

FINAL PROJECT REPORT

(ONGC-CPBT PROJECT)

:TITLE:

**“SPATIAL DISTRIBUTION AND SOURCE APPORTIONMENT OF PAHs IN
DRINKING WATER AND SOIL OF SURROUNDING AREAS OF OILFIELDS OF
BORHOLA AREA OF JORHAT.”**

Submitted to,

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INTRODUCTION

1.1 DEFINITIONS AND PROPERTIES OF PAHs

Polycyclic aromatic hydrocarbons (PAHs), also known as PolyAromatic hydrocarbons or Polynuclear Aromatic Hydrocarbons, are potent atmospheric pollutants that consist of fused aromatic rings and do not contain heteroatoms or carry substituents (Fetzer J. C., 2000). Polycyclic Aromatic Hydrocarbons (PAHs) are a group of organic contaminants that form from the incomplete combustion of hydrocarbons, such as coal and gasoline. PAHs are an environmental concern because they are toxic to aquatic life and because several are suspected as human carcinogens (Van Metre *et al.*, 1996).

PAHs often are byproducts of petroleum processing or combustion. Many of these compounds are highly carcinogenic at relatively low levels. Although they are relatively insoluble in water, their highly hazardous nature merits their positioning in potable waters and wastewaters (Eaton *et al.*, 2005).

National Research Council in 1997 defined PAHs as 'PAH compounds are a generally hazardous class of organic compounds found in petroleum and emissions from fossil fuel utilization and conversion processes. PAHs are neutral, non-polar organic molecules that comprise two or more benzene rings arranged in various configurations. Members of this class of compounds have been identified as exhibiting toxic and hazardous properties, and for this reason the USEPA [U.S. Environmental Protection Agency] has included 16 PAHs on its list of priority pollutants to monitor in water and wastes.' The 16 PAHs identified by USEPA are-

1. Naphthalene,
2. Acenaphthylene,
3. Acenaphthene,
4. Fluorene,
5. Phenanthrene,
6. Anthracene,
7. Fluoranthene,
8. Pyrene,
9. Benzo(a)anthracene,
10. Chrysene,
11. Benzo(b)fluoranthene,
12. Benzo(k)fluoranthene,
13. Benzo(a)pyrene,
14. Dibenz(a,h)anthracene,
15. Benzo(g,h,i)perylene,
16. Indeno(1,2,3-cd)pyrene.

Naphthalene is the simplest example of PAH but according to International Union of Pure and Applied Chemistry (IUPAC), the simplest PAHs are Phenanthrene & Anthracene which contain three fused aromatic rings (G.P Moss, IUPAC nomenclature for fused-ring systems).

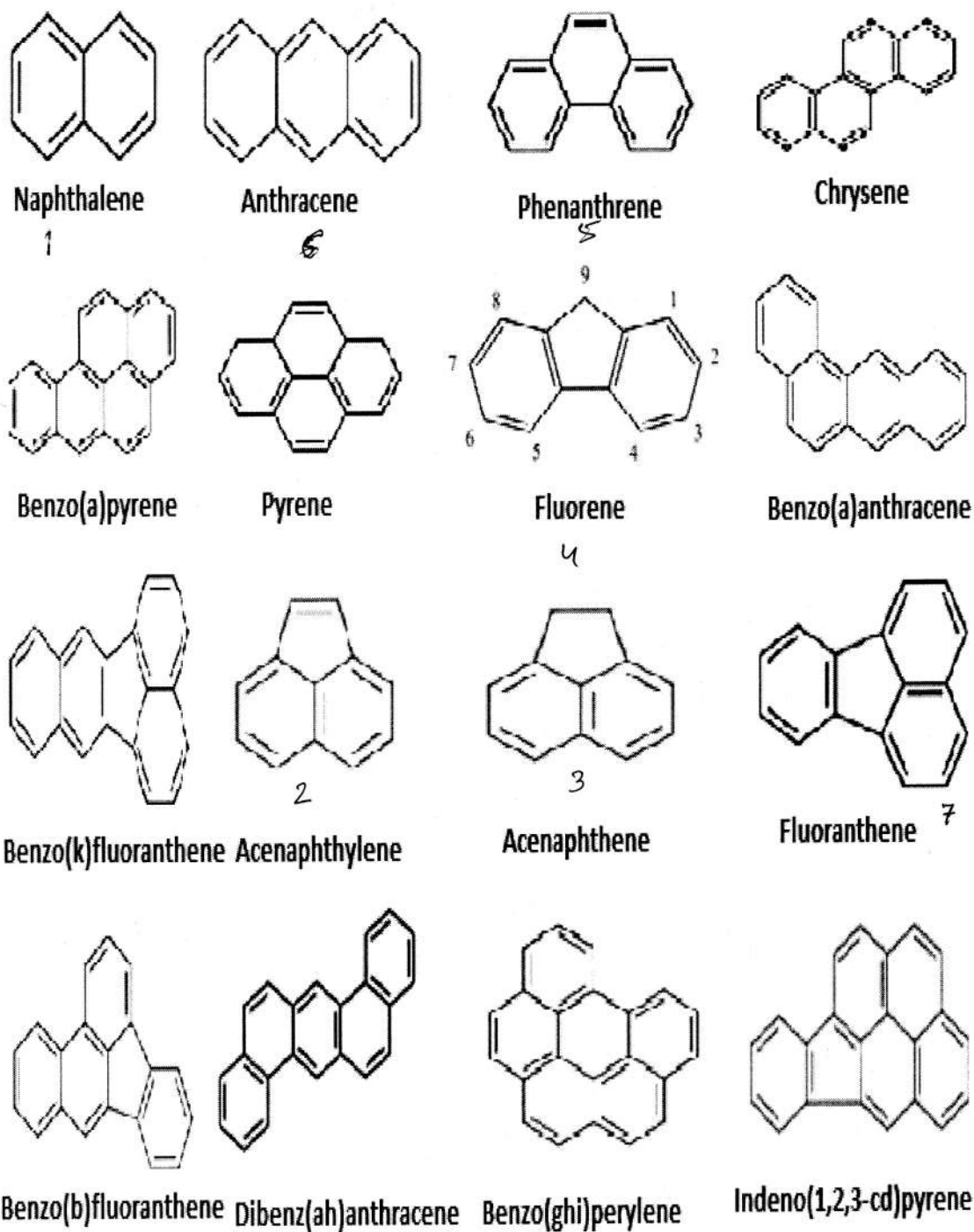


Figure 1: Chemical Structures of 16 PAHs

These Polycyclic Aromatic Hydrocarbons belong to the group of Persistent Organic Pollutants (POP). Many PAHs decompose in soil in the span of a few years (Naphthalene, Anthracene) and some compounds, such as Benzo(g,h,i)perylene, are persistent in spite of degradation processes in the soil environment like microbial activity, photo-degradation, hydrolysis etc (Starke *et al.*, 1991).

PAHs are lipophilic in nature (Luch A., 2005). It means their tendency to be present in water is less than that of soil or oil particles. Because of these properties, PAHs in the environment are found primarily in soil, sediment and oily substances, as opposed to in water or air. (M. T. Piccardo *et al.*, 2001). It is estimated that more than 90% of the total burden of PAHs resides in the surface soils where they accumulate. PAHs are retained in the soil matrix for a long time after adsorption to the soil organic matter (Huang *et al.*, 2003).

Studies have found that the amount of human exposure to PAHs through soils was higher than through air or water.

