ATMOSPHERIC DEPOSITION OF POLYCYCLIC AROMATIC HYDROCARBON: STUDY FROM GUWAHATI, ASSAM

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TO

MY HUSBAND MIRZANUR RAHMAN

DECLARATION

I hereby declare that the thesis entitled ***"Atmospheric Bulk Deposition of Polycyclic Aromatic Hydrocarbon: Study from Guwahati, Assam"***, submitted to the **Department of Environmental Science, Tezpur University**, Tezpur, Assam in partial fulfillment for the award of the degree of Doctor of Philosophy in **Environmental Science** and it has not been previously considered for the award of any degree, diploma, associateship, fellowship or any other similar title or recognition from any University, Institute or other organizations.

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CERTIFICATE OF THE PRINCIPAL SUPERVISOR

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All help received from various sources have been duly acknowledged.

No part of this thesis has been submitted elsewhere for award of any degree.

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CERTIFICATE

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The committee recommends for the award of the degree of Doctor of Philosophy.

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(Karishma Hussain)

ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAHs) are unique class of organic pollutants containing two or more fused aromatic rings, which are toxic and potential carcinogens. They are extensively studied compounds and their occurrence has been reported from various places over the world which indicates their ubiquitous nature in our environment. USEPA has already listed 16PAHs [naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene and Indeno(1,2,3-c,d)pyrene] as most priority ones to be analysed in various environmental matrices.

Main objectives of our work are 1) to ascertain the seasonal variability in the concentrations of 16 priority PAHs in atmospheric bulk deposition, 2) Source apportionment of PAHs in different matrices using marker compounds, 3) to study relationship of PAHs with carbon and some heavy metals such as Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn and 4) to establish association of PAHs signatures in bulk deposition to PAHs signatures in soil, street dust, river water and sediment.

Our study area was Guwahati city of northeastern India. Bulk deposition, soil and street dust sampling was carried out in five sampling locations selected based on their landuse pattern (industrial site, commercial site, institutional site, residential site and forest site). River water and bank sediment samples were collected from Bharalu River which passes through the urban stretch of Guwahati. The sampling sites were selected based on the various anthropogenic activities in the surrounding area of the river.

Bulk deposition samples were collected through a stainless steel funnel with surface area of 0.11m^2. Samplers were open for both dry and wet deposition for a period of about one month during February 2011 to February 2012. Triplicate of the samplers were placed at five selected sites at an average height of 7m, in addition to which a field blank sampler was also placed. Soil and street dust samples were collected seasonally during monsoon, post-monsoon and pre-monsoon. Five samples were collected from each site covering the entire area, pooled and homogenized by coning and quartering to make a composite sample. River water and bank sediment samples were collected during post-monsoon and pre-monsoon season. Three river sediment samples were collected from each location within a distance of 1km. Triplicate sediment samples were pooled homogenized by coning and quartering to make composite sample.

Bulk deposition samples were extracted by organic-aqueous phase extraction method as recommended by Ollivon et al. [1]. Soil and street dust samples were extracted through ultrasonic extraction [2]. River sediment samples were also ultrasonically extracted [3]. River water samples were extracted through liquid-liquid extraction method [4]. All the extracted samples were chromatographically clean-up according to the method recommended by USEPA [5]. Finally samples were analysed in HPLC equipped with UV [6].

Organic carbon (OC) was analysed in TOC analyser equipped with NDIR detector [Analytikjena, multi N/C HT1300 (solid samples) and HT 2100 (liquid samples)]. Black carbon (BC) concentration was determined by thermochemical oxidation method (CTO-375) as put forwarded by Gustafsson et al. [7], 1997. Heavy metals analysis was done in ICP-OES (Perkin Elmer Optima 2100 DV).

∑PAHs concentration in bulk deposition were ranged between 2.2ng/ml and 1035ng/ml with mean value of 71±140ng/ml. Whereas benzo(a)pyrene concentration were ranged from BDL-5.6ng/ml with mean of 0.2±0.9ng/ml. The maximum concentrations of ∑PAHs and BaP were observed to be on higher side than many industrial cities over the world. Total PAHs concentration was found to be contributed mainly by LMWPAHs (low molecular weight) with high dominance of 2 and 4-ring PAHs which could be due to their high water solubility. Seasonal variations of PAHs concentrations were also observed and maximum concentrations were detected during dry season of the year. Prevailing atmospheric condition with low wind activity, subsidence state and inversion condition as evident from the vertical temperature profile is attributed as possible cause for high PAHs accumulation during dry season. PAH scavenging was found to be affected by various meteorological parameters such as temperature, relative humidity, wind speed and wind direction. Temperature and relative humidity were found to influence mainly the dispersion of LMW PAHs. Toxic equivalency factors (TEFs) of PAHs were estimated to determine carcinogenic potential of individual PAH relative to BaP as BaPeq [Benzo(a)pyrene equivalent] concentration. Mean BaPeq concentration of ∑PAHs was found to be maximum at industrial site (4.6±10ng/ml) which was 11.5 times higher than forest site (0.4±0.5ng/ml). Moreover, the exposure risk was observed to be maximum during dry season. Source emission signatures also showed seasonality for the study period. Diagnostic ratios of the PAHs favoured for pyrogenic origin. Two sources were identified and quantified by PCA-MLR (Principal Component Analysis Multiple Linear Regression). Source 1 represented mixed inputs from diesel, coal and wood combustion and source 2 from gasoline vehicles. Source contributions estimated by the model were found to ~ 90% and ~10% for source 1 and 2 respectively.

Mean concentrations of ∑PAHs (USEPA 16) in soil samples were found to be 5570.7±7830ng/gm (799.7-19492ng/gm), 19292.1±19932ng/gm ((1271.4-51299.7ng/gm) and 9052.3±11508 ng/gm (1639.7-29492ng/gm) during monsoon, post-monsoosn and pre-monsoon season respectively. PAHs profile was found to be dominated by 2- and 4-ring PAHs which could be attributed to multi-hop nature of LMWPAHs with continuous cycle of atmospheric deposition and re-suspension. Mean BaPeq concentration of ∑PAHs was found to be maximum (557±828ng BaPq /gm) during pre-monsoon season with high exposure risk. Diagnostic ratios of marker species and their association with heavy metals indicated for pyrogenic origins of PAHs in soil with fossil fuel combustion as one of the major source of PAHs. Coal and diesel engine combustion was found to be significant source during pre-monsoon season. High dependencies of PAHs on BC/OC (black carbon/organic carbon) ratios were found indicating that BC could be interfering with the association of PAHs and OC. However, such relationships showed seasonal bias and high positive dependencies were found during pre-monsoon season only.

Mean ∑PAHs concentration in street dust samples were observed to be 8500.8±4608ng/gm (2248.8-13550ng/gm), 23294.7±15164ng/gm (1394.7-43789ng/gm) and 14770.5±9899ng/gm (5153.5-28796.3ng/gm) during monsoon, post-monsoon and pre-monsoon respectively. However, mean BaPq concentration was found to be maximum during pre-monsoon season 541.7±550ng/gm. PAHs profile in street dust was also found to be dominated by 2 and 4-ring PAHs. BC was also found to be an important factor controlling seasonal PAHs concentration in street dust. Diagnostic ratio and correlation of PAHs with heavy metal recommended pyrolytic source origin with fossil fuel and vehicular combustion as major signature source of PAHs in street dust samples of the city. Strong seasonality in sources of PAHs was indentified and signatory local source influence was recognized during pre-monsoon season.

Concentration of ∑PAHs in Bharalu water was found to be in the range 3.4-72.9ng/ml with mean value of 29.8±22ng/ml. Moreover, ∑PAHs concentration was found to be on higher side during pre-monsoon season than that of post-monsoon season. PAHs Profile was found to be dominated mainly by 3-, 4- and 5-ring compounds. Predominance of HMWPAHs (high molecular weight) (throughout the study period) despite of their low solubility in water could be attributed to their continuous input as urban waste or discharge of wastewater into Bharalu River. Mean BaPq concentration was found to be 2.2±3ng/ml for ∑PAHs. PAHs in water of Bharalu River were found with severe ecosystem risk during both the sampling season which was estimated using risk quotient (RQ). Only, BaA and IP showed significant correlation with OC in Bharalu River water. Sources of both petrogenic and pyrogenic origin of PAH was identified by using diagnostic ratio. Pyrogenic sources were found to be mainly from diesel and wood combustion.

∑PAHs concentration in Bharalu River sediment was varied from 337.6-23140ng/gm with mean value 4968.2±8135ng/gm during post-monsoon season, while they ranged from 608.8-8618.6ng/gm with mean concentration of 3812.4±2820 ng/gm during pre-monsoon season. The PAHs profile was found to be dominated by 3, 4 and 6-ring PAHs in sediment. Mean BaPeq concentration of ∑PAHs was observed to be maximum during pre-monsoon season (197.5±317ng BaPeq/gm). PAHs in aquatic sediment of Bharalu River resulted in severe ecosystem risk mainly during post-monsoon season. No significant correlation was observed for sediment PAHs with organic carbon (OC) content. However, naphthalene and chrysene showed significant correlation with black carbon (BC). The diagnostic ratios revealed mixed petrogenic and pyrogenic sources of PAHs in Bharalu River sediment contributed mainly from diesel and gasoline combustion in case of pyrogenic source.

PAH signatures of bulk deposition correlated significantly with signatures of soil (r=0.79), street dust (r=0.65), surface water (r=0.51) and sediment (r=0.50) which could support the hypothesis that atmospheric deposition is the major contributor of PAHs in soil, street dust, surface water and sediment.

From the observations it might be concluded that meteorological parameters played a significant role in atmospheric deposition of PAHs with temperature-dependent scavenging for LMWPAHs. Exposure risk for PAHs in all the environmental matrices was found to be maximum during dry season. High ecosystem risk was observed in Bharalu River water and sediment. Vehicular and coal combustion were identified as signature source for PAHs emission in various environmental compartments in Guwahati. In the dispersion of PAHs both in soil and street dust BC was found to play a very important role mainly during pre-monsoon season. Finally, atmospheric bulk deposition was revealed as significant contributor to other environmental matrices of the environment.

Key Words: PAHs, BaP, atmospheric deposition, season, carbon, heavy metal, source

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Acen	Acenapthene
Acy	Acenaphthylene
Anth	Anthracene
BaA	Benzo(a)anthracene
BaP	Benzo(a)pyrene
BbF	Benzo(b)fluoranthene
BC	Black Carbon
BDL	Below Detection Limit
BgP	Bezo(g,h,i)perylene
BkF	Benzo(k)fluoranthene
Chry	Chrysene
CMB	Chemical Mass Balance
CPAHs	Carcinogenic PAHs
DBA	Dibenz(a,h)anthracene
EPA	Environmental Protection Agency
Flu	Fluorene
Flan	Fluoranthene
GC-MS	Gas Chromatography Mass Spectrometry
HMW	High Molecular Weight
HPLC	High Pressure Liquid Chromatography
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IP	Indeno(1,2,3-cd)pyrene
LLE	Liquid-Liquid extraction
LMW	Low Molecular Weight

LOD	Limit of Detection
Naph	Naphthalene
NDIR	Non-Dispersive Infra-Red Radiation
PAH	Polycyclic Aromatic Hydrocarbon
PCA	Principal Component Analysis
PCA/MLR	Principal Component Analysis Multiple Linear Regression
PCBs	Polychlorinated biphenyls
Phen	Phenanthrene
POPs	Persistent organic pollutants
PM	Particulate matter
Pyr	Pyrene
OC	Organic Carbon
SOCs	Semivolatile Organic Compounds
StdDev	Standard Deviation
TLC	Thin layer chromatography
TSPM	Total suspended particulate matter
USE	Ultrasonic extraction
UVD	Ultraviolet Detector
∑PAHs	Sum of 16 PAHs

Chapter 1

Introduction

Chapter1: Introduction

1.1 Urban Environmental Quality

Over the past few decades economic expansion and industrial growth have been the triggering factor of global change in environmental quality with rising desire for prosperous economy, especially in the developing countries. Traditional urban developments at the cost of environmental degradation lead to emergence of many environmental issues including air, water and soil pollution [1]. The continuous addition of motorization results in a sharp increase in the concentration of pollutants in the urban air which subsequently adding to soil, street dust, water and sediment [2]. It is estimated that vehicular emission attributes about 40-80 % of the air quality crisis [3].

Rapid growth of cities in urban India illustrates a picture of transformation - feudal towns to cities, cities to metropolis and metros to megapolis. This in turn demands for increased energy-based goods and services [3], which in turn release many hazardous chemicals in the environment. The direct consequence of all these developments is degradation of environmental quality. Studies also reveal a close relationship of human health effect with the actual level of exposure to pollutants [4].

Extensive research is already being performed in many such areas including inorganic and organic pollutants in the environment with major developments in case of organic pollutants in last few decades [5].

Since industrialisation, many organic chemicals that are naturally occurring (e.g. petroleum) and synthetic are released into the environment from various anthropogenic activities. The presence of more than 600 organic compounds have already been reported in various matrices of the environment that belong to the classes of petroleum hydrocarbons, polycyclic aromatic hydrocarbons, ketones, aldehydes, volatile organohalogen compounds, monocarboxylic acids, pesticides, alcohols, dicarboxylic amines, fatty acids, saccharides and amino acids [6].

