The average concentration of total PAHs and PCBs in all samples was 11.14 μg g^{-1}, 6.76 μg g^{-1} and 13.44 μg Kg^{-1}, 20.38 μg Kg^{-1}, 12.91 μg Kg^{-1} and 29.19 μg Kg^{-1}. The maximum concentration of PAHs and PCBs were found to be in winter season.

Key words: Polycyclic aromatic hydrocarbon, Poly chlorinated biphenyl, Mathura-Agra region

INTRODUCTION

Polycyclic Aromatic Hydrocarbon (PAHs) is chemicals containing two or more fused benzene rings in a linear, angular or cluster arrangement. PAH contain carbon and hydrogen only. They are usually generated under inefficient combustion conditions, such as insufficient oxygen by primary natural sources[1,2]. The lighter PAH (2-3 rings), which are generally not carcinogenic, are mostly found in the gas phase, while the heavier PAH (with more than three rings) are rapidly attached to existing particles usually absorption or condensation upon colling of fuel gas[3].

Poly chlorinated biphenyl are a family of 209 chemicals with varying numbers of chlorine atoms attached in varying positions to two connected benzene rings. PCBs are xenobiotic and have potential to persistence and bioaccumulation as reported at Alcock and Johnston[4]. Wilcke et al.[5] pointed out that PCBs have adverse toxic effect on environment and humans. These chlorinated oils have a low degree of reactivity. The environmental occurrence of PAHs and PCBs has been associated with adverse effects on public health[6-8]. Both pollutants released into the environment arise from anthropogenic sources, such as burning of fossil fuels, petroleum refinery, industrial processes and electrical equipment. PAHs and PCBs have been implicated in causing immune system disorders, dermatological problems, reproductive abnormalities, neuro behavioral effect and cancer. Although the conclusive cause and effect relationships are difficult to prove[9].

Available online at www.sadgurupublications.com
*Author for correspondence; E-mail: m.sharma333@yahoo.com; Ph.: 09997540133, +91 9412255300

The present study aimed to investigate the concentration of PAHs and PCBs and reduce PAH and PCB exposure to the people living in this area at roadside oil-sludge of Mathura-Agra region[10-12].

EXPERIMENTAL

Materials and methods

Regional site description

Agra, the city of Taj (a first place wonder of our world) is located the North Central part (27°10, N 78°02'E) of India. The climate during summer is hot and dry with temperature ranging from 32°C to 48°C. In winter, the temperature ranges from 10.5°C to 30.5°C. The atmospheric pollution load is high because of the downward wind, pollutants may be transported to the different areas mainly from an oil-refinery situated in Mathura, roadside transformers and power station Agra site.

Sample collection

For the purpose of sample collection Mathura-Agra region was divided into two parts based on locations outer of Mathura Refinery roadside area and Sikandra power station, road side transformer Ramnagar Pulia chowk the centre of Shahganj-Bodla Road. A total of 300 oil-sludge samples were collected (75 from each location) for analysis. The collected samples were sieved through 20 mesh sieve and stored in polybags in a refrigerator.

Extraction and analysis

10 g of oily-sludge sample were extracted from 45 minutes with *n*-haxane (2.0-10.0 mL) in an ultrasonic bath extractor.

(a) Chemicals: All solvents were GC pure quality and were purchased from Supelco and Sigma-Aldrich Inc. (Germany). A working stock solution was prepared form PAHs compound and PCBs congeners mix standard containing 10 mg of each in 1 mL of heptane.

(b) Instrumentation: Analysis of PAHs and PCBs sample was done by GC. GC (Hewlett-Packard, Aligent) equipped with μECD, μFID detector, split/splitless injection system, and capillary columns, the extract are ready for analysis by GC method 8275. Nitrogen, 42 mL min^{-1} used as a carried gas. Gas chromatography system is characterized in Table 1.