1.2 SOURCES OF POLYCYCLIC AROMATIC HYDROCARBONS:

Polycyclic Aromatic Hydrocarbons can have varied types of sources. Many researchers have reported that PAHs can be found in crude oil, fossil fuel combustion, wood combustion, forest fires, volcanoes, atmosphere etc. So, summarizing all the sources, it can be said that PAHs have broadly two types of sources. Those are-

1.2.1 NATURAL SOURCES:

- a) Forest Fires (Blumer & Youngblood, 1975).
- b) Volcanic eruptions (Ilnitsky *et al.*, 1977).
- c) Degradation of biological materials, which has led to the formation of these compounds in various sediments and fossil fuels (White and Lee, 1980).

1.2.2 ANTHROPOGENIC SOURCES:

Anthropogenic sources are of two types-

a) PYROGENIC: This type of source is formed by incomplete combustion of organic matter, smelting, garbage, incinerators, forest fires, vehicle engines (diesel).

b) PETROGENIC: It includes crude oil and petroleum products such as kerosene, gasoline, diesel fuel, lubricating oil, and asphalt.

c) DIAGENETIC: Diagenetic PAHs refer to PAHs from biogenic precursors, like plant terpenes, leading to the formation of compounds such as retene & derivatives of Phenanthrene and chrysene (Hites *et al.*, 1980). Perylene is another common diagenetic PAH.

1.3 IMPACTS OF POLYCYCLIC AROMATIC HYDROCARBONS ON HEALTH AND ENVIRONMENT:

1.3.1 HEALTH EFFECTS OF POLYCYCLIC AROMATIC HYDROCARBONS:

Many of the PAHs have deleterious effects on mammals including humans such as respiratory, immunological, neurological, genotoxic, and reproductive (Gupta *et al.*, 1993; Mumford *et al.*, 1993; Szczeklik *et al.*, 1994). In the aquatic environment, the effects of PAHs on invertebrates include inhibited reproduction, delayed emergence, and increased mortality while the effects on fish include fin erosion, liver abnormalities, cataracts, and immune system impairments (Neilson, 1994; Salizzato *et al.*, 2000; USEPA, 2009). PAHs may create toxicity in organisms, by interfering with cellular membrane function and the coupled enzyme systems, and metabolites of PAHs may bind to DNA which causes biochemical disruptions and cell damage in organisms (Hawthorne *et al.*, 2002). Therefore, the presence of PAHs in the environment is of significant environmental concern due to their high toxicity and persistence.

Increased PAHs content in agricultural soil does not usually lead to acute intoxication of humans. On the other hand, health problems can be sometimes connected with symptoms of chronic intoxication. Carcinogenic, mutagenic, teratogenic effects, genotoxicity, an increased level of cholesterol in the blood or reproduction defects were observed after long-term POPs exposure and confirmed by toxicological experiments (Janosek *et al.*, 2007).

Among the 16 PAHs identified by USEPA as toxic organic pollutants for biota, seven compounds, namely Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Chrysene, Dibenzo(a,h)anthracene, and Indeno(1,2,3-c,d)pyrene, are

considered human carcinogens. The remaining nine compounds, namely Acenaphthene, Acenaphthylene, Anthracene, Benzo(g,h,i)perylene, Fluoranthene, Fluorene, Naphthalene, Phenanthrene, and Pyrene, are considered non-carcinogens. The First human carcinogen discovered was Benzo(a)pyrene.

PAHs cause direct toxic effects such as reduced survival, growth or reproduction in terrestrial invertebrates like *Folsomia fimetaria*. Along with that, it also affects other physiological traits making organisms more susceptible to additional stresses (Sjursen *et al.*, 2001).

Altered swimming behavior was exhibited by herring larvae hatched from eggs exposed to weathered *Exxon Valdez* oil containing 1 ppb PAHs (Carls *et al.*, 1999). Total carcinogenic PAHs as low as 1.0 mg/kg have been shown to induce tumors in brown bullhead catfish.

PAHs are known to cause reproductive toxicity in birds and can be the result of exposure of either adult birds or eggs; e.g. chronic exposure for up to 5 months to Benzo(a)pyrene resulted in complete infertility in female pigeons (Hough *et al.*, 1993).

High oral doses of Benzo(a)pyrene have caused bone marrow depression in mice, decreasing especially proliferating haematopoietic cells (Anselstetter and Heimpel, 1986). Mice that were fed high levels of one PAH during pregnancy had difficulty in reproduction and so did their offspring. These offspring also had higher rates of birth defects and lower body weights. It is not known whether these effects occur in people (ATSDR, 1996). B(a)P has decreased fertility and caused embryotoxicity. It increased primordial oocyte destruction, decreased the number of corpora lutea, caused resorptions, decreased the number of pups and decreased fetal weight in rats and mice.

1.3.2 ENVIRONMENTAL EFFECTS OF POLYCYCLIC AROMATIC HYDROCARBONS:

In soil most PAHs are strongly sorbed to the organic matter, making them relatively unavailable for degradation processes (Wild *et al.*, 1995). PAHs can therefore remain in the soil for many centuries, posing a long-term threat to the environment (Howsam, 1998). The consequences of soil contamination with oil derivatives are strongly felt in agriculture, where they adversely affect soil properties like, chemical and air-water relations, as well as the structure of soil, which loses its biological activity and does not regain it even after

several years (E. Kaimi *et al.*, 2006; M. Wyszowski *et al.*, 2009; M. Khamehchiyan *et al.*, 2007). The oily components cover both soil particles and parts of crop plants, hindering their growth and disturbing the microbiological processes in soil (E. Kaimi *et al.*, 2006).

Soil microbes degrade some of the PAHs in soil. It is necessary for the environment. But, hydrocarbon levels higher than 10% wt. are associated with varying degrees of inhibitory effects on soil microbes (Huesemann, 1994b).

Increased concentration of PAH in soil causes transfer of these PAHs into the plant vascular system by the soil solution or by binding of PAHs to organic substances in the external root layer. This soil load with PAHs could cause the plant contamination with PAHs (Zohair *et al.*, 2005).

Borhola oil fields, under the Damodar Valley project (DVP) of Eastern (India) Regional Business Centre (ERBC), Oil and Natural Gas Corporation Limited (ONGCL), India, with an operational area of approximately 300 acres, have been producing crude oil at an estimated capacity of two million tonnes per annum since 1972. During normal operation, leakage and spillage of crude oil result in soil contamination at such locations as oil wells, sumps and pits, tank batteries, gathering lines and pump stations. During the rainy season, flooding and/or accidents, crude oil from the waste pit may spread to the surrounding fields causing pollution. Furthermore, due to incomplete combustion, the residual hydrocarbons may gradually percolate into aquifers, causing long-term environmental problems (Gogoi *et al.*, 2003).

So, in this research, spatial distribution, concentrations and sources of various PAHs on soil & drinking water of Borholla Oil drilling area will be figured out.

1.4 OBJECTIVES OF THE STUDY:

The objectives of the study can be categorized as-

1. To find out the spatial distributions of 16 PAHs in drinking water and soil of Borholla Oilfields and its surrounding areas.
2. To identify the sources of PAHs whether Petrogenic or Pyrogenic, by diagnostic ratio characteristics and statistical analysis (PCA)

MATERIALS AND METHODS

2.1 DESCRIPTION OF THE STUDY AREA

The samples were collected in oil drilling areas & its surrounding places of Borholla area, 40 kilometres away from Jorhat town.