1.2 Polycyclic Aromatic Hydrocarbon

Polycyclic Aromatic Hydrocarbons (PAHs) are among the most notorious semivolatile organic pollutants and are considered as hazardous air pollutants (HAP) in the group of the non-halogenated organic compounds along with benzene, phenols, aldehydes, etc. [7]. They are the class compounds with two or more fused benzoid rings made up of only carbon and hydrogen [8]. Based on the molecular structure PAHs are commonly classified into two categories namely low molecular weight (LMW) PAHs with four or fewer aromatic rings and high molecular weight (HMW) PAHs with five or more rings. The United States Environmental Protection Agency (USEPA) has notified 16PAHs as the most priority ones to be analyzed in different environmental matrices [9]; Among them, Benzo(a)anthracene (BaA), Benzo(a)pyrene (BaP), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF),,Chrysene (Chry), Dibenzo(a)anthracene (DBA) and Indeno(1,2,3-c,d)pyrene (IP) have been classified as possible or probable human carcinogens [10] and BaP can serve as an indicator of the whole group of PAH because of its recognisation as being carcinogens [11].

PAHs are formed in incomplete combustion processes of any organic matter including fossil fuels and vegetation [12]. PAHs formation gets enhanced in thermochemical processes operating under rich fuel conditions [13]. The hydrogen abstraction–C_2H_2 addition (HACA) mechanism is now popularly considered as the major reaction route leading to the formation of PAHs in combustion flames [14-23]. In the combustion environment the simple gaseous PAH molecules, such as naphthalene, phenanthrene, pyrene, etc., can undergo sequential build-up process and eventually lead to formation of larger PAHs, fullerenes, bowl-shaped nanostructures, and solid-phase species including carbonaceous dust, graphene particles, and soot [14].

Depending on volatility and molecular weight PAHs can adsorb on soot surface and can remain in the gas phase as well [13]. Such particles then appear in different environmental matrices such as ambient air, soil, street dust, water, sediment etc. and can be inhaled by human being or consumed with food, leading to major health problems, such as tumors, birth defects, and a variety of pulmonary diseases [24].

1.2.1. Molecular Structure and Physico-Chemical Properties of PAHs

Molecular structure of 16 PAHs are shown in Figure 1.1 and Physical properties of the 16 PAHs were shown in Table 1.1. PAHs are weakly volatile and sparingly soluble in water. The solubility of PAHs in water decreases with increase in molecular weight of PAH. Solubility of 16 studied PAHs are shown in Annexure A. PAHs dissolve effectively in organic solvent and are lipophilic in nature which is measured by water – octanol partition coefficients (K^{ow}). All PAHs are solid having high melting and boiling points. Although PAHs are chemically inactive they easily bond to particulate matter. PAHs become highly thermo and photosensitive when adsorbed on dust surface and are degraded at high temperature (50°C) and on exposure to light especially ultraviolet and visible light [25]. Photo-oxidation is one of the principal pathway of PAHs decomposition and their secondary metabolite production in the atmosphere [26].

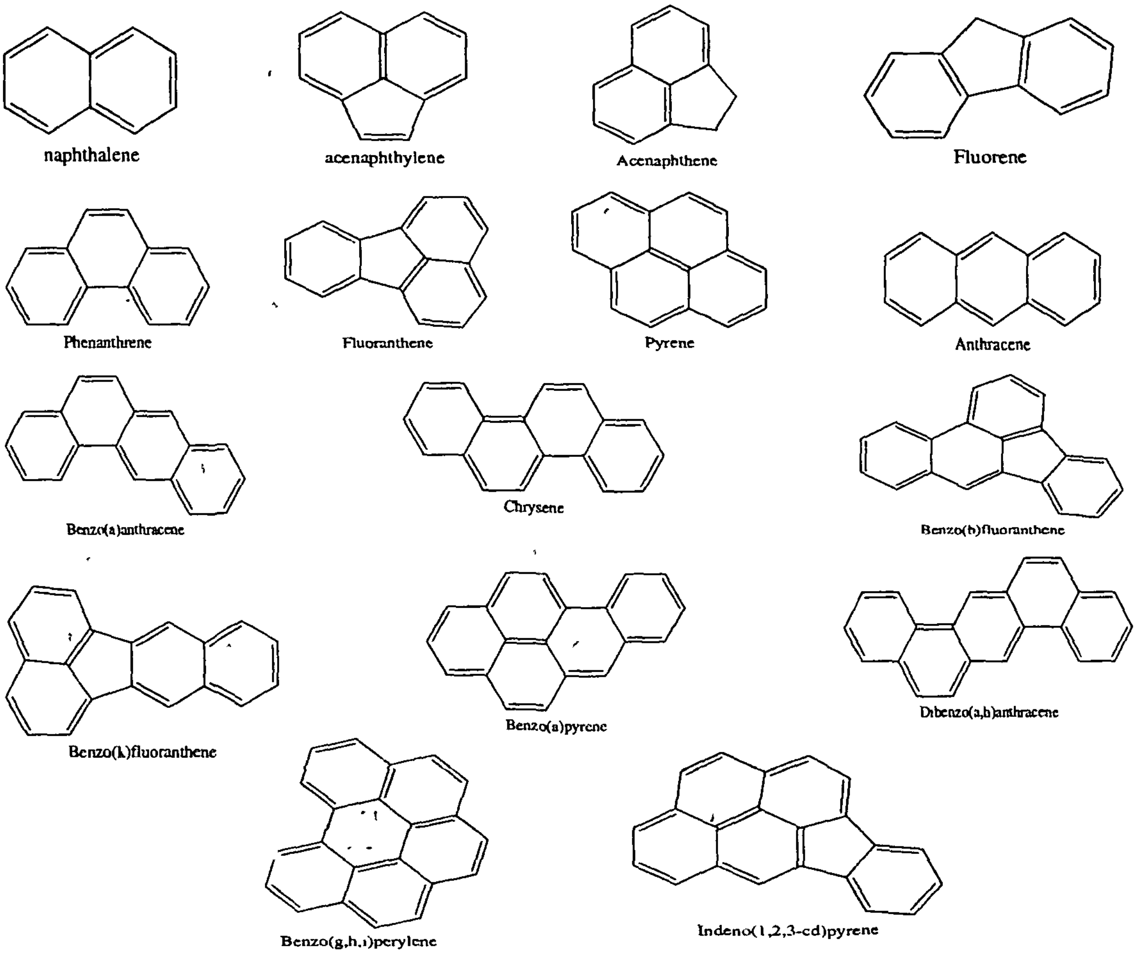


Figure 1.1: Molecular Structures of PAHs

Table 1.1 Physical properties and chemical formulae of 16 PAHs

Compound	Formula	Molecular Weight	Melting Point °C	Boiling Point °C	Vapour Pressure kPa
Naphthalene	$C_{10}H_8$	128.18	80.2	218	1.1×10^{-2}
Acenaphthylene	$C_{12}H_8$	152.20	92-93	265-280	3.9×10^{-3}
Acenaphthene	$C_{12}H_{10}$	154.20	90-96	278-279	2.1×10^{-3}
Fluorene	$C_{13}H_{10}$	166.23	116-118	293-295	8.7×10^{-5}
Phenanthrene	$C_{14}H_{10}$	178.24	96-101	339-340	2.3×10^{-5}
Anthracene	$C_{14}H_{10}$	178.24	216-219	340	36×10^{-6}
Fluoranthene	$C_{16}H_{10}$	202.26	107-111	375-393	6.5×10^{-7}
Pyrene	$C_{16}H_{10}$	202.26	150-156	360-404	3.1×10^{-6}
Benzo(a)anthracene	$C_{18}H_{12}$	228.30	157-167	435	1.5×10^{-8}
Chrysene	$C_{18}H_{12}$	228.30	252-256	441-448	5.7×10^{-10}
Benzo(b)fluoranthene	$C_{20}H_{12}$	252.32	167-168	481	6.7×10^{-8}
Benzo(k)fluoranthene	$C_{20}H_{12}$	252.32	198-217	480-471	2.1×10^{-8}
Benzo(a)pyrene	$C_{20}H_{12}$	252.32	177-179	493-496	7.3×10^{-10}
Dibenzo(a,h)anthracene	$C_{22}H_{14}$	278.35	266-270	524	1.3×10^{-11}
Benzo(g,h,i)perylene	$C_{22}H_{12}$	276.34	275-278	525	1.3×10^{-11}
Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	276.34	162-163	530	ca.10^{-11}

1.2.2. Toxicity and Carcinogenicity of PAHs

Environmental PAHs have harmful effects on different types of organisms of the ecosystem [27]. PAHs attract considerable attention among researchers with the continuous rise in death toll caused by cancer which account for about 13% of all human deaths worldwide in 2007 [28]. Carcinogenic and mutagenic properties of a few PAHs members have already been well established by researchers [29-45] in experimental animals and humans. It is revealed from studies on experimental animals that PAHs may trigger various health effects, such as cytotoxicity, immunotoxicity, genotoxicity, carcinogenicity, reproductive toxicity etc [7]. Organizations including United States Agency for Toxic Substances and Disease Registry (ATSDR), the International Agency for Research on Cancer (IARC), the Department of Health and Human Services (DHHS), the National Occupation Safety and Health Administration (OSHA), and the US-EPA classify PAHs as carcinogenic materials. Carcinogenic classifications of selected PAHs put forward by various agencies are given in Table 1.2.

Benzo(a)pyrene (BaP) is termed as index or 'gold standard' of the whole group of PAHs due to its high carcinogenic potency [32, 35]. Carcinogenicity of BaP through inhalation was tested only in hamsters [46, 47]. Risk analysis inferred that about 9 per 100000 individual spending a lifetime in ambient air exposed to average level of BaP of 1 ng/m^3 may die from respiratory tract cancer [40, 47]. LMW PAHs are generally associated with relatively lower toxicity than HMWPAHs (5 or 6 rings). Car exhausts (petrol, diesel), domestic coal-stove emissions and tobacco smoke releasing mainly 4- to 7-ring PAHs are found to exhibit nearly all the carcinogenic potential [48]. Elevated levels of DNA adduct, mutations, reproductive effects, and cancers of lung, respiratory tract and urinary bladder are found to be associated with exposure to PAHs [49, 50]. According to Pankow et al. [51] 1993 carcinogenic risk of inhaled PAHs depend upon whether it enters into lung in the gas form or particulate; in case of particulate PAHs carcinogenicity prevails for longer period of time.

Table 1.2 Carcinogenic classifications of PAHs by various agencies

Agency	PAHs Compounds	Carcinogenic Classification
U.S. Department of Health and Human Services (HHS)	• Benzo(a)anthracene • Benzo(b)fluoranthene • Benzo(a)pyrene • Dibenzo(a,h)anthracene • Indeno(1,2,3-cd)pyrene	Known animal carcinogens
International Agency for Research on Cancer (IARC)	• Benzo(a)anthracene • Benzo(a)pyrene	Probably carcinogenic to humans
	• Benzo(a)fluoranthene • Benzo(k)fluoranthene • Indeno(1,2,3-cd)pyrene	Possibly carcinogenic to humans
	• Anthracene • Benzo(g,h,i)perylene • Benzo(e)pyrene • Chrysene • Fluoranthene • Fluorene	Not classifiable as to their carcinogenicity to humans

	• Phenanthrene • Pyrene	
U.S. Environmental Protection Agency (EPA)	• Benzo(a)anthracene • Benzo(a)pyrene • Benzo(b)fluoranthene • Benzo(k)fluoranthene • Chrysene • Dibenzo(a,h)anthracene • Indeno(1,2,3-cd)pyrene	Probable human carcinogens
	• Acenaphthylene • Anthracene • Benzo(g,h,i)perylene • Fluoranthene • Fluorene • Phenanthrene and • Pyrene	Not classifiable as to their carcinogenicity to humans

1.2.3. Sources of PAHs

Although some PAHs in the environment arise from natural sources of combustion such as forest fires and volcanoes along with some minor biogenic sources;

emissions from anthropogenic activities predominate [52, 42, 43]. Anthropogenic sources of PAHs can be broadly classified into stationary and mobile sources. Stationary sources of PAHs include residential heating, industrial activities (e.g. aluminium production and coke manufacture), incineration and power generation. Diesel and gasoline engine vehicular exhaust are categorised as mobile sources of PAHs [5]. In general, Stationary fuel sources are considered to be responsible for over 97% of PAH emissions [53]. However, the profile is different in case of an urban area with high traffic density [5].

Anthropogenic sources of PAHs can also be categorised as petrogenic and pyrogenic. Pyrogenic PAHs are resulted from incomplete combustion of any organic material while the petrogenic PAHs are found in oil and some of its product [54-56]. In general, the pyrogenic PAHs are comprised of larger ring than the petrogenic PAHs [57]. Pyrogenic PAHs production is favoured by an oxygen-deficient flame with temperature range of 650-900°C and fuels which are less oxidized [58].

Sources of PAHs can vary depending upon the prevailing activities, atmospheric conditions and topography of the area.