Table 1: Gas chromatography

Gas chromatography	Agilent 6890, Hewlett Packard – 5890 II Series
Detector	μECD, μFID, 320°, N_2 Make up, 60 mL min^{-1}
Column	Quartzitic capillary column HP-5 (50 m x 0.2 mm x 0.11 micrometer)
Gas carrier	Nitrogen 42 mL min^{-1}, H_2, 1.5 mL min^{-1} or average velocity 46 cm sec^{-1} constant flow
Injector temperature	250°C
Detector temperature	300°C
Oven	First ramp – 100 (hold 1 min) to 190°C at 30°C min^{-1} Second ramp – 190° to 280°C (hold 1 min) at 6°C/min.

RESULTS AND DISCUSSION

The climate of Agra can be broadly classified into three seasons, winter (November-February), summer (March-June) and monsoon (July-October). The statistical data for PAHs and PCBs for outside of Mathura Refinery, roadside transformers and power station waste oil-sludge are summarizes in Tables 2 and 3.

Table 2: Seasonal average concentrations of PAHs in waste oil-sludge at sample site of Agra-Mathura region

PAHs	Summer	Monsoon	Winter
Naphtalene	1.05 μg g^{-1}	0.95 μg g^{-1}	1.20 μg g^{-1}
Acenaphthylene	0.58 μg g^{-1}	0.42 μg g^{-1}	0.79 μg g^{-1}
Phenanthrene	0.47 μg g^{-1}	0.15 μg g^{-1}	0.56 μg g^{-1}
Anthracene	1.03 μg g^{-1}	0.62 μg g^{-1}	1.27 μg g^{-1}
Fluoranthene	1.26 μg g^{-1}	n.d.	1.70 μg g^{-1}
Pyrene	n.d.	n.d.	n.d.
Benzo (a) Anthracene	0.36 μg g^{-1}	n.d.	0.81 μg g^{-1}
Chrysene	3.71 μg g^{-1}	3.03 μg g^{-1}	4.10 μg g^{-1}
Benzo (b) fluoranthene	1.32 μg g^{-1}	0.95 μg g^{-1}	1.56 μg g^{-1}
Benzo (k) fluoranthene	n.d.	n.d.	0.30 μg g^{-1}
Benzo (a) Pyrene	0.27 μg g^{-1}	n.d.	n.d.
Benzo (ghi) perylene	1.09 μg g^{-1}	0.64 μg g^{-1}	1.15 μg g^{-1}
Total PAHs	**11.14 μg g^{-1}**	**6.76 μg g^{-1}**	**13.44 μg g^{-1}**

n.d. = not detected implies below limit

Table 3: Seasonal average concentrations of PCBs in waste oil-sludge at sample site of Agra-Mathura region

PCB Congeners	Summer	Monsoon	Winter
18	0.86 μg Kg^{-1}	0.42 μg Kg^{-1}	0.99 μg Kg^{-1}
28	n.d.	n.d.	0.25 μg Kg^{-1}
52	3.19 μg Kg^{-1}	2.82 μg Kg^{-1}	3.58 μg Kg^{-1}
101	1.92 μg Kg^{-1}	1.07 μg Kg^{-1}	4.00 μg Kg^{-1}
118	3.05 μg Kg^{-1}	2.00 μg Kg^{-1}	3.30 μg Kg^{-1}
153	0.42 μg Kg^{-1}	n.d.	2.14 μg Kg^{-1}
105	n.d.	n.d.	n.d.
138	1.48 μg Kg^{-1}	0.80 μg Kg^{-1}	3.00 μg Kg^{-1}
187	n.d.	n.d.	0.02 μg Kg^{-1}
128	3.40 μg Kg^{-1}	1.08 μg Kg^{-1}	3.96 μg Kg^{-1}
180	6.06 μg Kg^{-1}	4.72 μg Kg^{-1}	7.95 μg Kg^{-1}
Total PCBs	**20.38 μg Kg^{-1}**	**12.91 μg Kg^{-1}**	**29.19 μg Kg^{-1}**

n.d. = not detected implies below limit

The seasonally averaged concentrations of all measured total PAH and PCB for the entire samples collected were PAH (11.14 μg g^{-1}, 6.76 μg g^{-1} and 13.44 μg g^{-1}) and PCB (20.38 μg Kg^{-1}, 12.91 μg Kg^{-1} and 29.19 μg Kg^{-1}) (Table 2-3).