Borholla oil drilling area is situated at a distance of 40 kilometres from Jorhat town. The place is to the extreme south of Jorhat district. Borholla oil drilling area is operated & regulated by Oil and Natural Gas Corporation (ONGC). The co-ordinates of the place are 26°41.335 North & 93°66.635 East. This place is situated in foothills of Naga Hills and so its altitudes vary from 87 metres to 168 metres.

2.2 THE SAMPLING SITES

Samples from 15 different sites were analyzed covering the greater Borholla region. Those sites are described below-

SITE-1- Inside Group Gathering Station (GGS): This place has co-ordinates of 26°26.944 N & 94°10.434 E & altitude of 168 m. This place is storage for crude oil drilled out from various wells around Borholla. It is under ONGC, Assam-Aarakan Basin, Jorhat.

SITE-2- Gorajan: Co-ordinates- 26°26.385 N & 94°09.816 E, altitude- 115 m. This is a rural residential area having a church near it.

SITE-3- MK-3 Field: Co-ordinates- 26°24.168 N & 94°08.222 E, altitude- 109 m. This is an oil drilling area.

SITE-4- BR#6: Co-ordinates- 26°26.341 N & 94°09.996 E, altitude- 105 m. This is also an oil drilling area where well is there to collect the crude oil.

SITE-5- Borholla Town-I: Co-ordinates- 26°26.877 N & 94°07.901 E, altitude- 98 m. This is a commercial place with hotels & shops lined along the main road.

SITE-6- Negheri: Co-ordinates- 26°26.648 N & 94°07.165 E, altitude- 91 m. This is a village area nearby to a tea garden.

SITE-7- Bojalkota Mini Primary School: Co-ordinates- 26°24.099 N & 94°08.807 E, altitude- 89 m. This is a roadside area and also surrounded by residences of villagers.

SITE-8- Bekajan-6: Co-ordinates- 26°23.905 N & 94°10.075 E, altitude- 119 m. This is a village area with densely spaced residences.

SITE-9- Balijan Miching Gaon-II: Co-ordinates- 26°25.281 N & 94°09.962 E, altitude- 106 m. This is also a densely populated rural area.

SITE-10- Rajabahar Namghar: Co-ordinates- 26°29.287 N & 94°09.909 E, altitude- 92 m. This place is on Borholla main road opposite to paddy fields. There are also some houses near to this place.

SITE-11- Gorajan Tiniali (Serali): Co-ordinates- 26°27.484 N & 94°08.910 E, altitude- 99 m. This is a junction of three roads one of which leads to the Borholla town, one to GGS.

SITE-12- Borholla Town-II: Co-ordinates- 26°26.723 N & 94°07.690 E, altitude- 90 m. This place is near to the Borholla main market. It is commercial place with some residences.

SITE-13- Lonpuria: Co-ordinates- 26°26.063 N & 94°07.032 E, altitude- 76 m. This area is close to Borholla town but it is a completely residential place.

SITE-14- Nangol Gaon, Phukanchuk: Co-ordinates- 26°27.035 N & 94°07.699 E, altitude- 76 m. This is a fully residential place.

SITE-15- Kherema Gaon, near A.T. Road: Co-ordinates- 26°27.317 N & 94°08.393 E, altitude- 87 m. This place is on the main road & close to Borholla town. On the other side of the road, there are large tea gardens.

2.3 SAMPLING PERIOD

The sampling was done in two seasons-

1. **Pre-Monsoon:** In the month of April on 28th & 29th, 2011.

2. **Post-Monsoon:** In the month of October on 20th & 21st, 2011.

2.4 COLLECTION OF SAMPLES

Water samples were collected from both tube well and hand pump. Soil samples were collected from surface layer using dust pan and kept in aluminium foil. Using of metallic equipment was restricted as it can contaminate the samples. Site descriptions including land use type and major environmental features were recorded at the time of sampling. The exact geographic coordinates for each sampling point per location were obtained with the aid of Global Positioning System.

2.5 PRETREATMENT

The soil samples were at first dried in natural condition and crushed into finer structures. After that, they were sieved and made prepared for the next procedures. No such pretreatment was required for water samples. Both the samples were kept in refrigerator until analysis.

2.6 PARAMETERS ANALYSED

2.6.1 Temperature:

Soil and water temperature was measured by using mercury thermometer in the field during the collection of sample.

2.6.2 pH

Principle: pH of soil is the measure of the 'hydrogen ion activity' and depends largely on relative amounts of the adsorbed hydrogen and metallic ions. Thus, it is a good measure of acidity and alkalinity of a soil-water suspension and provides a good identification of the soil chemical nature. pH of soil suspension highly depends on the soil: water ratio and increases with dilution. pH of the samples were measured by using pH meter (WTW /Cond 340i). For soil sample a suspension was prepared using soil:water in a ratio of 1:5.

2.6.3 Conductivity

Principle: Conductivity is a measure of the current carrying capacity, thus, gives a clear idea of soluble salts present in the soil. Conductivity of the samples were measured by using Conductivity meter (WTW pH/Cond 340i). For soil sample a soil suspension was prepared using soil:water in a ratio of 1:5.

2.6.4 Organic Carbon: (Walkley and Black Method)

Principle: The organic matter present in the soil is digested with excess of potassium dichromate and sulphuric acid, and the residual unutilized dichromate is then titrated with ferrous ammonium sulphate.

The elementary carbon present as graphite, charcoal etc is not attacked in this method and only organic carbon is determined. The recovery of the carbon in this method is not 100%. Only about 60-90% of the total organic matter is recovered depending upon the kind.

Reagents: Potassium Dichromate solution, 1 N, Sulphuric Acid, Phosphoric Acid, Ferrous Ammonium Sulphate 0.4 N, Diphenylamine indicator

Calculation:

a) $\% C = 3.951/K \times (1-T/S)$

b) $\% \text{ Organic matter} = \% C \times 1.724$

Where, K= Weight of sample in g for soil, ml for water.

S= ml Ferrous solution with Blank titration.

T= ml Ferrous solution with sample titration.

2.6.5 Polycyclic Aromatic Hydrocarbons: Analysis of PAHs includes the following steps:

A. **Extraction:** Water samples were extracted by using EPA method 3510C. This method describes a procedure for isolating organic compounds from aqueous samples. A measured volume of sample, usually 1 liter is serially extracted with methylene chloride using a separatory funnel. Soil samples were extracted by sonication using Dichloromethane.

B. **Concentration:** Concentration of the organic fraction extracted from both water and soil samples were done as per EPA Method 3500. The solvent after concentration exchanged to cyclohexane.

C. **Purification:** Purification of the concentrated samples of both water and soil collected were done by EPA method 3630C or Silica gel Clean-up Method. Silica gel (silicic acid) is a regenerative adsorbent of silica with weakly acidic properties. It is produced from sodium

silicate and sulfuric acid. Silica gel can be used in column chromatography for the separation of analytes from interfering compounds of a different chemical polarity.

D. Analysis: The analysis of extracts from soil samples was carried out using a High Performance Liquid Chromatography (HPLC) system (waters) using EPA method 610. This method provides for both high performance liquid chromatographic (HPLC) and gas chromatographic (GC) approaches for the determination of PAHs. By this method 16 EPA priority PAHs can be determined using HPLC with an UV- detector (model 2489, Waters) at a wavelength of 254 nm. The method of operation was gradient type with a combination of acetonitrile and deionised filtered water as the mobile phase and a stationary phase made up of silica gel loaded in Empower C₁₈ HPLC column(serial no. 02453011213619, part no. WATO54275) of dimensions 4.6x250mm.