1.2.4 Distribution in the Environment (Air, Soil, Street Dust, Water and Sediment)

PAHs are ubiquitous pollutant in the environment mainly arising from anthropogenic sources [59, 42, 60, 61]. Atmospheric PAHs are derived from combustion and volatilization [58]. Aerial movement is one of the major pathways for environmental distribution and transboundary deposition of PAHs [62]. Remote areas far from emission sources also get exposed to PAHs as they undergo long range transport [63, 64]. Eventually, PAHs settle down in soils, street dust and enter into aquatic environment [65, 66]. Soil and street dust acts as direct sink of atmospheric PAHs near to traffic and other combustion sources. From these environmental compartments rain water and storm water easily washed away PAHs to nearby aquatic bodies. Due to hydrophobic nature, PAHs in aquatic environment are preferably partitioned and accumulate into the particulate phase of sediment [5]. PAHs thus, occur in multicompartmental system of the environment [67, 68] and paved the way for multiple routes of exposure to this class of carcinogen. Figure 1.2 illustrates distribution PAHs in various environmental matrices.

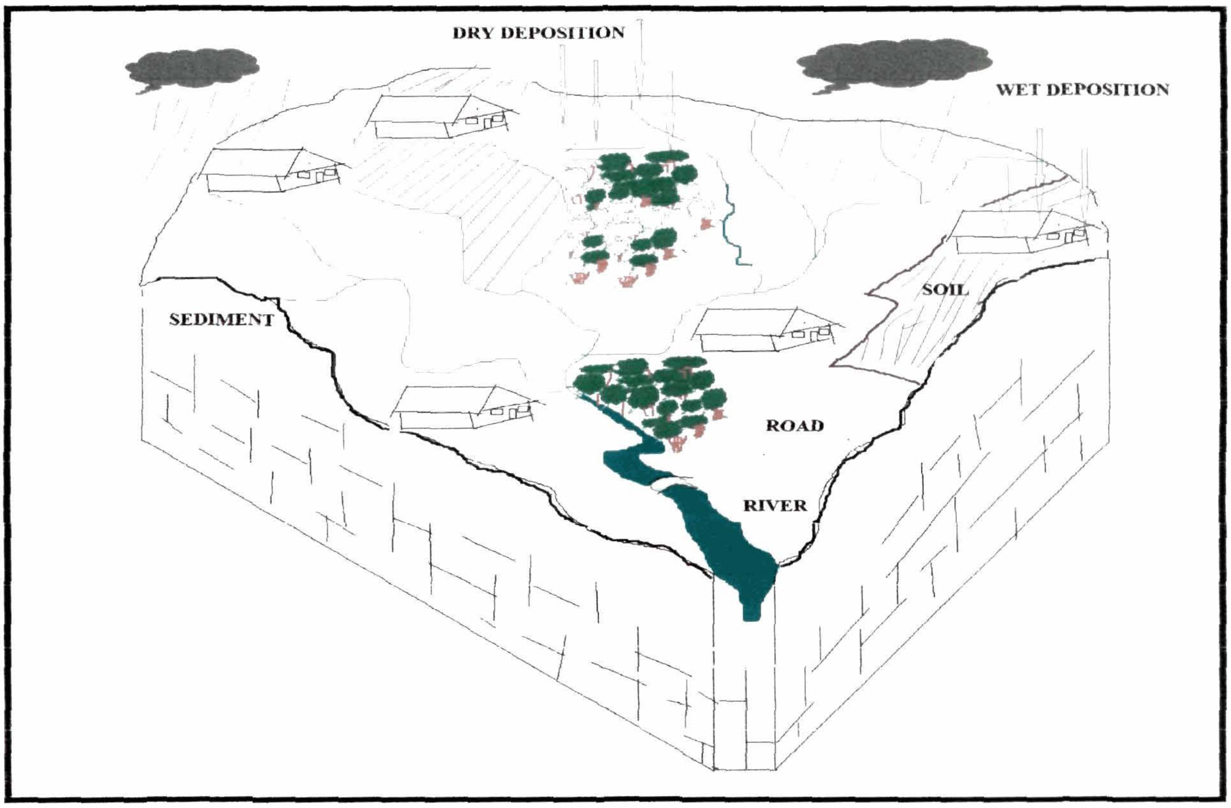


Figure 1.2: Distribution of PAHs in the environment. This diagram is a modification to that of Norville watershed in Massei et al. [63]

1.3 PAHs in the Atmosphere

It is fully established that atmospheric transfer is the principal pathways for the global distribution of PAHs [62]. Once in the atmosphere, depending on their physical and chemical properties such as vapour pressure, Henry's law constant and solubility, PAHs get distributed between gas, particle and droplet phase [69-72]. At ambient temperature, the 2 and 3-ring PAHs are mainly found in the vapour phase, while 4 to 6 PAHs occur in the particle phase as recorded in the literature [73-76]. Oxidative and photolytic reactions and atmospheric fallouts are two major pathways for wash-out mechanism of PAHs from the atmosphere [77-78]. According to Bidleman et al. [70], PAHs associated with both vapour and particle phase are removed from the atmosphere by atmospheric bulk (dry+wet) deposition. Deposition of PAHs is also influenced by particle phase concentration and meteorological factors [79]. Extensive studies have been carried out to explore relationship between meteorological parameters and PAH concentrations. Significant relationship of PAHs with temperature and relative humidity were also documented by Pankow et al. [51] and Chetwittayachan et al. [80]. Moreover, temperature variation found to have more influence on gas phase LMW PAHs dispersion than on particulate phase HMWPAHs [81].

1.3.1 Gas to Particle Distribution of PAHs in the Atmosphere

PAHs in the atmosphere occur both in vapour and particulate phase of mainly the fine fraction (<1 μm) because of their semi-volatile property [82, 83]. This phase partitioning plays an important role in fate and distribution of PAHs in the environment. While cycling through various matrices of the environment, gaseous exchanges take place at various surfaces such as sea, vegetation, soil etc [84-86]. Gas/particle partitioning of semivolatile organic pollutants both in urban and rural atmosphere allow us to understand various aspects such as their partition and subsequent influence on health-effect [51], their removal by dry and wet deposition from an airshed [87-91], formation of secondary pollutants by photolysis [92] and their removal by advection [91].

Gas/particle partition of PAHs is controlled by the molecular weight of the compounds, temperature, humidity and precipitation [93, 94]. In general, low-volatile PAHs with > 5 rings undergo relatively high temperature condensation and are mostly adsorbed to airborne particles [94, 95]. Moreover, they are categorised as “single-hop” persistent organic pollutants (POPs) due to their low mobility and they are subjected to rapid deposition and retention close to the source [95-97]. On the other hand, the LMW PAHs with 2-3 rings are are characterised by low temperature condensation and exist mostly in the gas phase [93-95, 98-99]. This group of PAHs are classified as “multi-hop” chemicals due to their high or moderately high mobility [95]. Therefore, LMW PAHs experience world-wide atmospheric distribution and preferentially accumulate in polar latitudes [94, 95]. Semi-volatile (4-ring) PAHs can occur both in particle and gas phase and are most influenced by of environmental factors [93]. They are mostly found to be settled and enriched in mid latitudes [95].

Individual PAH compounds behave differentially under different meteorological and climatic conditions depending upon their molecular weight and structure. Meteorological parameters, especially, temperature and relative humidity play a significant role in dissipation of LMW PAHs [51, 100]. Vapour pressure controlling volatilization have been found to be regulated by temperature, humidity and wind speed. With increase of temperature, volatilization of PAHs from soil, atmospheric particles, water and vegetation increases [101, 81]. Thibodeaux et al. [102] reported an increase in absorption of semivolatile organic compounds as relative humidity approaches 100%. Such increase at very high relative humidity is due to partitioning into the liquid or nearly-liquid water when the gas phase is nearly saturated with water.

1.3.2 Air Water Gas Exchange of PAHs

Air-water transfer processes for PAHs consists of volatilization and absorption of gases, dry deposition with particles, wet deposition by rain or snow, i.e., particle and gas "washout", spray transfer, and bubble scavenging [103].

Air-water transfer is controlled by Henry's law, according to which the concentration of PAHs in water is proportional to the partial pressure of PAHs in air

$$p_a = H_a X_w$$

where p_a is the partial pressure in air, H_a is Henry's constant (both in pressure units), and X_w is the mole fraction in water. The lower is the Henry's constant it is more likely that PAHs will partition from air to water [104].

1.4 Atmospheric Pollutant Removal Processes

Anthropogenic activities are primarily accountable for release of chemical pollutants into the environment. If all the pollutants remain in various environmental compartments as it is, their ambient levels should equal to the aggregate amounts released. However, this is not the case in general, as each environmental compartment in nature has some active naturally occurring removal or "self-purification" processes [105].

PAHs distributed between trace gases and particles are subjected to removal mechanism such as oxidative and photolytic reactions and ultimately from the atmosphere by two pathways namely wet and dry deposition [77].

Dry deposition refers to transport of pollutants from the atmosphere in the absence of precipitations onto surfaces. On the other hand, wet deposition is scavenging processes by which pollutants are encapsulated by hydrometeors and consequently dropped to the Earth's surface [106].

Once released airborne PAHs are carried by the prevailing meteorology before being removed from the atmosphere by different scavenging processes. Wet deposition such as rain, sleet, snow, hail and dry deposition are considered as the major mechanisms of removal of PAHs from the atmosphere. The wet removal mechanism of gaseous PAHs is better understood than particulate PAHs [88]. The scavenging mechanism through in-cloud or below cloud, collection efficiency of falling precipitation, solubility and size particles has been well explored in literature [107, 108].

Non reactive gaseous organic compounds are washed out by rain according to the Henry's Law equilibrium between the gas and aqueous phases [88]. According to Pankow et al. [87], the total degree of scavenging of a given compound when there is no exchange of material between the particulate and dissolved phases in the rain can be expressed as follows:

$$W = W_g(1-\phi) + W_p\,\phi$$

Where W is the overall scavenging ratio:

$$W = [\text{rain, total}] / [\text{air, total}]$$

W_g is the gas scavenging ratio:

$$W_g = [\text{rain,dissolved}] / [\text{air, gas}]$$

W_p is the particle scavenging ratio:

$$W_p = [\text{rain, particulate}] / [\text{air, particulate}]$$

and ϕ is the fraction of the atmospheric concentration which is associated with particles. For compounds which (1) are scavenged to some degree from the atmospheric particulate phase; and (2) remain on particulate material inside the raindrop, W will differ from the equilibrium W_p value. The second state become necessary as material which is moved to the dissolved phase will undergo rapid reequilibriation with the atmosphere.

Dry deposition is a function of prevailing atmospheric state and the surface level concentration of PAHs. PAHs adsorbed particle size greater than 20 μm are susceptible to settle in the vicinity of the source due to their high settling velocity. However, only minor percentage of PAHs removal occurs through this mechanism as PAH are predominantly adsorbed on particles diameter of <10 μm [109].

An illustration of sources, transport, and deposition of pollutants via the atmosphere is shown in Figure 1.3.

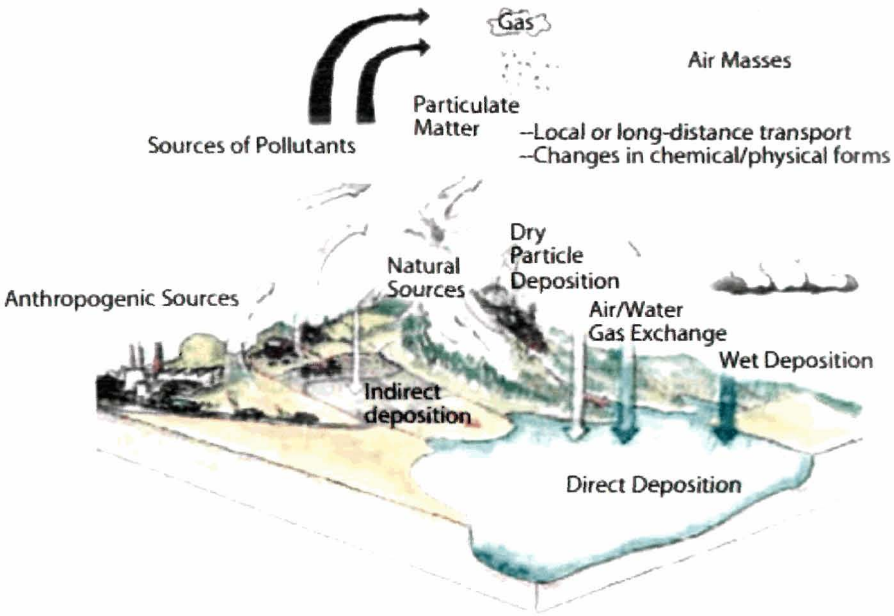


Figure 1.3: Diagram of the sources, transport, and deposition of pollutants via the atmosphere (US EPA 2002).

1.5 Bulk Deposition of PAHs

Broadly, the atmospheric deposition can be divided into wet and dry deposition [110-112]. The overall flux for both the mechanisms is contributed by processes such as scavenging of vapour and particles, particle sedimentation, and surface gas absorption. It is needed to measure both dry and wet deposition to determine the total atmospheric deposition of PAHs [113]. Bulk samplers record the grand total of all the atmospheric removal processes as they do not differentiate between the two [72].

The atmospheric bulk deposition of individual PAHs are influenced by various parameters, such as the compound's Henry's law constant and vapour pressure, the particle size distribution, the gas/particle partitioning, meteorological conditions and the size of raindrops [114, 78]. Thus, the dispersion of PAHs in the environment is controlled by their physical and chemical properties as well as by climatic conditions [115].