The concentrations for all the individual ten PAHs in different seasons are shown in Fig. 1.

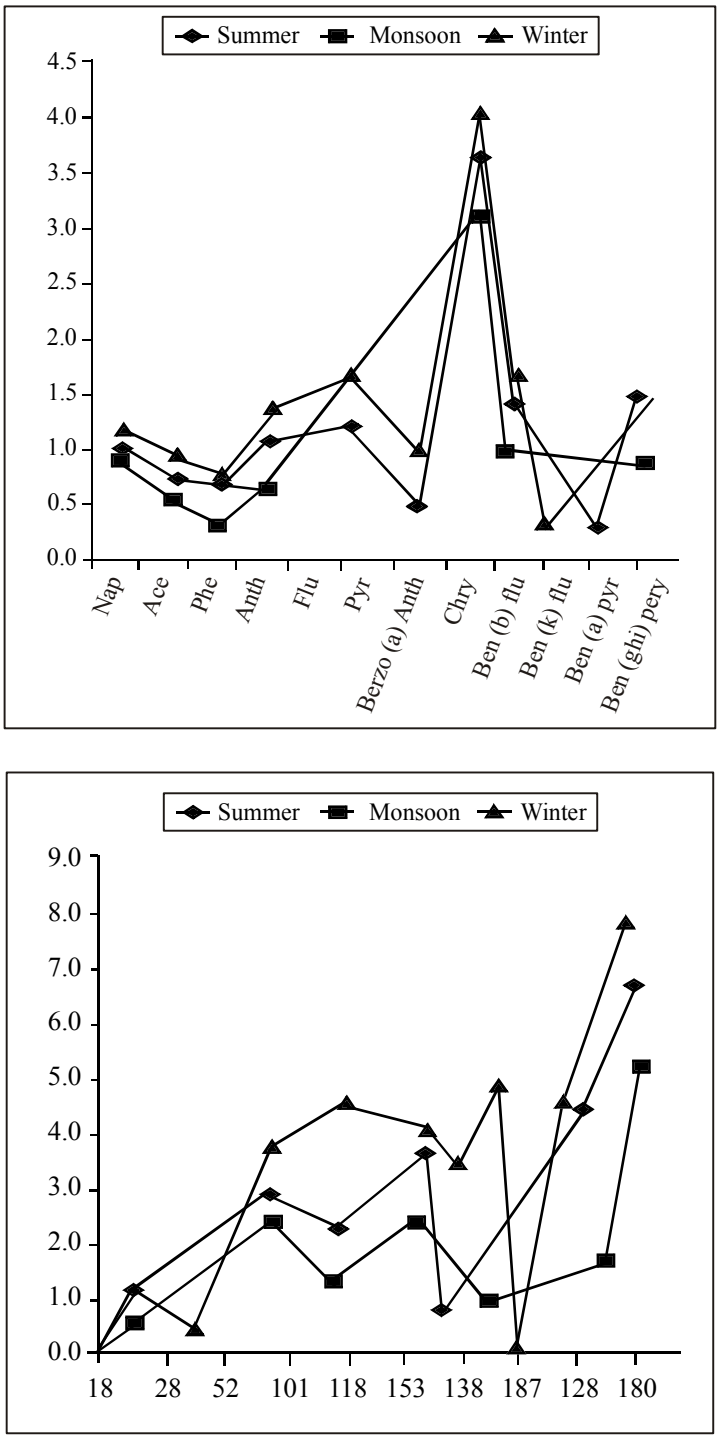

Fig. 1: Seasonal trends of PAHs concentration at sample sites

The concentration for PAHs (in summer) are shown in Fig. 1 i.e. Naphthalene (1.05 μg g^{-1}), Acenaphthylene (0.58 μg g^{-1}), Phenanthrene (0.47 μg g^{-1}), Anthracene (1.03 μg g^{-1}), Fluranthene (1.26 μg g^{-1}), Benzo (a) Anthracene (0.36 μg g^{-1}), Chrysene (3.71 μg g^{-1}) Benzo (b) fluoranthene (1.32 μg g^{-1}), Benzo (a) Pyrene (0.27 μg g^{-1}) and Benzo (ghi) Perylene (1.09 μg g^{-1}).

The concentration for PAHs (in monsoon) are shown in Fig. 1, i.e. Naphthalene (0.95 μg g^{-1}), Acenaphthylene (0.42 μg g^{-1}), Phenanthrene (0.15 μg g^{-1}), Anthracene (0.62 μg g^{-1}), Chrysene (3.03 μg g^{-1}), Benzo (b) fluroranthene (0.95 μg g^{-1}) and Benzo (ghi) perylene (0.64 μg g^{-1}).

The concentration of PAHs (in winter) are shown in Fig. 1, i.e. Naphthalene (1.20 μg g^{-1}), Acenaphthylene (0.79 μg g^{-1}), Phenanthrene (0.56 μg g^{-1}), Anthracene (1.27 μg g^{-1}), Fluoranthene (1.70 μg g^{-1}), Benzo (a) Anthracene (0.81 μg g^{-1}), Chrysene (4.10 μg g^{-1}), Benzo (b) Fluranthene (1.56 μg g^{-1}), Benzo (k) Fluoranthene (0.30 μg g^{-1}) and Benzo (ghi) perylene (1.15 μg g^{-1}).