RESULTS AND DISCUSSION

3.1 pH AND CONDUCTIVITY:

pH of Pre-monsoon water samples varied from 6.52 to 7.99 with the average of 7.19 ± 0.44 . So, pH of Pre-monsoon water was slightly acidic to slightly basic. The pH range of the Post-monsoon water samples was from 7.4 to 8.9 and average is 8.1 ± 0.35 . So, it was found to be basic in nature. pH in the soil of Pre-monsoon season has been found in the range from 5.69 to 8.37 and average of 7.32 ± 0.80 . So, it can be concluded that, Pre-monsoon soil was slightly acidic to basic in nature. In the same way, pH of Post-monsoon soil ranges from 5.6 to 9.43 with average of 7.32 ± 0.94 . So, Post-monsoon soil was also slightly acidic to basic in nature.

Conductivity of Pre-monsoon water sampled from Borholla was found in between $285 \mu\text{S}/\text{cm}$

and $1522 \mu\text{S}/\text{cm}$, whereas, of the Post-monsoon water samples, it was found to be in between

$134 \mu\text{S}/\text{cm}$ to $1136 \mu\text{S}/\text{cm}$. A decrease in the conductivity property of water is noticed in the

Post-monsoon season. Again, the soil solution in the Pre-monsoon season has conductivity in

the range from 92 $\mu\text{S}/\text{cm}$ to 665 $\mu\text{S}/\text{cm}$ and that of the Post-monsoon soil was found in between

29 $\mu\text{S}/\text{cm}$ to 271 $\mu\text{S}/\text{cm}$.

3.2 SPATIAL DISTRIBUTIONS OF 16 EPA PAHs:

One of our objectives was to find out the spatial distributions of 16 PAHs in drinking water and soil collected from the 15 sites of Borholla oilfield. Therefore, we have classified the 15 sites as given in the Table-1.

Samples were analyzed for both pre-monsoon as well as post-monsoon seasons. A difference in the concentrations of PAHs were expected depending upon both site and season. It was found that, the concentrations of individual PAHs in the Borholla oilfield & its surrounding areas varied from 0.003 mg/Kg to 52.28 mg/Kg in soil and 0.003 mg/L to 42.22 mg/L in water. The highest level of total PAH concentration was recorded in soil sample marked as Site-15 under Zone-B (52.28 mg/) in the Post-monsoon season sampling followed by water sample marked as Site-12 under Zone-B (42.22 mg/L) in the Pre-monsoon season. These, above mentioned sites are near a commercial establishment with District Main road with passage of a large number of vehicles. The concentrations of 6 PAHs considered as Carcinogens including Flu, BbF, BkF, BaP, IcdP and BgP by the USEPA and WHO were from 0.003 mg/Kg to 2.286 mg/Kg in soil samples, whereas, in case of water samples, the range was found to be from 0.003 mg/L to 1.82 mg/L. Dai *et al.*, (2008) found the concentrations of 6 PAHs 0.45 mg/Kg to 161.11 mg/Kg in soil of Ji'nan City, China.

Zones	Sites	Position	Elevation
Oil contaminated areas	Site-1: Inside GGS	26°26.944 N, 94°10.434 E	168 m
	Site-3: MK 3 Field	26°24.168 N, 94°08.222 E	109 m

(Zone-A)	Site-4: BR#6	26°26.341 N, 94°09.996 E	105 m
Road Side Areas (Zone-B)	Site-5: Borholla Town (Hotel Rajbhog)	26°26.877 N, 94°07.901 E	98 m
	Site-10: Rajabahor Namghar	26°29.287 N, 94°09.909 E	92 m
	Site-11: Gorajan Tiniali (Serali)	26°27.484 N, 94°08.910 E	99 m
	Site-12: Borholla Town (Nesimuddin Ahmed)	26°26.723 N, 94°07.690 E	90 m
	Site-15: Kherema Gaon, near A.T Road (Probhat Sonowal)	26°27.317 N, 94°08.393 E	87 m
	Site-7: Bojalkota Mini Primary School	26°24.099 N, 94°08.807 E	89 m
	Residential Area-I (Zone-C)	Site-2: Gorajan (Hand Pump), near Church	26°26.385 N, 94°09.816 E
Site-13: Lonpuria (Neelakanta Baruah)		26°26.063 N, 94°07.132 E	76 m
Site-14: Nangal Gaon, Phukanchuk (Tulu Devi)		26°27.035 N, 94°07.699 E	76 m
Residential Area-II (Zone-D)	Site-6: Negheri	26°26.648 N, 94°07.165 E	91 m
	Site-8: Bekajan-6	26°23.905 N, 94°10.075 E	119 m
	Site-9: Balijan Miching Gaon II	26°25.281 N, 94°09.962 E	106 m

Table-1: Sampling sites classified into zones with locations & elevations

The concentrations of individual PAHs compounds in different sites in the oilfield of China varied significantly, which were in the range of 120-14863 ng/g. The highest level of total PAHs was recorded in soil sample with 82393 ng/g and the following high concentrations were 42227 ng/g and 12837ng/g. The higher concentrations detected for the sites were near to the oil platform and the crude oil contamination was visible (Xianyuan *et al.*, 2010).

Gbadebo *et al.* (2010) found that the values of the PAH in both Gbokoda X & Gbokoda Y oil wells ranged from 18.44–20.52 mg/kg (18440-20520 $\mu\text{g}/\text{kg}$) for cuttings and from 13.72–23.60 mg/kg (13720-23600 $\mu\text{g}/\text{kg}$) for drilling muds in Southwestern Nigeria.

Surface soils from the outskirts of Beijing, China, contained total concentrations of 16 PAHs (16 priority pollutants proposed by the United States Environmental Protection Agency) ranging from 16 to 3884 ng/g (0.016-3.884 mg/Kg) with a mean value of 1347 ng/g (1.347 mg/Kg) (Ma *et al.*, 2005).

Sl. No.	Names of PAHs	Abb*	Molar mass (g/mol)	Molecular Formula	No. of Rings	Boiling Point (°C)	Melting Point (°C)
1	Naphthalene	Nap	128	C ₁₀ H ₈	2	218	80.26
2	Acenaphthylene	Any	152	C ₁₂ H ₈	3	280	91.8
3	Acenaphthene	Ane	154	C ₁₂ H ₁₀	3	279	93.4
4	Fluorene	Fle	166	C ₁₃ H ₁₀	3	295	116-117
5	Phenanthrene	Phe	178	C ₁₄ H ₁₀	3	340	99
6	Anthracene	Ant	178	C ₁₄ H ₁₀	3	340	218
7	Fluoranthene	Flu	202	C ₁₆ H ₁₀	4	375	110.8
8	Pyrene	Pyr	202	C ₁₆ H ₁₀	4	404	145-148
9	Benzo(a)anthracene	BaA	228	C ₁₈ H ₁₂	4	438	158
10	Chrysene	Chr	228	C ₁₈ H ₁₂	4	448	254
11	Benzo(b)fluoranthene	BbF	252	C ₂₀ H ₁₂	5	481	168
12	Benzo(k)fluoranthene	BkF	252	C ₂₀ H ₁₂	5	480	217
13	Benzo(a)pyrene	BaP	252	C ₂₀ H ₁₂	5	495	179
14	Dibenz(a,h)anthracene	DaA	278	C ₂₂ H ₁₄	5	524	262
15	Benzo(g,h,i)perylene	BgP	276	C ₂₂ H ₁₂	6	500	278
16	Indeno(1,2,3-c,d)pyrene	IcdP	276	C ₂₂ H ₁₂	6	536	163

*Dai *et al.* 2008

Table-2: Different properties of PAHs with their abbreviations

3.3 PAH PROFILE

The attributions of different numbered ringed PAHs are presented in Figure-2 to Figure-5.