Generally, dry air PAHs that do not get transported far from emission sources and so they have short life of few to ten hours [116, 113]. On the other hand, the aqueous phase PAHs have life time of approximately ten to hundreds hours [116]. In-cloud and below-cloud scavenging of particulate and gas phase PAHs travel over long distances. Thus dry deposition preponderates in urban/industrial areas while wet deposition in remote areas [117, 113]. Consequently, in order to evaluate deposition loadings due to atmospheric deposition, it appears inevitable to include both dry and wet depositions [118].

During the past few decades, PAH in bulk deposition (dry + wet) have been widely studied [77-78, 115, 118-123]. The present study is the first one taken up in South Asia.

1.5.1 Sampler Characteristics and Challenges with Bulk Deposition Measurement

To estimate PAHs deposition two methods are found to be used very often. The first method utilizes gaseous and particulate phase PAHs concentration. Here, deposition flux is determined by multiplying PAHs concentration and deposition velocity [124, 125]. However, uncertainties are found to be associated with it while estimating the deposition velocity which is controlled by parameters such as particle size, meteorological conditions, properties of the receptor surface, and physical and chemical properties of the particle [126].

In the second method, gas and particulate phase PAHs are collected passively on an artificial surface, such as metal pans, coated or uncoated glass fiber filter (GFF), plates filled fluid, greased surfaces and water surface [72, 77, 118, 127-132]. In this method, deposition flux is estimated from PAHs concentration and sampling period. Although the second method also has some artefacts such as degradation of PAHs due to atmospheric radicals, solar radiation etc., re-volatilization from collection surface and particle blow-off due to high wind speed [122, 123], yet this method is considered more accurate and so widely used compared to first one [123]

1.6 PAHs Deposition on Soil

Combustion products that are released into the atmosphere are deposited back onto the soil surface. Soil is, therefore, considered as the medium for accumulation and integration of many pollutants [99]. Soil contamination with PAHs is a growing problem mainly in urban areas due to increased consumption of energy [133]. Such increase over time is an indicator of increased emission associated with industrialization and urbanization besides emission from motor vehicles.

Emissions arising from motor vehicles are usually contributed by a mix of tailpipe emissions, wear and tear of brakes and tyres and re-suspension of street dust [134, 135]. Generally higher presence of HMWPAHs typically means contribution from combustion sources (pyrogenic) and, on the other hand, LMW PAHs are often considered to be petrogenic. Much of the combustion derived PAHs are present in top layer of soil [97] and human exposure of PAHs through soil has been reported to be greater than that of air and water [136]. Smith et al. [137] reported ≈95% PAHs burden in soil in contrast to ≈0.2% in air.

Primary input of PAHs into soil surface is by air to surface precipitation [138, 139]. Soil is, therefore, considered as one of the major sinks of atmospheric PAHs [140]. Further, volatilization, irreversible sorption, leaching, accumulation by plants and biodegradation are the possible pathways for dispersion of PAHs [141]. Soil PAHs can also be considered as a source of air and sediment contamination because of their distribution by surface runoff and dust re-suspension [142]. PAHs concentration in soil consociates well with their representative levels in air [143], house dust [144] and urban street dust [145, 146]. Soil therefore can be a good index for PAHs pollution and environmental risk [147].

Hydrophobic nature and stable chemical structure of PAHs favour adsorption onto soil particles, thus PAHs can sustain in soil matrix for longer time [148, 149]. Thus, PAHs are persistent and poorly degraded contaminants of the soil. PAHs concentration is significantly regulated by soil organic carbon (OC) content [147]. Higher level of soil organic matter could make PAHs become more resistant to degradation [150].

Black carbon (BC) is also considered to play a major role in distribution of PAHs in soil due to their co-emission and high sorption capacity for PAHs [151, 152]. BC is recognized as strong adsorbent for hydrophobic organic compounds. This adsorption also reduces toxicity and biodegradability of organic contaminants in soil [153]. Thus the fate and behaviour of contaminants are the principal factors to their risk assessment and remediation [154].

1.7 PAHs Deposition on Street Dust

Street dust is chemically most identical to the principal portion of atmospheric aerosol and exhibit a vital relationship through continuous process of re-suspension into and re-deposition from atmosphere [138]. Rapid urbanization triggering transport of increasing population and goods by large number of motor vehicles have given rise to intensifying levels of pollution along roadways [155]. Traffic density and rate of deposition are assumed to be the main determining factor for PAHs concentration in street dust [156-158].

Street dust is often considered as the direct sink of deposited PAHs near to sources mainly from traffic. It is very much reasonable that closer to the highway faster deposition of exhaust aerosol droplets occurs; while going away dust particles that are dispersed with wind interfered their adsorption [159] and subsequently affect other environmental matrices (e.g. air, water, soil and plants) [160]. This in turn increases significant exposure risk for human population [161] mainly for those who live by roadside. Although atmospheric removal of anthropogenic and biogenic sources of PAHs contribute to street dust load [162], part of street dust PAHs may transfer back to atmosphere through the mechanism of evaporation and wind raise [163]. PAHs are easily washed out from street dust by rain to drainage and then move to nearby water bodies such as river, estuaries etc. [164, 165]. More than 95% contribution fraction of PAHs from dry deposition was could be found on street dust [162] and motor vehicles account for a significant aid to total PAHs load in street dust.

PAHs in urban street dust are originated from multiple sources such as weathered materials of road surfaces, automobile exhaust, lubricating oils, gasoline, diesel fuel, tire particles, construction materials and atmospherically deposited materials [166].

Moreover, street dust is a major source for many heavy metals resulting mainly from wear and tear of vehicles. The high concentration of heavy metals causes deleterious effects on various terrestrial creatures and human beings (including internal body organ damage) [167-171]. Therefore, greater oxidative damage resulting from occupational co-exposure to PAH and metals [172] may increase the carcinogenic potential of this group of compounds. Therefore, simultaneous characterization of PAHs and metals in street dust would be the better way of understanding the health risks involved. Also, the use of both organic and inorganic tracers in the source apportionment studies is found to improve source resolution [173].

1.7 PAHs Deposition on Water and Sediment

Surface water and sediment consists important information regarding anthropogenic activities adjacent to a water body. Primary pathways of PAHs entering aquatic environments include direct wet or dry deposition from atmosphere, runoff from land, roads, pavements, roofs, guttering and industries [174, 175] and direct water outlet [58]. In general anthropogenic sources of PAH's in aquatic environment can be both pyrogenic and petrogenic. Pyrogenic sources of PAHs include combustion of organic matter like petroleum fuel, coal and biomass. Petrogenic PAHs (from crude and refined petroleum products) can enter aquatic environments through accidental oil spills, municipality and urban runoff and industrial processes. Stormwater is a major delivery route of PAHs to the receiving water bodies irrespective of types of sources of PAHs in urban areas. Therefore, to address effective control and remediation of these pollutants their source and sink have to comprehend well [176].

In urban soils non-homogenous distributions of PAHs is observed [177]. Upon entering aquatic systems, PAHs preferably tend to settle, partition or adsorb onto non-aqueous phase such as soil or sediment due to their hydrophobicity [178] and high octanol/water partition coefficients. Adsorption to solid particles makes them less susceptible to degradation [179]. So, the presence of PAHs in water system of a river can also be used as an indicator of their presence in sediment.

Due to their mutagenic and carcinogenic effects to land and water organisms [180], distribution and sources of PAHs in aquatic environment near urban centres have received much attention. The Water Framework directive 2000/60/EC considered 16 PAHs as priority substances due to their environmental behaviour and their toxic effects. High toxicity, high stability in the environment and lipophilic nature of PAHs enable them to transport through food chains with human being as final destination [7, 181-182]. The EU Directive 98/83/EC, relevant to drinking water, has set a limit of 0.10 μgl^{-1} for the sum concentration of BbF, BkF, BgP and IP and 0.010 μgl^{-1} for BaP [183]. Thus, monitoring of these compounds in surface water can provide inputs for potential toxic effect assessment of these pollutants in addition to decision-making for management authorities [184].

1.9 Organic Molecules as Tracers

Organic molecular tracers are discrete quantifiable organic compounds that are exhausted from single source or group of sources. Classes of such molecular tracer compounds include alkanes, cycloalkanes, PAHs, steranes, fatty acids, sterols and methoxyphenols. Preferably, these tracer molecules are expected to originate from one distinct source type. However, in reality they can originate from multiple sources with different time-dependent source contribution. For a wide range of natural and anthropogenic sources (e.g., traffic, biomass burning, food cooking), characteristic unique molecular marker has already been identified [185].

To identify sources of PAH, parent PAH ratios have been extensively used [186-193]. Understanding of the respective discrimination ability (relative thermodynamic stability) of individual parent PAHs, the attributes of different PAH sources and the variation in PAH composition between source and sink (the relative stability of various PAH isomers and PAHs from separate sources) are essential requirement while using parent PAH ratios for source apportionment in various environmental matrices [193]. Computation of PAHs ratio are usually confined to PAHs within a given molecular mass in order to reduce various contradicting factors such as differences in volatility, water solubility, adsorption, etc. [194, 195]. For parent PAHs, it is inferred that combustion and/or anthropogenic input is from an increase in the part of the less stable, "kinetic" PAH isomers compare to the more stable, "thermodynamic" isomers [196] and to support such interpretation the stability of the lighter PAH isomers has been computed [190] Thus, the use of these indices depend on the fact that PAHs dispersion is regulated by thermodynamic properties during low temperature processes and by kinetic characteristics during high temperature processes, such as pyrolysis of organic matter [197]. As Phenanthrene is thermochemically more stable than anthracene, molar fraction of phenanthrene produced is much higher than that of anthracene at low temperature. On the other hand, high temperature combustion such as incomplete burning of organic matter is characterized by low value of Phe/Ant ratio [198].

As shown in Table 1.3, extensive studies have established and prescribe a specific value of PAH diagnostic ratio for a particular source category. Ravindra et al. [199, 200] used IP/(IP+BgP) ratio for diesel and coal combustion, whereas Kavouras et al. [201] established diesel emission ratio of IP/(IP+BgP) to be between 0.35 and 0.70 (Table 1.3). Thus, based on only one proposed diagnostic ratio, it would be challenging to discriminate diesel emission from coal combustion. Source identification can be upgraded by using various other ratios with their relative comparison [202]. However, use of multiple ratios (more than two) for potential source identification can also lead to ambiguous interpretation [120].

Table 1.3 PAHs diagnostic ratio for source apportionment

Diagnostic Ratio	Value	Sources	References
IP/(IP+BgP)	0.18	Cars	Grimmer et al. [203]
	0.37	Diesel	Ravindra et al. [199]
	0.56	Coal	Ravindra et al. [200]
	0.62	Wood burning	Kavouras et al. [201]
	0.35-0.70	Diesel Emission	Kavouras et al. [201]
Flu/(Flu+Pyr)	>0.5	Diesel	Rogge et al. [204, 205]
	<0.5	Gasoline	Mandalakis et al. [206] Fang et al. [207] Ravindra et al. [199, 200]
BaP/(BaP+Chry)	0.5	Diesel	Khalili et al. [208]
	0.73	Gasoline	Guo et al. [209]
Flu/Pyr	>1	Pyrolytic	Baumard et al. [198]
	<1	Petrogenic	
Phen/Anth	<10	Pyrolytic	Baumard et al. [198]
	>15	Petrogenic	
Phen/(Phen+Anth)	>0.7	Fossil fuels	Kauvoras et al. [210]
	<0.7	Biomass burning	
Anth/(Anth+Phen)	>0.1	Pyrolytic	Yunker et al. [193]
	<0.1	Petrogenic	
Flan/(Flan+Pyr)	>0.5	Pyrolytic	Yunker et al. [193]
	<0.5	Petrogenic	
Naph/Phen	<<1	Petrogenic	Dahle et al. [211]
BbF/BkF	>0.5	Diesel	Pandey et al. [212]
BaP/BgP	0.5-0.6	Traffic	Park et al. [213]

		emission	
	1.25	Cattle manure	Pandey et al. [214]
IP/BgP	<0.4	Gasoline	Caricchia et al. [215]
Pyr/BaP	~10	Diesel engine	Oda et al. [216]
	~1	Gasoline engine	Oda et al. [216]
Flan/Pyr	0.6	Vehicular	Neilson [217]
LMW/HMW	Low	Pyrolytic	
	High	Petrogenic	
CPAHs[a]/∑PAHs	~1	Combustion	Prahl et al. [218] Takada et al. [145] Mantis et al. [219] Ravindra et al. [200, 220] Gogou et al. [221]

[a] CPAHs=fluorene + pyrene + benz[a]anthracene +chrysene + benzo[b]fluoranthene + benzo[k]fluoranthene + benzo[a]pyrene + indeno[123-cd]pyrene and benzo[ghi]perylene

1.10 Objectives

The research problem undertaken here is primarily focussed to understand the distribution and source-sink relationship of PAHs among various environmental matrices including atmosphere, soil, street dust, river water and sediment. They are associated to each other through a range of mechanisms such as pollutant build up in the atmosphere, atmospheric deposition on various other environmental matrices, pollutants build up in different environmental compartments and pollutant wash-off from one to another environmental compartment. This indicates the significance of the research to assess atmospheric bulk deposition of PAHs regulated by various meteorological parameters and its influence on other environmental matrices. Regarding this the important mechanisms which required to be addressed are atmospheric PAHs bulk deposition, PAHs build up directly in different environmental matrices and transfer of PAHs among the matrices. The research study thus promotes a vigorous approach to foresee the influence of atmospheric bulk deposition on other environmental matrices. Taking this into consideration, this study has the following objectives:

1) To ascertain the seasonal variability in the concentrations of 16 priority PAHs in atmospheric bulk deposition.
2) Source apportionment of PAHs in different matrices using marker compounds.
3) To study relationship of PAHs with carbon and some heavy metals
4) To establish association of PAHs signatures in bulk deposition to PAHs signatures in soil, street dust, river water and sediment.