From Fig. 1, it is clear that 2 and 3 ring compounds (Nap, Ace, Phe, Anth) are found in low concentration than 4, 5, 6 ring compounds (Flu, Ben (a) Anth, Chry, Ben (b) Flu, Ben (k) Flu, Ben (a) Pyre, Ben (ghi) Pery) are found in high concentration because the reason behind this is that 2 and 3 ring compounds are of lighter molecular weight and therefore they are highly volatile in nature while the compounds of 4, 5, 6 ring are not volatile due to their high molecular weight; 4, 5, 6 ring compounds are carcinogenic and mutagenic.

The concentrations for all the individual ten PCBs in different seasons are shown in Fig. 1.

The concentration for PCBs (in summer) congeners are shown in Fig. 2 i.e. 18 (0.86 μg Kg^{-1}), 52 (3.19 μg Kg^{-1}), 101 (1.92 μg Kg^{-1}), 118 (3.05 μg Kg^{-1}), 153 (0.42 μg Kg^{-1}), 138 (1.48 μg Kg^{-1}), 128 (3.40 μg Kg^{-1}), and 180 (6.06 μg Kg^{-1}).

The concentration for PCBs (in monsoon) congeners shown in Fig. 2 i.e. 18 (0.42 μg kg^{-1}), 52 (2.82 μg Kg^{-1}), 101 (1.07 μg Kg^{-1}), 118 (2.00 μg Kg^{-1}), 138 (0.80 μg Kg^{-1}), 128 (1.08 μg Kg^{-1}) and 180 (4.72 μg Kg^{-1}).

The concentration for PCBs (in winter) Congeners shown in Fig. 2 i.e. 18 (0.99 μg Kg^{-1}), 28 (0.25 μg Kg^{-1}), 52 (3.58 μg Kg^{-1}), 101 (4.00 μg Kg^{-1}), 118 (3.30 μg Kg^{-1}), 153 (2.14 μg Kg^{-1}), 138 (3.00 μg Kg^{-1}), 187 (0.02 μg Kg^{-1}), 128 (3.96 μg Kg^{-1}) and 180 (7.95 μg Kg^{-1}).