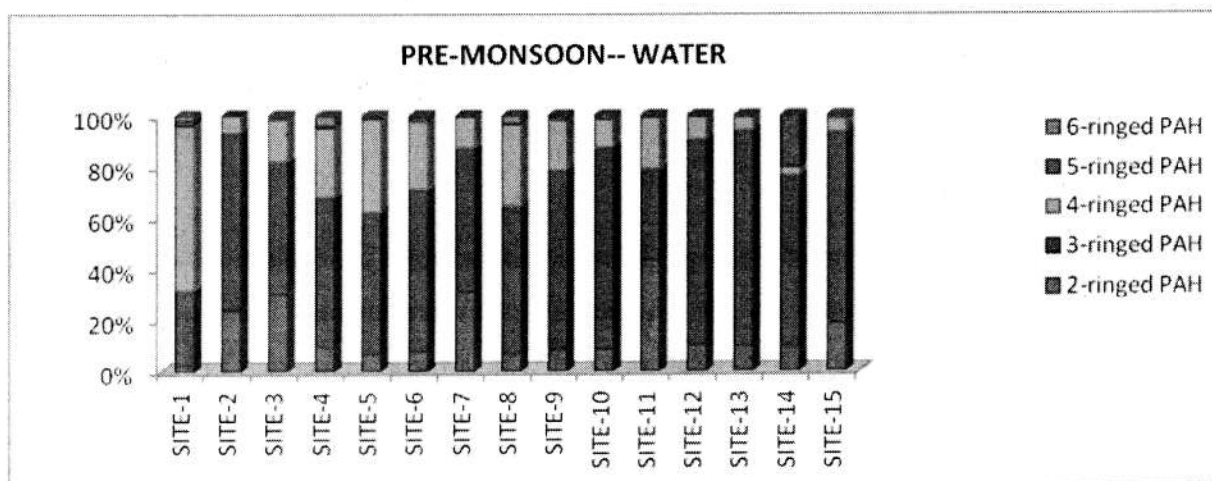


Figure-2: Distribution of PAHs in the Pre-monsoon water samples

In Pre-monsoon water, 3-ringed PAHs were found with highest abundance. PAHs with next highest abundance were of 2-ringed structure that is Naphthalene. In Post-monsoon water samples, relative abundance of 3 & 4-ringed PAHs were found to be maximum with 10%-60% and second most abundant PAHs were of 2-rings. In case of Pre-monsoon soil, the PAHs with the highest abundance were of 3&4 rings with followed by 2-ringed PAHs. In site 5, 5- ringed PAHs are dominant. In Post-monsoon soil samples, 2, 3 & 4-ringed PAHs were recorded to have highest abundance.