1.11 Research Hypothesis

1. Atmospheric deposition is the major contributor of PAHs in soil, road dust, surface water and sediment.
2. Atmospheric bulk (wet+dry) deposition is influenced by various meteorological parameters such as temperature, relative humidity etc.
3. BC, OC and heavy metals play an important role in PAHs distribution in the environment.

1.12 Scope

The research study primarily focused on establishing an extensive approach to assess atmospheric bulk deposition of PAHs regulated by various meteorological parameters and its influence on other environmental matrices. The scopes of the research study were:

1. The research focused on PAHs generated by various land use related activity in the selected urban study sites of Guwahati, a major city of Brahmaputra valley.

2. The research addressed processes namely atmospheric PAHs bulk deposition, PAHs build up directly in different environmental matrices and transfer of PAHs among the matrices.
3. Sample analysis mainly focused on PAHs, heavy metals, BC and OC.
4. Possible spatial and temporal variations including seasonality were taken into consideration.
5. PAH marker compounds were adopted for source identification
6. Statistical model - PCA-MLR was used for computation of source identification and respective contribution of each source.
7. Variations of PAHs source signature as a function of seasonal variations was also determined.

1.13 Innovation and Contribution to Knowledge

Understanding the mechanism and pathways of PAHs dispersion in an urban environment play a vital role in mitigating pollution. Mathematical models can also be developed from such studies to project PAHs loading, their removal mechanism and exposure risk assessment for health effect in an urban settlement with varying land use scenario.

Relevant outcomes of this research study are

1. The contribution of atmospheric bulk deposition PAHs to other environmental matrices and how they are interlinked with each other.
2. How meteorological parameter govern the process of atmospheric PAHs removal.

Chapter 2

Review of Literature

Chapter2: Review of Literature

2.1 Worldwide Scenario of PAHs

2.1.1 Atmospheric Deposition of PAHs in all Environmental Matrices Worldwide

PAHs have been extensively studied. For most of the developed countries, background levels of PAHs are available. Researchers from different parts of the world have reported several studies on atmospheric deposition of PAHs for last three to four decades.

Among earlier studies, Lunde et al. [221] performed study on organic micro pollutants in precipitation in Norway. Snow and rain samples were collected and analyzed for 4 chemical groups namely alkanes, polycyclic aromatic hydrocarbons, phthalic acid esters and fatty acid ethylesters. Both particle adsorbed and water dissolved phase organic components were fractionated for analysis. They reported presence of alkanes and PAHs in precipitation samples and considered fossil fuel to contribute these organic micro pollutants in precipitation.

Noort et al. [222] determined the temporal variation of PAHs concentration in rain during three precipitation events. The rain samples were collected simultaneously at ground level and at an altitude of 200m. The concentration of Phen and Flan was remarkably higher in former than that of later as reported in the study. The presence of Phen was considered to be result of below-cloud gas-phase scavenging. The range of studied PAHs was BDL to110 ng/l.

To estimate PAHs fluxes [223] within the Lake Michigan basin to coastal waters adjacent to the Chicago urban area and found that dry deposition loading for PAHs were three times higher than that of wet deposition.

Polkowska et al. [6] estimated PAHs in atmospheric precipitation including rain and snow in Poland. Phen, Flan and Pyr were the dominant PAHs in precipitation samples. Seasonal attributes were recognised in both rain and snow with maximum PAHs concentrations during winter which was attributed by them to be primarily from residential heating. Another significant PAHs source was identified as traffic emission by them.

Bulk deposition and gas exchange of PAHs were estimated in the Galveston Bay, Texas by Park et al. [224] and reported atmospheric PAHs in vapour phase and in the rain dissolved phases. They had found Phen and Naph to be the dominant individual PAHs in air vapour and rain dissolved phases. Particulate phase of both air and rain samples were found to be dominanted by 5and 6-ring PAHs. Moreover, air to surface water gas exchange was recognized as principal deposition process for PAHs compare to wet deposition. Combustion and petroleum deposition were identified as major sources of PAHs in the studied area. Levels of PAHs in bulk (wet and dry) precipitation were conducted by Manoli et al. [78] in the main plain of central Macedonia in Northern Greece. They observed maximum PAHs concentration during cold months. For deposition flux, the greatest values were revealed during large precipitation events coinciding with high PAHs concentrations. PAHs in bulk deposition were found to influence that of surface water as their signatures showed strong association.

In an urban region of Poland, Grynkiewicz et al. [119] estimated 16 PAHs in bulk precipitation (dissolved in water and adsorbed on solid particles) in which compounds were recovered using solid phase extraction method and analysed in GC-MS. In this study Naph, Phen+Anth, Flan and Pyr were found to be dominant compounds with high concentration values. On the other hand, trace level of Acy, Acen, Flu, BbF+BkF, IP, BaA and BgP were also reported. High PAHs concentration in winter samples and major contribution of coal fed heating to average PAHs load was observed. Vehicular traffic was identified to be a major source of total PAHs in precipitation.

Similar method of PAHs estimation was adopted by Golomb et al. [113] while determining wet and dry deposition of PAHs near New England coastal water. In this study wet (rain and snow) samples were received into a shielded, temperature controlled collecting bottle and an exposed water surface was used as a collector for gaseous and particulate dry PAHs deposits. High wet and dry deposition was observed during heating season. It was also reported that precipitation during non-convective events brought more wet deposition of PAHs than convective events. In this study chemical mass balance (CMB) model was used for apportionment of sources and identified diesel and gasoline fuelled vehicle and wood burning as major sources of PAHs.

Seasonal variation of PAHs in atmospheric precipitation in a rural site of Lake Balaton, Hungary was examined.[225] and higher level of 3-6 ring PAHs was observed during the winter (3-350ng/l) than during the summer (1-54ng/l) with highest wet deposition rate of 412 $\mu gm^{-2}year^{-1}$. The most abundant compounds in snow samples reported by the group were Phen, Flan and Pyr.

Atmospheric bulk deposition PAHs was also studied by Ollivon et al. [118] during 1999-2000 in Paris, France. High abundance of Flan and Pyr was observed in bulk deposition samples by them. Vivid seasonal variation was observed with the highest concentration during winter. Temperature was found to play an important role in scavenging of LMWPAHs. The heating contributed 41% to the overall annual PAH load. In other study Montelay-Massei et al. [115] estimated PAHs in bulk deposition during 2001-2002 on weekly basis at Evereux, West of Paris (France). Similar trends were reported and dominant Phen, Flan and Pyr were the species contributing 69% of total PAHs. Moreover, LMW PAHs were found to correlate well with high rainfall. Principal Component Analysis (PCA) was used to identify meteorological influence as well as seasonal variability in that study.

Bulk deposition of PAHs at remote, rural village and an urban area of Beijing-Tianjin, North China were studied during 2007-2008 [123]. High deposition flux of Phen (35.3%) and Flan (25.7%) were observed. Highest deposition during fall was estimated which indicate high exposure risk during this season in that season. Spatially, urban areas (8.28$\mu g/m^2/day$) received high deposition flux than that of rural ones (3.91 $\mu g/m^2/day$).

PAHs flux in various environmental compartments viz. ambient air, atmospheric deposition, soils, sediments, runoff and surface waters was monitored in Seine estuary, France to identify the major pathways of transport and accumulation through a mass balance model. Transport of PAHs from the atmosphere to watershed outlet was *investigated for two rural and urban experimental watersheds within the Seine Estuary.* High loading for atmospheric input of PAHs was observed in rural areas relative to urban areas, where atmospheric loading was found to be negligible [63].

Yan et al. [226] conducted a large-scale survey on distribution and deposition flux of PAHs in rainwater samples in Shanghai, China and reported annual deposition flux of PAHs was found to be 4148 kg/yr in collected samples. Naph, Phen, Anth and

Flan were revealed as the most dominant PAHs in rainwater. Along with diagnostic ratios together with back trajectory analysis was also performed by them to identify the pollutant sources. Combustion of grass, wood and coal were suggested to be major contributors of PAHs in that study. Air mass from Southern part of China was observed to enrich PAHs in Shanghai.

2.1.2 PAHs in Soil

Study of PAHs in soil has been performed extensively from various part of the globe. Some Researchers also tried to estimate atmospheric signature in soil and vice-versa.

Aamot et al. [227] investigated levels of nine selected PAHs in surface soils from southern and central Norway. Concentration in southern Norway was observed to be higher than that of central Norway in general; which was approximately ten times higher in case of 4 and 5-ring PAHs. Atmospheric transport was found as major contributor source of PAHs in soil after comparing with air quality data in south Norway. Atmospheric signature in soil was confirmed with the analysis of peat cores from ombrotrophic bogs, which is considered as a potential approach to assess temporal variation of atmospheric PAH deposition. Naphthalene concentration in soil was found to be very high compared to many other studies. Similar study was carried out in seven locations across the Seine River basin, France was estimated by Montelay-Massei et al. [228]. They observed distinct spatial variation with concentration industrial and urban areas to be in order of magnitude higher than those at the remote areas. High percentage contributions of carcinogenic PAHs (approximately 40%) were reported. This study also highlights the potential use of soil sampling to estimate spatial differences in atmospheric inputs of PAHs based on differences in regional and local atmospheric emissions.

Association of PAH with total organic carbon (TOC) was observed for Norwegian soil samples [229]. In UK-woodland soil HMWPAHs found to be correlated with black carbon (BC) which was considered as PAHs from combustion source. Four and more ring PAHs were found to be dominant in the UK soil than that of Norwegian soil. The PAHs profile was regarded as indicator of fractionation that occurred during long-range atmospheric transport and deposition. Thus the LMWPAHs with lower K_{ow} values were found to be more susceptible to reach the most remote sites, whereas the HMWPAHs with higher K_{ow} values retained near to emission sources.

Spatial distribution and sources of PAHs in soil of Valasske Mezirici was investigated by Plachá et al. [230]. PAHs concentration in urban, agriculture and forest soil were analysed and found to be maximum at high altitude forest soil. The maximum PAH level was found to be higher than that of the forest soil in Western and Northern Europe. Meteorological condition with frequent calm condition associated with inversion state was considered as major contributing factor for such high PAH concentration at the high altitude forest. Industrial processes, transport and local heating activities were identified as significant source of PAHs in soil.

Wang et al. [231] reported air–soil gas exchange flux in Beijing–Tianjin region, North China with annual median PAHs flux of 42.2 ng/m^2/day from soil to air. Acy and Acen were observed as major contributor in total exchange flux. The air–soil gas exchange fluxes of PAHs were higher at the urban sites than those at the remote and rural sites. Seasonal variation also found to affect the mechanism with more gaseous PAHs volatilized from soil to air in summer with rise of temperature and increased rainfall. However, more gaseous PAHs were recognised to be deposited from atmosphere to soil during winter because of higher PAH emissions and lower temperature. The air–soil gas exchange of PAHs was not found to be influenced by TOC concentration.

2.1.3 PAHs in Street Dust

As compared to air and soil, street dusts have been a newer matrix in terms of studies relative with PAHs.

Among the earlier studies Takada et al. [145] reported molecular distributions of PAHs in street dust samples in Tokyo. Level of total PAHs concentration was found to be a few micrograms per gram of dust. Individually, 3- and 4-ring PAHs such as Phen, Flan and Pyr were recognised as dominant ones in the street dust. It was observed that automobile exhausts were the major source of PAHs in streets with high traffic density, whereas in residential area stationary sources of heating were identified as significant source. Pengchai et al. [232] also studied PAHs profile in urban road dust in Tokyo. This study mainly aimed to explore source identification of PAHs in road dust using cluster analysis combined with PCA. Seven categories of PAHs sources were recognised including diesel and gasoline vehicle exhaust, vehicle exhaust, tire, asphalt or bitumen, asphalt-pavement, petroleum products and the combustion products except for those in vehicle engines.

Seasonal variation in street dust was reported by Netto et al. [233] in the center of Niteroi, a tropical city located in the State of Rio de Janeiro, Brazil, at the margins of Guanabara Bay. The maximum PAH concentrations were found in the month of July when the temperature was minimum. Individually, maximum geometric mean was detected in case of Pyr, Flan and Naph. Carcinogenic PAHs contribution was found to vary from 29 to 45%. PAHs showed significant correlations with daily mean and minimum temperature, as well as the overall temperature during sampling period. This indicate that meteorological parameter mainly temperature play an important role in PAHs distribution in street dust.

Liu et al. [234] perfoemed study of PAHs in road dust samples collected from central Shanghai during winter and summer. Seasonal variation was reported with higher level of total PAHs during winter than that of summer. Moreover, spatial variation was observed with high concentration levels at industrial site, traffic site and commercial sites during both the seasons. HMWPAHs were found to be dominated in all areas. Mix source of traffic and coal combustion was identified for road dust PAHs using PCA. Pyrogenic and petrogenic source contribution were 71.0% and 11.4% respectively during winter, while 64.9% and 14.1% respectively during summer.