The sampling site of PCBs congeners 18, 28, 101, 153, 138, 128 are found in low concentration, while the congeners 52, 118, 180 are of high concentrations.

The concentrations for all the individual PCBs are shown in Table 3. PCBs congeners are present in the sample. Ten congeners are found 18, 28, 52, 101, 118, 153, 138, 187, 128, 180 and 105 are not identifying. Amongst the PCBs congeners 138 was the most abundant sample.

PCBs congeners 101, 118 and 180 are of high concentration due to their high molecular weight which makes these congeners carcinogenic and mutagenic.

The congener's pattern varied as a function of emission sources and the oil-sludge. These variations are a result of pysico-chemical properties, solubility and the relative stability of the different PCB congeners in the atmosphere.

Seasonal variation

Agra climate classified into three seasons; summer, monsoon and winter. Tables 2 and 3 summarizes the seasonally averaged concentrations of all measured PAHs and PCBs in waste oil sludge at sample site of Agra-Mathura region.

The concentration of PAHs in summer, monsoon and winter are dominating in site i.e., 11.14 μg g^{-1}, 6.76 μg g^{-1} and 13.44 μg g^{-1} and the concentration of PCBs in summer, monsoon and winter are dominating in site i.e. 20.38 μg Kg^{-1}, 12.91 μg Kg^{-1} and 29.19 μg Kg^{-1}, respectively.

The differences in PAH and PCB concentration in waste oil-sludge in due to the collected at different sample sites. Although the trends of seasonal variation of all PAHs and PCBs at all the sites is similar in nature i.e. maximum concentration of PAH and PCB were found to be in winter followed by summer and monsoon seasons.

This trend can be easily visualized in Fig. 1. Differences in concentration of PAH and PCB in oil-sludge can be explained with the different meteorological conditions of these seasons. Temperature is a very important factor in determining the leachability or mobility of sample.

In this region, summer is generally characterized by high temperature ranging from 35°C to 48°C. The concentration of PAH and PCB at present site increases with increasing temperature as biodegradation and volatility accompanied by rising temperature, resulting the lower PAH and PCB in the summer than in winter season.

In contrast, in the winter season at low temperature microbial breakdown of PAH and PCB is decreased resulting the higher concentration of PAH and PCB at this season. While during the months of monsoon season the region is generally experienced with the frequent rain showers and washout effects of pollutants. In contrast, the concentration of soil PAH and PCB was observed to be lower in monsoon.

Concentration variations of samples during the different seasons depends on some several factor like PAH and PCB molecular structure, vapour pressure, solubility and the relative stability of different PAH and PCB in the atmosphere.

CONCLUSION

This investigation was conducted adjacent to the seasonal variation in different sample sites. The total mean concentration of PAHs were found to be 11.14 μg g^{-1}, 6.76 μg g^{-1} and 13.44 μg g^{-1} and PCBs concentration were found to be 20.38 μg Kg^{-1}, 12.91 μg Kg^{-1} and 29.19 μg Kg^{-1} in waste oil-sludge at Agra-Mathura region. A set of PAHs and PCBs samples was found in oil-sludge including Fluoranthene, Chrysene, Benzo (b) flu (High molecular weight, PAHs) and PCBs congeners 52, 118, 180 (High molecular weight), respectively.

PAHs and PCBs are released into the environment from some industrial and anthropogenic sources, such as fossil fuels, refused burning, industrial processes. This activity induces severe damage to the environment. The results obtained by varimax rotated factor analysis are found to be statistically significant. The carcinogenic potency of PAH and PCB compounds were calculated and found to be insignificant at the present level of emissions in Agra region.

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