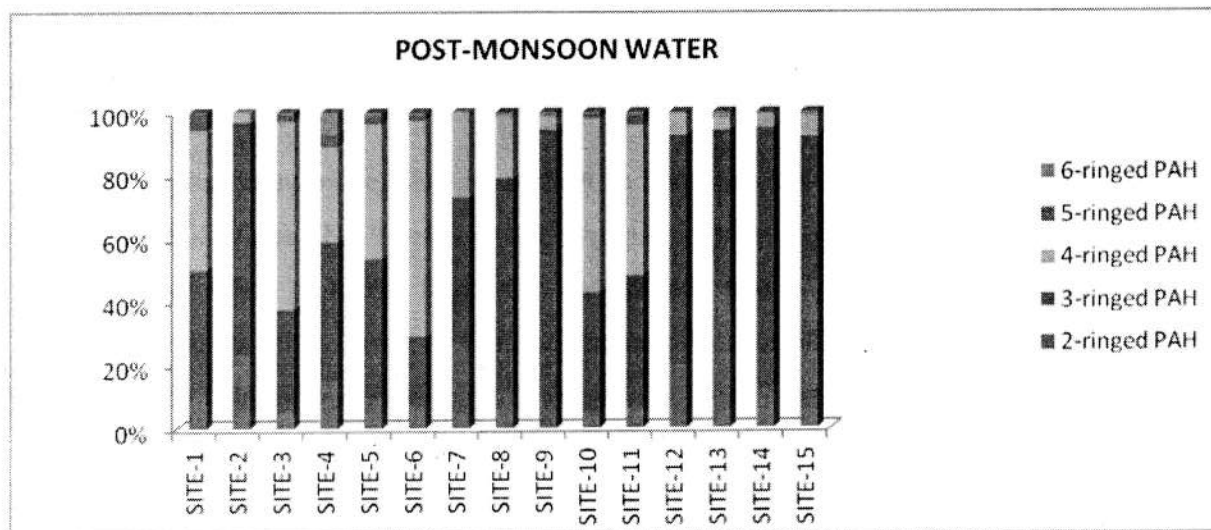


Figure-3: Distribution of PAHs in the Post-monsoon water samples

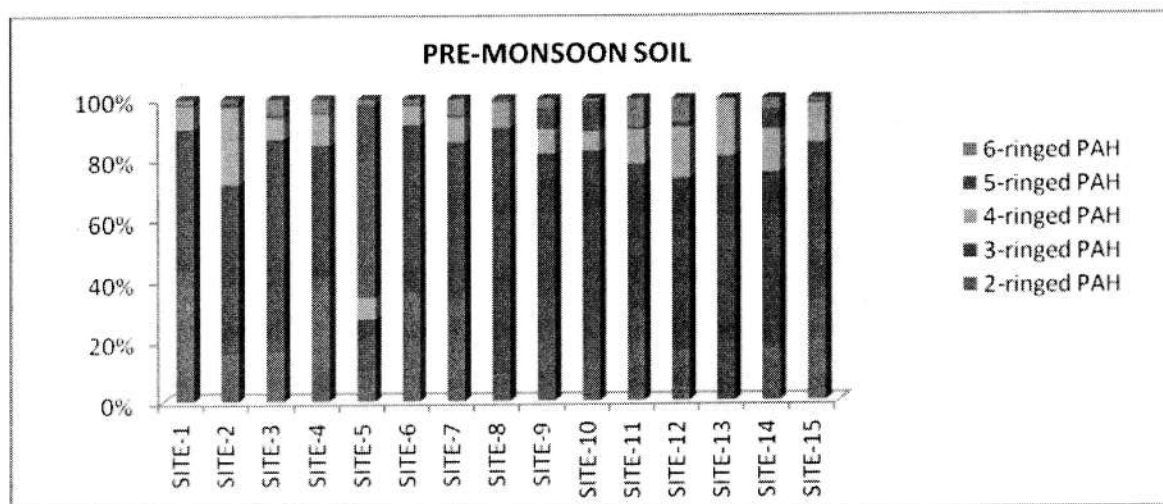


Figure-4: Distribution of PAHs in the Pre-monsoon soil samples

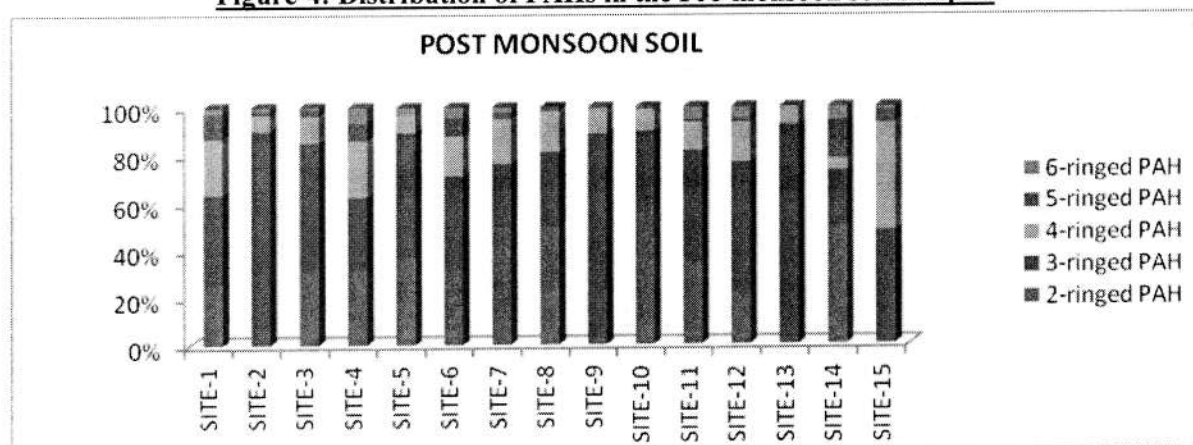


Figure-5: Distribution of PAHs in the Post-monsoon soil samples

High abundance of Nap in both Pre-monsoon as well as Post-monsoon water samples may be due to greater solubility of Nap in water in comparison to other PAHs due to low molecular weight (Du *et al.*, 2010). Again, high abundance of 2-ringed PAHs in soil may be due to combustion and also may be due to traffic related sources as most of the areas selected for sampling were close to Main road. Post-monsoon soil samples have a noticeable abundance of 4-6 ringed PAHs as compared to Pre-monsoon soil samplings which indicate that this abundance may be due to atmospheric wet deposition, which remained in the soil because of their non-degradation & non-volatility.

PAH profile in soil from an oilfield of China showed less abundance of Nap but high abundance of 5 ringed PAHs and overall PAH profile evaluated was 5+ringed > 4-ringed > 3-ringed > 2-ringed (Du *et al.*, 2010).

3.4 Percentage of six carcinogenic PAHs in total PAHs:

Among the 16 PAHs identified by USEPA as toxic organic pollutants for biota, six compounds, namely Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Dibenzo(a,h)anthracene, and Indeno(1,2,3-c,d)pyrene, are considered human carcinogens. The following figures showed their percentage contribution in the total PAHs concentration. The figures illustrated below summarized that the contribution of six carcinogenic PAHs was very less compared to the other PAHs except in site: 4 of the post monsoon water sample and site: 5 of the pre monsoon soil sample. The site for is a drilling site so the crude oil may be the cause of higher concentration of these PAHs. On the other hand site 5 is in town area so higher concentration is attributed to vehicular sources, also this site is at back side of a hotel so fossil fuel burning is may be the another cause.

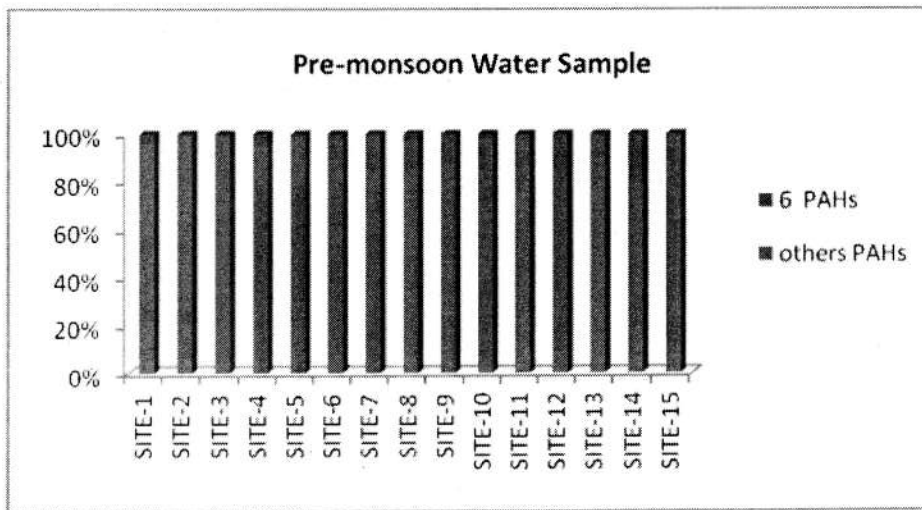


Figure-6: Profile of 6 carcinogenic PAHs with other PAHs in the Post-monsoon water samples

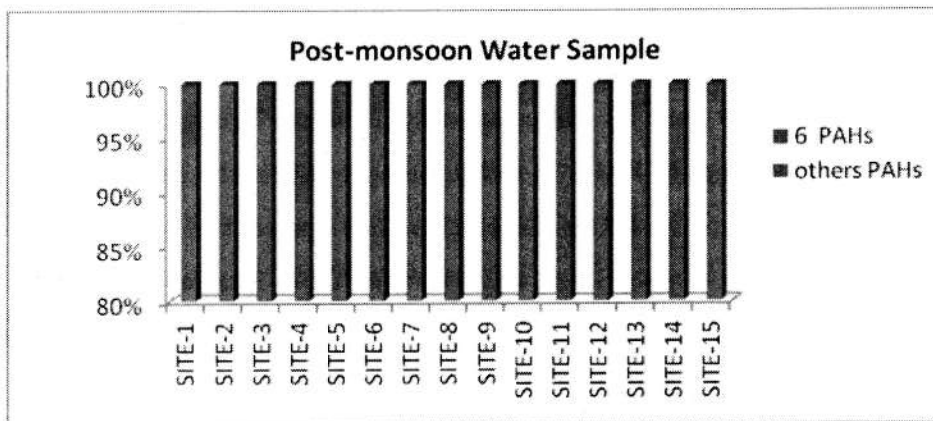


Figure-7: Profile of 6 carcinogenic PAHs with other PAHs in the Post-monsoon water samples

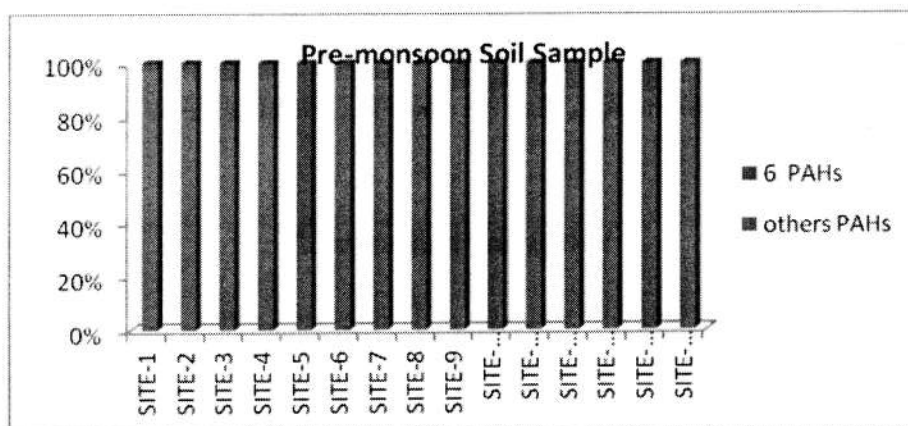


Figure-8: Profile of 6 carcinogenic PAHs with other PAHs in the Pre-monsoon soil samples