Samimi et al. [160] investigated PAHs contamination level in the form of settle dust in different types of samples including street dust, soil and water of a western highway in Tehran, Iran. Very high PAHs contamination was observed in the vicinity of the highway. Naph and phen were found as most common individual PAH in all the samples. The presence of these compounds was an indication of emission from incomplete combustion of vehicular fuels and their subsequent adsorption to atmospheric suspended particles which were finally settled in surface of street dust, soil and water near to highway.

2.1.4 PAHs in River Water and Sediment

PAHs behave in a very complex manner in aquatic environment. More so, natural water bodies often act as sink of PAHs from both atmosphere and terrestrial runoff. Biological risk is also directly associated with aquatic environment. All these facts usher researchers to get more interest in aquatic environment.

Smith et al. [235] measured PAHs in waters from three rivers which flow through the largest cities in south-eastern Australia. Smaller ring compounds were found to be more abundant with higher concentration than the larger ring ones in that study.

Skrbić et al. [236] estimated PAHs in the surface soil samples of Novi Sad city and bank sediment of Danube covering entire city and found that total PAHs content in bank sediments were higher than that of surface soil. Overall percentage contribution of BaP was found to be 6-14% of the total PAHs. The total carcinogenic potency for most of the sites was observed to be on higher side than recommended levels.

Spatial distribution of PAHs in surface water, suspended particulate matter (SPM) and sediment of Daliao River watershed composed of the Hun River, Taizi River, and Daliao River was investigated by Guo et al. [237]. Both diagnostic ratio and PCA was employed for source identification. Composition of PAHs was found to be dominated by 4-6 ring PAHs in the entire three medium. High occurrence of LMWPAH in water and SPM was recommended for recent local source and atmospheric deposition. High pollution load in water and sediment near industrial area indicated input from industrial wastewater.

To assess potential risk of PAHs from street dust to urban streams reflecting source-sink mechanism through stromwater Hongtao et al. [238] assessed PAHs in street dust particles and river sediments (Yangtze River Delta) in Xincheng, China. In street dust smaller particles found to have higher concentration. The sediments of the urban stream reaches in town were found to act as sinks for street dust PAHs. More so, total loads of PAHs in receiving water bodies is found to influenced by factors including particle size, land use and the hydrological conditions in the stream network as recommended by many researchers.

Major inputs and sources of PAHs into surface water, stream and precipitation along the Sacramento River, California was investigated by Kim and Young [239]. Concentration of total PAHs was found to be higher in surface water than precipitation, however, dissoved PAHs content in both the matrix was observed to be almost similar. Individually Naph, Phen, Pyr and BgP were identified as most dominant compounds in both surface water and rain. In dissolved phase more than 4-ring PAH compounds were rarely occurred. During wet season significant input of PAHs in surface water was observed through indirect deposition (i.e., washoff of atmospheric particles previously deposited to land) in California's Mediterranean climate. During wintertime although there was remarkable increase in aqueous PAHs level no apparent seasonal change was noticed in dissolved PAHs concentrations. Marker PAH ratios suggested pyrogenic origin of rainwater PAHs whereas complex and variable origin of PAHs were recognised in case of surface water.

Li et al. [240] investigated PAHs in soil, water, sediment, and plant samples collected from Aojiang River and its estuary. The concentration of PAHs in soil, water, sediment and plant were found to be relatively high while considering the population size of the area. Petrogenic sources were identified in sediment using diagnostic ratio. The composition profile of PAHs in soil and sediment was found to be similar with dominance of 4–6 ring PAHs.

Chemical analysis and biotoxicity was assessed by Fu et al. [241] to estimate the distribution, source, ecological risk and ecotoxicity of PAHs in sediments of Huaihe River. Diagnostic ratio revealed mainly pyrogenic origin of PAHs in the river sediment. Some of the individual PAHs were found to pose occasional biological risk, however no sample was identified for frequent biological impairment. However, some of the sites were observed with very high carcinogenic potential value.

Levels, dispersion patterns, seasonal variation, and sources of PAHs in Hun River of Liaoning Province, China was conducted by Zhang et al. [242]. The total PAHs concentrations were prominently elevated periodically in the order of level period > flood period > dry period. Dominance of LMWPAHs was noticed particularly for 2-3-ring PAHs. Predominance of LMWPAHs with high concentration during flood period was considered as relatively recent local source of PAHs. Selected PAHs ratio was used for source identification which indicated petrogenic origin of PAHs during dry season, while mixed pyrogenic and petrogenic source during wet season. After comparing contamination level of PAH among different types of area it was prescribed that atmospheric deposition was the most important mechanism of PAHs entry into water system.

2.2 Indian Scenario of PAHs

While in many European countries studies on environmental PAHs initiated in the 1960s, most of the studies, on the similar lines, in India started in the early 1980s only. The preliminary studies were taken up with the cancer indicator BaP. The carcinogenic risks of BaP to people were studied in cities like Bombay (now Mumbai) and Ahmedabad. Later, with time, several groups from many parts of India started to study PAHs in various matrices including soil, sediment, water and atmospheric particulate matter.

2.2.1 Atmospheric PAHs

In comparison to other environmental matrices - soil, sediment and water - a good number of studies have been carried out on the atmospheric levels of PAHs in India so far. However, most of these studies were from major urban centres and their adjoining suburban and rural localities. Furthermore, source apportionment studies of PAHs from both urban and rural sites are also reported by several researchers.

Increasing incidence of lung cancer among various populations worldwide led to a growing concern among researchers about environmental carcinogens. Some PAHs like BaP for long been identified as a carcinogen and PAHs being ubiquitous in the environment, there is a tremendous increase in the studies on PAHs, especially BaP, were carried out in India in the last 3 decades.

In one of the pioneering study in India, BaP levels in air of general community, near domestic fire pots in kitchen and traffic junction in Ahmedabad were reported by Aggarwal et al. [243]. This study identified high BaP concentrations in urban conditions and opined that an association between urban-rural gradient of lung cancer incidences and environmental BaP exposure could be traced for many other developing countries of Asia or Africa and, therefore, intensive studies are required to understand the relationship of BaP and lung cancer. During the same period of time and with similar analytical methods (TLC / spectrofluorometry), Mohan Rao et al. [244] reported BaP concentrations in atmospheric particulate matter of urban, suburban and rural region of Bombay and made attempts to find a possible correlation of BaP with lung cancer incidences among different populations. Wide spatial variations of BaP levels were observed by Mohan Rao et al. [244] and they opined that such variation could indicate suitability for epidemiological investigations.

Urban PAHs size distribution in gas/particle phase in Mumbai was studied and found to be regulated by both size-dependent adsorption and absorption to urban fine mode aerosols. Range of average PAHs concentration in aerosol in Indian Institute of Technology (IIT) Bombay and Regional Telecommunications Training Centre Saki Naka, Mumbai was found to be 2.1×10^{-2}-4.2×10^{-2} µg/m^3 [245]. They presented a very interesting finding on the adsorptive behavior of PAHs; predominance of non volatile PAHs in the fine mode and semi-volatile ones in the coarse mode.

Later, Kulkarni et al. [246] reported ∑PAHs concentration range of 2.45×10^{-2}-3.88×10^{-2} µg/m^3 in particulate matter of IIT, Bombay and Saki Naka, in Mumbai with a dominance of Pyr and BaP+Chry both the sites.

As concerns over PAHs grew, groups in lesser known cities like Bhilai, started assessments with respect to health risks. Pandey et al. [212] measured PAHs in the ambient air particulates in Bhilai industrial city and emphasized on the need for assessment of PAHs in the light of risk posed to human health.

Researchers at NEERI conducted a very early study from 1991-2005 to see the ambient air quality status for PAHs level of SPM and RSPM in 10 major cities of India. In this study the highest concentration range of 283.9-2113.6 µg/m^3 was found in Kolkata. Descending order of concentration range was Chennai (243.8-1481µg/m^3) then Kanpur (197.4-2397.2 µg/m^3) then Mumbai (212.8-1402 µg/m^3) and then Delhi (186.9-1597.3 µg/m^3). So this can be concluded that Kolkata is the highest polluted metropolitan city in respect of PAHs [247].

Ambient PAHs were monitored in residential and industrial area of Delhi in 1998 during winter, summer and monsoon and this study was reported in CPCB [248]. The concentration of PAHs during winter, summer and monsoon was 30.3-60.9 ngm^{-3}, 16.0-29.3 ngm^{-3} and 9.4-27.8 ngm^{-3} respectively [249]. So, maximum PAHs level was observed in winter.

A pilot study was carried out to examine the PAHs profile in PM$_{10}$ in a residential site in New Delhi. The reported value in this study was also found to be comparable with that of TEERI [250] and also inferred that local source signatures are needed to get a complete picture of organic fractions of urban aerosols [251].

Simultaneous rain and air sampling was performed for thirteen rain event in Trombay, Mumbai during monsoon season in 2001. This study observed that with the increase of molecular weight the gas phase scavenging ratio of PAH also increased and for volatile PAHs the particle phase scavenging ratio values were found to be higher [252].

Suspended particulate matter samples were collected in Jawaharlal Nehru University Campus for PAHs analysis. Seasonal variation was investigated in the study and reported maximum concentration in winter and minimum during monsoon. Seasonality in source signatures was also revealed with major contribution from coal and wood combustion in winter samples. However, diesel and gasoline driven vehicles were identified as principal PAHs sources in atmospheric particulate matter throughout all seasons by using PCA [253].

Alternative fuel is the very way out for air quality improvement. Keeping this in mind Khillare et al. [254] investigated the comparative study of PAHs concentrations in PM$_{10}$ from three areas Daryaganj (DG), Moti Nagar (MN) and JNU in Delhi during Pre-CNG and Post-CNG period. This study revealed that use of alternative fuel could lead to 58-68% reduction of $\sum$PAH concentration.

Pandit et al. [255] carried out a study on PAHs in ambient air of creek area to investigate gas influx direction in air water interface. The study revealed active transfer of LMW dissolved PAHs into the atmosphere due to volatilization and deposition of HMW gas-phase PAHs into the surface water.

Levels of 3PAHs in the suspended particulate matter of an urbanised industrial site of India was monitored at two locations: the CISF building Sector 4, Bhilai, and the MPEB station at Bhilai-3, the twin city of Bhilai-Durg situated in the Mahanadi (Great River) basin of the Madhya Pradesh. Concentration range of BaA, BbF and BaP which are potentially weak and moderate carcinogens were BDL-1.56×10^{-1} µg/m3; BDL-1.28×10^{-1} µg/m^3 and BDL-1.01×10^{-1} µg/m^3 respectively in ambient air of Gwalior city, Madhya Pradesh (covering all Industrial, Commercial & Residential zones). Higher concentration was observed in winter at commercial areas & minimum at residential area. Enhancement in disintegration rate of organic compound in summer was the reported possible cause of such concentration trend [256].

PAHs in the suspended particulate matter and respirable suspended particulate matter were studied in airborne particulate matter in a petroleum refinery in west coast of India in six directions. A comparison of the PAHs concentrations showed that the average PAHs concentrations in major Indian cities were in the range of 5.81×10^{-1}–9.6925×10^{-1} µg/m^3, which is less than the PAHs concentration of 10.92-100.82 µg/m^3 around the refinery [257].

In Nunhai, an industrial site in Agra total PAHs concentration in TSPM from December 2005 to August 2006 was monitored. A relationship between PAH concentration and temperature was revealed where winter concentration of PAH was four-fold higher than summer. Higher fuel consumption coupled with lower mixing layer height, lower temperatures and less photodegradation were considered to be the possible cause of such high PAH level during cold periods [258]. Rajput et al. [259] conducted another similar study on PAHs in the same area from May 2006 to September 2006. The results indicated that PAHs concentrations were higher than many other industrial sites. Such higher concentration of PAHs revealed their higher emission rates in Nunhai as well as higher adsorption of gas phase PAHs by TSPM.

Masih et al. [260] measured PAHs in airborne particulate matter (PM$_{10}$) from four different sites of industrial, residential, roadside and agriculture area in Agra, amongst which industrial site recorded highest total PAHs concentration. The PAH concentrations in industrial (9.79×10^{-2} µg/m^3), residential (3.46×10^{-2} µg/m^3), and roadside (2.87×10^{-2} µg/m^3) areas of Agra are less than the concentrations found in Taiwan (0.1101µg/m^3) [industrial] [261] and 7.45×10^{-2} µg/m^3 [residential] [261] and in Italy/Chile (5.48×10^{-2}

/7.68×10^{-2} μg/m^3 [roadside]) [214, 262], respectively. In the present study, the concentration of PAHs (8×10^{-3} μg/m^3) in agricultural areas was found to be higher than in Malaysia/Taiwan (3×10^{-1}/5×10^{-1} ng m^{-3}). Another study in the same area for gaseous/particulate bound PAHs of outdoor rural environment was carried out. In this study the highest concentration was recorded during winter, lower in summer and lowest in rainy season [263].

In Ambathur, Kolathur, Saidapet, and Egmore representing urban, commercial, urban-residential, and industrial regions of Chennai PAHs in $PM_{2.5}$ was measured and found higher than (National Ambient Air Qulaity Standard) NAAQS annual average of 1ng/m^3, indicating an alarming pollution level in Chennai [264]. Singh et al. [265] monitored PAHs in PM_{10} and $PM_{2.5}$ at G.G.S.I.P University campus in eastern part of Delhi. This study found concentration of both PM_{10} and $PM_{2.5}$ higher than the prescribed limit of WHO and the NAAQ given by CPCB India. ∑PAH concentrations for PM_{10} and $PM_{2.5}$ were much higher in winter as compared to summer with predominance of 4-6 ring PAHs (80-95.8% of ∑PAHs).

Gupta et al. [266] measured 4PAHs (Pyr, BaP, BgP and BbF) in ambient aerosol particles using a five-stage impactor at six different sites in Delhi for both the coarse and fine fractions. It has also been observed that the PAHs concentrations, in most of the cases, increase with decrease in the particle size, with lowest concentration in >10.9 μm size and highest in <0.7 μm.

PAHs in ambient respirable particles PM_{10} from Jawaharlal Nehru University campus (JNU) in Delhi were recorded. Nearly 85% of the PAHs profile was dominated by combustion-derived large-ring compounds that were considered to be local in origin. In this study for the first time both organic and metallic characterisation in atmospheric particulate was conducted which revealed a better result for source apportionment [173].

A passive air sampling was carried out to estimate ambient PAHs in Imphal (urban), Thoubal (rural), and Waithou (mountain) of Manipur, Northeast India in the year 2009. The urban air was found to be most polluted compared to that of rural and mountain. The PAH profile was dominated by 2-3 rings PAHs. Seasonal variation was observed for PAHs with higher concentration during autumn and winter compared to spring and summer. Diagnostic ratio indicated sources of diesel and gasoline driven vehicles in urban and mountain sites while coal burning in rural site PAHs. Sources of PAHs were identified to be both local and long range transport of southern Indian cities including Indian coastal regions and from Bangladesh [267].

2.2.2 Indoor PAHs

Biofuels, including wood, dried animal-dung cake and crop waste, are used extensively for cooking energy in India. High concentrations of PAHs in particulate have been reported in indoor environments, during biofuel combustion for cooking. In India, 70% of population depends on such biomass fuels for domestic cooking, and 78% of the population thrives on the biomass fuels in general [243, 268, 269-270].

Raiyani et al. [270] investigated indoor PAHs in kitchens with varied fuel type in Ahmedabad and found over 75% of the PAHs were in the particulate size bins of <2μm.

Pandit et al. [271] conducted a study on PAHs of Particulate matter in Trombay, Mumbai for indoor and outdoor of three houses where kerosene was used as cooking fuel. This study revealed significant indoor pollution due to use of kerosene as fuel. Moreover, mean concentrations of some individual PAH compounds were found with higher values by approximately an order of magnitude in indoor cooking environments than outdoor cooking environments with the effective total daily exposure was two times higher than that from ambient.

As cooking stoves using biofuel are high in use in Indian conditions, size-resolved emission factors of PAH from such cooking environment in India were measured using a dilution sampler. Emission factors of ∑PAH for wood, briquette and dung cake combustion were in the range of 2×10^{-3}–3.2×10^{-3} mg/ g, 2.8×10^{3}–3×10^{-3} mg/ g and 3.1×10^{-3}–5.5×10^{3} mg/ g respectively for per mass of fuel burnt [272]. In a rural area of Lucknow in north India ∑PAHs in particle bound indoor cooking area was monitored. This study reported that the concentrations of carcinogenic PAHs were significantly high in breathing zone and in surrounding areas during cooking over chulha in rural India and was higher during winter than summer. PAHs concentrations were also increased considerably during biomass combustion. Thus the daily exposure to high concentrations of carcinogenic PAHs in indoor air environment could lead to chronic pulmonary illnesses in rural Indian women while cooking food [273]. Ansari et al. [269] conducted a study on PAH compounds in $PM_{2.5}$ and PM_{10} from North India, Bhithauli near Lucknow during cooking period and non-coocking period. The pollutant levels during cooking were significantly higher compared to the non cooking period. This study also confirmed that indoor pollution depends on the kind of biomass fuel used for cooking. In Agra PAHs in kitchen, living room and in outdoors at urban site was recorded, where maximum concentration was found in Kitchen. But the high BaP concentration was detected in roadside living room (37.75±3.74) [260]. In this study, BaP level of kitchen in both roadside and urban areas were showing similar trend.

To prove the hypothesis that PAHs emissions differ with variance of biomass fuel used, Singh et al. [274] determined emission factors and emission estimates of PAH emitted from dung cake, fuelwood and crop residue from rural household of six states of Indo-Gangetic Plains in India including Delhi, Uttar Pradesh, Punjab, Haryana, Uttarakhand and Bihar. The average emission factors of total PAHs from dung cakes, fuelwood and crop residue are found to be 59.5 ± 19.9 mg kg^{-1}, 52.5 ± 19.6 mg kg^{-1} and 40.9 ± 15.2 mg kg^{-1} respectively. The emission factor of particulate phase PAHs (56.5 mg kg^{-1}, 45.3 mg kg^{-1} and 35.8 mg kg^{-1}) was observed to be higher than that of gaseous phase PAHs (3.1 mg kg^{-1}, 7.2 mg kg^{-1} and 5.1 mg kg^{-1}) from dung cakes, fuel-wood and crop residue, respectively. Individually Anth, Flan, Pyr, BaA and Chry were found to be dominant in studied biomass fuels. Moreover, the average emission estimates of PAHs were determined as 2.95 ± 0.98 Gg yr^{-1}, 3.13 ± 1.08 Gg yr^{-1} and 0.66 ± 0.26 Gg yr^{-1} from dung cakes, fuelwood and crop residue, respectively.

Emission factors of PAHs were also estimated in emission from different religious and ritual burning practices including pyrolysis, flaming and smoldering in India where natural and synthetic biomaterials are used in different proportions. Five different types of religious and ritual places were selected for sampling which included Hindu Temples (HT), Muslim Holy shrines (MG), Buddhist Temples (BT), Hindu Marriage Places (MP) and Cremation Centres (Hindu Funeral Pyre) (CC). The average emission factors of total PAHs (TPAHs) was found to be 77.04±5.39, 99.09±6.02, 90.35±6.76, 22.78±1.57, and 77.15±6.16 mg kg^{-1} from MP, MG, BT, HT and CC respectively. Country level emission budget of particulate bound TPAHs was found to be

0.47 Gg $yr^{-1}$from religious and ritual burning practices which contributed 23% of the Indian emission budget of PAHs (2.07 Gg yr^{-1}) from unknown sources [275] .

Thus in Indian context, PAHs in air have been extensively studied in many urban and their adjoining areas. In various possible aspects of ambient PAHs concentrations from outdoor including particulates of different sizes, from various type of motor vehicles with different fuel used, in various urban junctions, in various period like pre CNG, post CNG etc to indoor considering variety of cooking fuel used with different possible cooking stoves, different rituals in Indian environment were considered for investigation. According to the WHO, India accounts for 80% of the 600,000 premature deaths that occur in South- East Asia annually due to indoor air pollution.

2.2.3 Soil PAHs

Soil is the main source of atmospheric dry and wet deposition. The carcinogenic potency of PAH load in traffic soil of Delhi was measured and found to be 21times higher than as compared to the rural soil. ∑BaP-equivalent concentration (BaPeq) concentration in traffic soil (1.00943 µg/g) [97] was higher than in the roadside soil of Shanghai, China (8.92×10^{-1} µgBaPeq g−1) [276], surface soils of Agra, India (6.50×10^{-1}µgBaPeq g−1) [277] and in soil from Tarragona County of Spain (1.24×10^{-1}µgBaPeq g−1) [278]. Ray et al. [279] monitored PAHs in the Soil of IGI airport Delhi. The airport soil was found to be 2.58 times more contaminated with PAHs, than background soil. In the roadside soil of Jalandhar, Punjab the total average concentration of PAHs was estimated to be 7.7×10^{-1}-46.46 µg/g [170]. While comparing with available literature data it was revealed that Jalandhar city's average of 16 PAHs during autumn (16.38 µg/g) and winter (4.04 µg/g), was quite high as compared to many other cities of the world such as Kota Bharu, Malaysia (1.45 µg/g); Fadzil et al. [280], Australia (3.30 µg/g); Yang et al. [96], but lower than few other cities of the world such as USA (58.68 µg/g); Rogge et al. [134].

PAHs distribution and human health risk was also assessed in urban soils of Kurukshetra, India [281]. Environmental and human health risk assessment was carried out in terms of parameters such as BaP total potency equivalent (BaPTPE), index of additive cancer risk (IACR), life time average daily dose (LADD) and incremental lifetime cancer risk (ILCR). The BaP total potency equivalent (BaP TPE) ranged between 8.9×10^{-4} to 0.87 mg kg^{-1} with average of 0.194 mg kg^{-1}. For adults and children the incremental life time cancer risk (ILCR) of PAHs was estimated as 8.1×10^{-6} and 4.2×10^{-5}, respectively. All the estimated parameters for environmental and human health risk assessment were lower than guidelines and acceptable levels. This inferred the area is safe in terms of human exposure to soil PAHs.

Among all these studies the maximum concentration of PAHs was reported from soil of IGI airport Delhi.

2.2.4 PAHs in water

A few studies were taken up so far to estimate PAHs in water in India. Moreover, source apportionment of resultant PAHs was also scanty. Sahu et al. [252] reported PAHs in rainwater from Trombay, Mumbai. In rainwater the LMWPAHs like Phen, Flan and Pyr were dominant than the HMW compounds. Another study was carried out for PAHs in sea water of Mumbai by Pandit et al. [255]. The result of this study revealed gaseous influx in air water interface. Water of Kolleru lake wetland, east coast of India, Andhra Pradesh reported with range of total PAHs concentration 5.6×10^{-2}-2.38×10^{-1} μg/L and maximum concentration of BaP was 9.1×10^{-2} μg/L [282]. Malik et al. [283] recorded the USEPA 16 PAHs in rainwater of Lucknow city. Here also it was found that the LMWPAHs like Acy (three ring PAHs) dominated over the HMW compounds which may be due to higher water solubility for LMWPAHs. The results of this study were in accordance with that reported by Sahu et al. [252] in the rainwater of Mumbai city (India) and in the rainwater of Turkey [284], however, relatively lower levels have been reported in the rainwater of Singapore [285]. Rainwater of Lucknow was the highest reported total PAHs till now.

2.2.5 River Sediment PAHs

As river and lake are the main source of water for majority of Indian population, their sediment toxicity with PAHs is now a major concern for researchers along with its ecotoxicological effects. In the bank sediment of one of the important river of India, Yamuna, level of PAHs was measured. A comparison with earlier studies across the world reveals that PAH concentrations reported here were on the higher side [286]. Amaraneni [282] reported PAHs in the sediment of Kolleru lake wetland in east coat of India, Andhra Pradesh. The result of the study indicated that the lake need proper management as this lake is often used for prawn culture. In the Gomti river sediment, Lucknow USEPA 16 PAHs was measured. This study revealed that some sites of the river may lead to occupational risk for PAHs [287].

As mangrove has many ecological importance for the environment; PAHs in sediment cores of Sundarban mangrove wetland was also monitored. This study found that from an ecotoxicological point of view, the study sites appear to be moderately polluted [288]. Choudhory et al. [289] studied PAHs in sediment Cores from the deepest part of Nainital and Bhimtal respectively, the two Kumaun Himalayan lakes, northwest India in Uttarakhand. The concentrations in the lakes are much higher than in other remote lakes over the world. Among all these studies of PAHs on sediment, concentrations in Nainital and Bhimtal having great ecological significance was found to be highest and is of major concern.

2.3 Sources of PAHs in Environmental Matrices, Indian Context

Researchers had applied various methods for source apportionment of PAHs. Due to similar chemical nature certain PAHs and their ratios were used by researchers as marker for source study in the environment. Also multiple regression and principal component analysis were frequently used for source identification of PAHs.

Results of diagnostic ratio of BaP/BgP indicated a greater contribution of the traffic sources to the ambient concentrations of PAHs in two stations of Bhilai [212]. The qualitative source apportionment presented in particulate of Mumbai indicated the large amount of Pyr was likely from cooking-fuel combustion (animal manure, kerosene and liquid petroleum gas) in addition to vehicular emissions. At the Bombay IIT site, primarily vehicular emissions along with cooking fuel emissions were the likely contributors while industrial oil burning was an additional contributor at Saki Naka, accounting for the higher concentrations of Pyr and Chry/BaA [246].

With growing concern among researchers for vehicular sources of PAHs mainly in urban areas; PAHs profile in Indian cities with various types of vehicles with unique use of fuel was reported. PAHs in the exhaust from three different types gasoline driven vehicles cars, autorickshaws and scooters in Delhi was monitored. The percentage contribution of BaP to ∑PAHs was 1.1%, 2% and 2.6% for cars, autorickshaws and scooters respectively. The reason for such high concentration of PAHs in the present study as compared to the concentration reported elsewhere could be the age of the vehicles, driving condition, quality of the fuel, engine conditions etc [290]. A similar type of study in Delhi in two different type vehicles (buses and truck) which use diesel as fuel was performed. The PAHs concentration was found to be higher in case of truck than bus [291].