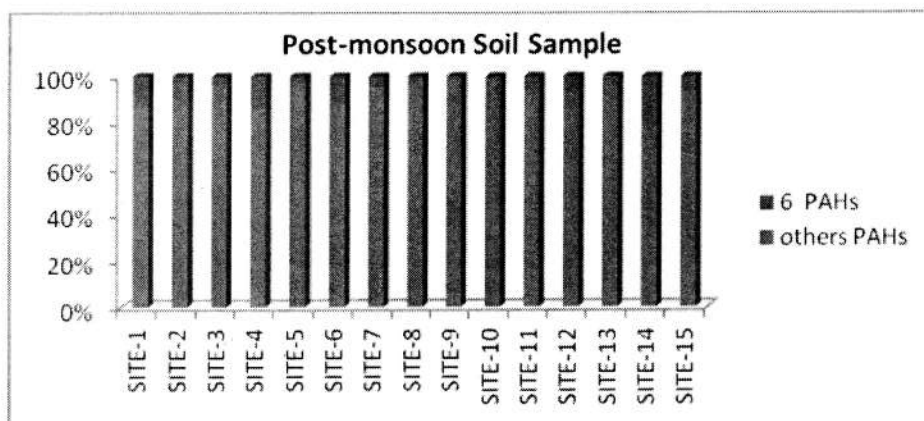


Figure-9: Profile of 6 carcinogenic PAHs with other PAHs in the Post-monsoon soil samples

3.5 SOURCE APPORTIONMENT OF PAHs BY DIAGNOSTIC RATIOS:

PAHs ratio have been widely used for source apportionment studies. It is essential to identify the origin and potential sources of PAHs in soil in order to assess the environmental risk and control environmental pollution by PAHs. Researchers have prescribed individual PAHs ratio for source diagnosis of these compounds in environment. Table-3 summarizes some of ratios quoted in literature which had been used to distinguish whether PAHs compounds found in the environment were derived from petrogenic or pyrogenic sources.

Usually, **Phe/Ant ratio <10** and **Flu/Pyr ratio >1** indicate that PAHs come from pyrogenic source and **Phe/Ant >15** and **Flu/Pyr <1** indicate petrogenic origins of PAHs (Baumard *et al.* 1998). According to Yunker *et al.* (2002) **Flu/(Flu+Pyr) <0.4** and **Ant/(Ant+Phe) <0.1** represent Petrogenic source, while, **Flu/(Flu+Pyr) >0.4** and **Ant/(Ant+Phe) >0.1** represent Pyrogenic source. The ratios of Phe/Ant, Flu/ Pyr and Flu/ (Flu+Pyr), Ant/(Ant+Phe) are listed in Table-3.

Ratios	Values and indicative of		Reference	
	Petrogenic source	Pyrogenic source		
R1	Phe/Ant	>15	<10	Baumard <i>et al.</i> , 1998

R2	Flu/Pyr	<1	>1	Yunker <i>et al.</i> , 2002
R3	Ant/(Ant+Phe)	<0.1	>0.1	
R4	Flu/(Flu+Pyr)	<0.4	>0.5	

Table-3: PAHs ratios and values for source diagnosis

Phe/Ant ratio (R1) of the Pre-monsoon soil samples varied from 0.05 to 0.93, whereas, this ratio in the Post-monsoon soil samples ranged from 0.10 to 21.2. Again, Flu/Pyr ratio (R2) in the Pre-monsoon soil was found to be in the range from 1.4 to 3.5 and for the Post-monsoon soil, it was 1.10 to 18.0. Both these ratios indicated towards Pyrogenic origin for the PAHs detected in those areas. The Ant/ (Ant+Phe) ratios (R3) for Pre-monsoon and Post-monsoon soils were found as 0.51-0.94 and 0.04-0.90 respectively. Flu/ (Flu+Pyr) ratios (R4) for Pre-monsoon soil as well as Post-monsoon were 0.59-0.77 and 0.54-0.94 respectively. These ratios also indicated dominance of Pyrogenic source.

Phe/Ant ratios (R1) of the Pre-monsoon & Post-monsoon water samples varied from 0.07 to 6.26 and 0.26 to 10 respectively. Again, Flu/Pyr ratio (R2) in the Pre-monsoon water was found to be in the range from 1.19 to 3.08 and for the Post-monsoon water samples, it was found as 1.10 to 4.80. The Ant/ (Ant+Phe) ratio (R3) for Pre-monsoon water was 0.13-0.93 and of the water in the Post-monsoon season, it was 0.09-0.78. Flu/ (Flu+Pyr) (R4) ratios for Pre-monsoon and Post monsoon water samples were 0.54-0.75 and 0.20-0.72 respectively. All these ratios showed that the source of PAHs detected in the Borholla area were mostly Pyrogenic.

The Phe/Ant and Flu/Pyr ratios in the soils from all the locations in the Oil exploration areas in Niger Delta, Nigeria, ranged from 6.0 to 9.2 and from 1.2 to 1.5, respectively. These values strongly affirmed a predominant pyrogenic origin, with minor petrogenic contributions, of PAHs in the soil samples (Sojину *et al.*, 2010). The Flu/Pyr ratios in all samples collected from Ji'nan City in China ranged from 0.72 to 1.40 and Phe/Ant ratios ranged from 0.99 to 24.85. Data from each sample were grouped according to the origins of these PAHs in soils. It can be seen that there was a strong pyrogenic influence on soil PAHs (Dai *et al.*, 2008). The Ant/ (Ant + Phe) ratio for soils in Natural Reserve (Isola delle Femmine) (Italy) is 0.060–0.23. Such Ant/ (Ant + Phe) ratios suggest combustion sources in the investigated and reference areas (Orecchio, 2010).

3.6 SOURCE APPORTIONMENT OF PAHs BY PCA (PRINCIPAL COMPONENT ANALYSIS):

Diagnostic ratios provide only qualitative information about the contributions of various sources to PAHs. Quantitative assessments can be done with PCA. PCA was used to separate PAHs that have similar sources and modes of input. The use of PCA for identification of PAH sources is simply based on the similarity in the PAH profiles of emission sources and receptors (Lee *et al.*, 2004). The primary function of PCA is to reduce the number of variables while retaining as much as possible of the original information, therefore variables with the similar characteristics were grouped into factors (Fang *et al.*, 2004). PCA was done for soil and water samples separately for both Pre-monsoon and Post-monsoon samples using SPSS version 16 statistical package. PCA was conducted on the priority pollutant PAH data set (16 variables× 15 samples) also revealed the presence of an apparent mixing trend. The results of PCA showed which factors were able to explain the primary portion of the data variance. Therefore individual PAHs representative of each factor was taken as source tracers. The results are summarized below:

In the Pre-monsoon water samples, PCA revealed two factors responsible for PAHs in drinking water samples of Borholla area. The first factor accounted for 68.62% of the total variance and had high loading of Acenaphthene, Acenaphthylene, Fluorene, Phenanthrene, Anthracene. This profile of PAH was consistent with the emission characteristic of PAH composition in coal combustion in China (Y. Chen *et al.*, 2005). It was also similar to that of biomass burning (Simoneit, 2002; Tahir *et al.*, 2006). Therefore, this factor is possibly a representative of coal or wood combustion sources. High loading of Anthracene reflects coal-combustion source (Harrison *et al.*, 1996; Li *et al.*, 2003). The second factor accounted for 31.38% of the total variance which is dominated by Benzo(a)pyrene, Benzo(g,h,i)perylene, Benzo(a)anthracene and Anthracene. This profile of PAH was similar to the PAH composition in vehicle exhaust in city tunnels on the Pearl River Delta (Wang *et al.*, 2007) and also consistent with that in other studies on vehicle emission PAHs (Harrison *et al.*, 1996; Li and Kamens, 1993; Venkataraman *et al.*, 1994). Thus this factor is mainly associated with vehicular emission source also a contribution of biomass and fossil fuel burning. Thus these factors may be associated with mixed source.

The PCA of Post-monsoon soil samples revealed three factors. Factor 1 contributed about 45.05% of the total variance with high loading values of Acenaphthene, Acenaphthylene, Fluorene, Phenanthrene, Anthracene, Benzo(a)anthracene, thus its main source is wood, biomass and coal combustion (Y. Chen *et al.*, 2005). The second factor accounted for 30.79% of the total variance, dominated by Benzo(k)fluoranthene, Indeno(1,2,3-cd) pyrene which indicates vehicular emission sources (Harrison *et al.*, 1996). The third factor accounted for 15.34% of the total variance dominated by Benzo(a)pyrene, This factor was mainly from petrol vehicle emission sources as Pyrene is characterized by petrol power cars tracer (Harrison *et al.*, 1996).

The Principal Component Analysis revealed that the PAHs contamination over the whole area of Borholla is due to the mixed effects of wood and coal combustions as well as vehicular exhaust. So, it can be concluded that the PCA results are consistent with the results obtained from diagnostic ratios and source of the PAHs detected in that place is Pyrogenic.

3.6 CORRELATION BETWEEN ORGANIC CARBON (OC) AND TOTAL PAH CONCENTRATIONS

Organic Carbon, in the Soil samples of Pre-monsoon season, was found in the range from 0.76% to 2.18%, while, in the Post-monsoon season, it was found in the range from 1.73% to 4.08%. We compared these OC values with their respective Total PAH concentrations. We found a very weak correlation ($r=0.54$) in Pre-monsoon and $r=0.42$ in Post-monsoon) between OC and Total PAH concentrations.

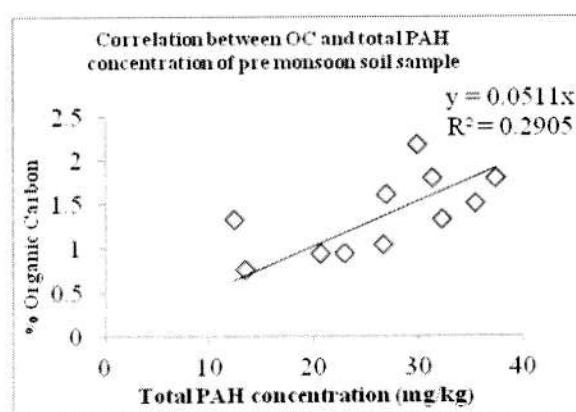


Figure-6: Correlation between OC and total PAH concentration of Pre-monsoon Soil samples

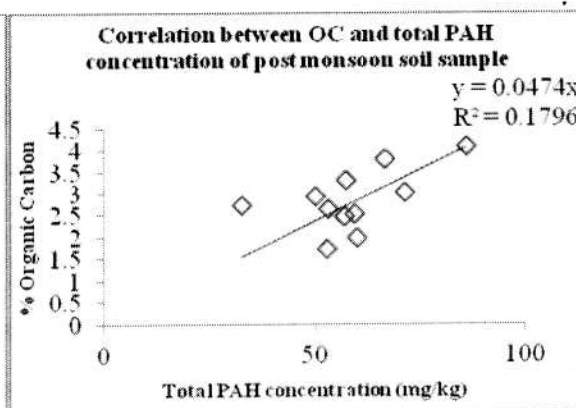


Figure-7: Correlation between OC and total PAH concentration of Post-monsoon Soil samples

Ana *et al.*, (2009) also found no correlation between OC and PAHs in the soils of Eleme in the Niger Delta, Nigeria ($r=0.044$). This probably may be due to some variations soil properties and environmental factors. Santino Orecchio in 2010, found a weak positive correlation between total PAH concentration & organic matter content ($r=0.60$) which indicates other elements probably play a major role in determining the level of contamination (e.g. proximity to sources, soil characteristics, vegetation type, altitude or latitude). It may be due to influenced by deposition from particulate matter, suggesting that the partitioning between organic matter and PAHs is not a dominant process in the soils. No significant correlation was observed between OC and PAH concentrations in the Kota Bharu soils also (Fadzil *et al.*, 2008).

CONCLUSION

The study on polycyclic aromatic hydrocarbons (PAHs) in the Borholla Oilfield areas shows a very high concentration of PAHs over the whole area. A noticeable increase in the concentrations of PAHs in the Post-monsoon season has been noticed which indicates that the wet deposition can be held responsible for the recharge of PAHs in the soil after monsoon which may had been percolated through the deeper layers of soil to the ground water ultimately resulting in the increase of PAH concentrations in water in the Post-monsoon season. This fact is supported by the result of our experiment, which proves that the sources of all the PAHs detected in the Borholla Oilfield are Pyrogenic. This result is obtained by doing the statistical analysis i.e. Source diagnostic ratios and Principal Component Analysis. As PAHs have tendency to remain attached with soil particles, concentrations of PAHs were expected to be higher in soil than in water and this fact is also established by the results of my study Organic carbon percentage has been found to have very weak positive correlation with total PAH concentrations. This study shows that the PAH contamination in the whole Borholla area is not due to the crude oil itself or crude oil explorations activities but mainly due to the wood and fossil fuel combustions and vehicular exhaust.

ONGC-CPBT

Statement of expenditure of the ONGC-CPBT research project

1. Name of Principal Investigator: Prof. Kali Prasad Sarma
2. Deptt. Of Principal Investigator: Environmental Science
3. University: Tezpur University
4. Grant no.: ONGCA/FTG/ONGC-CPBT/2010-11.
4. Title of the Research Project: Spatial distribution and source apportionment of PAHs in drinking water and soil of surrounding areas of oilfields of Borhola area of Jorhat.
5. Effective date of starting the project: March, 2011.
6. Duration: 1 year
6. a. Period of Expenditure: From 2011 to 2012

b. Details of Expenditure:

Sl.N o.	Item	Amount received (in Rs)	Expenditure Incurred (in Rs)
1	Salary (project fellow @Rs 5000/- pm)	60,000/-	60,000/- (Since the project fellow received Rajiv Gandhi National Fellowship for the financial year 2011-2012 from the month of August an amount of Rs. 40,000/- has been refunded later.)
2	Equipment	4,70,000/-	Rotary evaporator (3,20,000/-) Sonicator bath (50,630/-) The remaining amount was used in purchasing of some small equipments
3	Chemical and glassware	50,000/-	- 50,000/-
4	Calibration standards	30,000/-	30,000/-
5	Travel	15,000/-	15,000/-
6.	Contingency	10,000/-	10,000/-
	Total	6,35,000/-	6,35,000/- (Rupees Six Lakhs Thirty-five Thousand only)

It is certified that the grant of Rs 6,35,000/- (Rupees Six Lakhs Thirty-five Thousand only) received during 2011-2012 from ONGC-CPBT for the Research Project entitled "Spatial distribution and source apportionment of PAHs in drinking water and soil of surrounding areas of oilfields of Borhola area of Jorhat", has been fully utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University.



SIGNATURE OF PRINCIPAL INVESTIGATOR

26/04/2013