Qualitative analysis using marker compounds suggested that biomass and/or refuse burning and motor vehicle exhaust emissions were found to be primary contributors to the organic fraction of ambient PM_{10} in the residential sites of southern Delhi [251]. Molecular diagnostic ratio analysis for PAHs in PM_{10} suggested that diesel emission was the major source contributor in 1998 and gasoline for 2004 in Delhi [254]. Source apportionment study in total PAHs concentration in TSPM at Nunhai, Agra through correlation analysis revealed that LMWPAH was mainly due to primary emission from diesel exhaust while the HMWPAH were formed during combustion process, while good correlations between BkF, IP, Flan and Pyr indicated the contributions from gasoline and diesel combustion. Molecular diagnostic ratios of Flan/(Flan+Pyr), BaP/(BaP+Chy) and BaA/(BaA+Chy) with values 0.38, 0.8 and 0.66 respectively were indicating contributions from diesel combustion whereas IP/(IP+BgP) and IP/BgP ratios of 0.33 and 0.49 respectively were comparable to that for diesel and gasoline emissions. Moreover IP/BgP and BaP/BgP ratio indicated the dominant contribution from traffic emissions [258]. With same source identification method in another study of Agra, prevalent contribution of sources such as vehicular emission from gasoline and diesel engine were identify to contribute particulate PAHs [259]. Factor analysis of PAHs in airborne particulate (PM_{10}) from Agra implied that the sources were strongly linked to land use at each particular site [260]. The correlation analysis of PAHs in Agra during winter season (November 2006 to February 2007) suggested that gas utilities, cooking (frying and oil combustion), smoking and incense burning were mainly attributed to PAHs in indoor environment [260]. Source apportionment of

Gaseous/particulate bound PAHs of outdoor rural environment in Agra with correlation and factor analysis indicated cooking/diesel fumes, burning of biomass fuel (cow dung cakes/wood/coal) as potential sources of PAHs [260]. Factor analysis suggested that vehicular emissions of petrol and diesel-driven engines inclusively contributing to PAHs in $PM_{2.5}$ as probable sources in Chennai [264]. The results of diagnostic ratio and enrichment factor analyses in PAHs in PM_{10} and $PM_{2.5}$ at G.G.S.I.P University campus in Delhi showed that vehicular and anthropogenic emissions related to combustion, industrial processes as well as natural sources associated with the transport of dust from the roadside area were the major pollutant sources for PAHs [265]. The principal sources identified for PAHs in ambient aerosol particles at six different sites in Delhi were vehicular emission and coal combustion. Some contribution from biomass burning was also detected [266]. Principal component analysis–multiple linear regression (PCA-MLR) technique revealed mainly four sources with their respective percentage contribution of crustal dust (73%), vehicular emission (21%), coal combustion (4%) and industrial emission (2%) for PAHs in PM_{10} from JNU campus in Delhi that was further validated by hierarchical cluster analysis (HCA) [173].

The use of PAHs and inorganic (metals) tracers like Fe, Mn, Cd, Cu, Ni, Pb, Zn, Cr etc being co-emitted from similar sources such as biomass burning, coal and petroleum combustion, vehicular emissions, coke and metal production etc. improve the process of source apportionment to get higher resolution results. In Indian context a few such studies were performed by Sarkar et al. [173], Amaraneni [282], Singh et al. [265], which reported their similar emission source. So, this is another very important aspect to be explored for researchers while executing PAH study.

In some of the studies source apportionment of PAHs in soil and sediment through marker compounds and statistical analysis was also adopted. In the source apportionment study of bank sediment of Yamuna river the value of Phen/Anth ratio, 0.69 ± 0.54 (<10) and BaA/Chry ratio, 3.16±2.87 (>1) in the studied samples demonstrate the classical role of pyrogenic sources. While average value of Flan/Pyr ratio, 0.92±0.62 suggested common sources i.e. combustion as well as petroleum also. In the present study average of ratios Anth/Anth+Phen, Flan/Flan+Pyr, and BaP/BaP+Chry at all the sites showed that PAH in river sediments are derived primarily from combustion sources including fossil fuels (gasoline, crude oil, and coal) and biomass (wood and grasses) [286]. Factor analysis and isomer pair ratios suggested pyrogenic origin of PAHs in the Soil of IGI airport Delhi [279]. Principal Component Analysis (PCA) provided the fingerprints of vehicular traffic emission and coal combustion in the urban traffic sites in Delhi and IP/BgP ratio indicated that PAH load at the traffic sites is predominated by the gasoline-driven vehicles [97]. According to observed molecular indices, PAHs contamination in the river Gomti seemed to be originated both from the high temperature pyrolytic process as well as from the petrogenic source, indicating a mixed PAH input pattern [287]. To assess the PAH sources in the sediment of Nainital and Bhimtal lake, diagnostic ratios were calculated including: (i) ∑LMW (Naph, 2-methylnaphthalene, 1-methylnaphthalene, Acy, Acen, Flu, Phen and Anth) to ∑HMWPAHs (1-methylpyrene and 2-methylpyrene) and (ii) Phen to Anth. Nainital sediments reveal a dominance of LMW over HMWPAHs. In contrast, the Bhimtal sediments were found to be dominated with HMWPAHs completely. This implied that PAHs in these lakes were derived from petrogenic sources [292, 293] and are mainly of anthropogenic origin [289]. The PAH diagnostic ratios indicated that the PAHs in the sediment cores of Sundarban mangrove wetland were mainly of pyrolytic origin, mainly transported by surface runoffs [288].

Moreover, Indian soil (Delhi soil) PAHs witnessed a significant correlation with black carbon which could be used as a better predictor for PAHs presence [151]. So, this is another very important aspect of PAHs study having a lot of scope for researchers of this country.

In Indian context the preliminary studies of PAHs mainly begins with the most toxic indicator of PAHs i.e. BaP and their concentration in the ambient environment. The frontline analysis of these compounds was performed with spectrofluorometer [243,244].

In the 1990s PAHs study extended from just BaP to a group of 8PAHs and then 12PAHs compounds. Accordingly the analytical methods also upgraded with HPLC system with UVA detector and HPLC with florescence and GCMS detector [212, 245]. In the 21st century the scope of majority of studies now look into USEPA recognized 16PAHs concentrations or the no of compounds are selected according to the importance and viability of the work. For PAHs study sample preservation and method development often encounter some limitations. In most of the Indian studies on PAHs, researchers are following the classical methods of USEPA or methods developed by the researchers of western countries. Going through all these literature, it seems there is a very urgent need for detailed and systematic study of PAHs in various environmental matrices in Indian conditions. This part of South Asia with different climatic, topography, green cover, cultural and ethnic groups thus encourages divergent scopes of monitoring of environmental exposure to PAHs.

In India, although different aspects of atmospheric PAHs were assessed by researchers, studies on atmospheric bulk deposition of PAHs are observed to be scarce. Atmospheric bulk deposition of PAHs is the comprehensive pathway for transfer of these compounds to other environmental matrices. In India, prevailing atmospheric conditions during different seasons of the year are unique. Thus, the factors governing bulk deposition of PAHs in India are quite discrete from that of other parts of the world. As we have for the first time attempted to estimate PAHs in bulk deposition and their signature in other environmental matrices, these information will act as baseline for further studies of bulk deposit PAHs in Indian context.

Chapter 3

Materials and Methods

Chapter3: Materials and Methods

3.1 Study Area

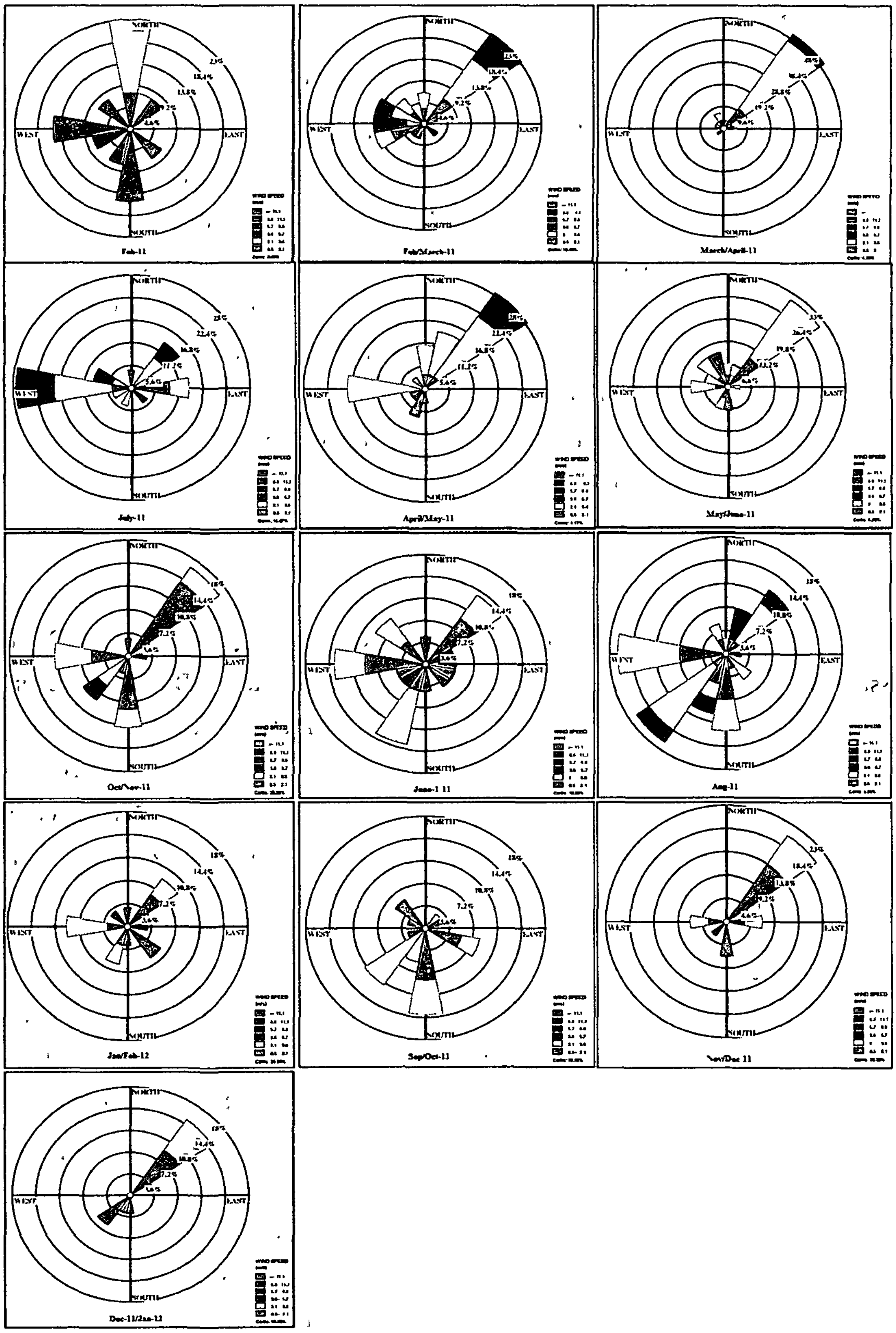
The study was carried out in Guwahati which is often considered as the gateway of northeast India. It is a very rapidly growing city situated between the bank of Brahmaputra River and the foothills of Shillong plateau. The city has a geographical area of 340 km^2. It has a dense human population with high density of vehicular traffic. According to 2011 census Guwahati metropolitan region has recorded a population of ~1 million which is an increase of about 8% to the 2001 census. According to the district transport office information Guwahati metropolitan region witnessed a vehicular growth (light motor vehicle and heavy motor vehicle) of about 87% from 2000 to 2012 with 58,638 number of vehicles on road condition in the year 2013.

Its geographical coordinates are 26° 10' 0" North and 92° 49' 0" East. The city is situated on an undulating surface with its altitude varying from 49.5 to 55.5m above mean sea level. Guwahati has a warm and humid climate and the monsoon brings heavy rainfall. The summer and winter are extreme with mean maximum and minimum of 31.8° C and 25.5° C in summer and 23.6° C and 10.2° C in winter respectively. Monthly mean of temperature (T), relative humidity (RH), wind speed (WS), wind direction (WD) are shown in Table 3.1. Windrose of Guwahati during entire study period from February 2011 to February 2012 is illustrated in Figure 3.1. From the windrose it was observed that wind in Guwahati was mainly north-easterly type. However, with the onset of monsoon wind pattern got shifted to westerly and south-westerly direction.

Table 3.1 Sampling periods and mean monthly weather attributes

Month	Monthly mean Temperature (°C)	Monthly mean Relative Humidity (%)	Monthly mean Rainfall (mm)	Monthly mean Wind Speed (Km/hr)	Monthly mean Wind Direction Degrees
Feb-11	19.9	70.9	23.4	0.96	85.6
Feb/March-11	23.2	65.5	47.3	1.67	227.7
March/April-11	24.9	70.6	32 2	2.16	194
Apr/May-11	27.2	70.7	78.5	2.39	116
May/Jun-11	20.8	59.4	143.1	1.88	181.1
Jun1-11	24.5	60.4	171.5	1.69	185.8
Jul-11	28.1	76.6	182.7	2.07	191.1
Aug-11	28.8	87.5	421.7	2.31	198.8
Sept/Oct-11	29.1	85.2	227.4	1.08	188
Oct/Nov-11	29.1	85.5	5.2	1.05	192.5
Nov/Dec-11	28.5	87.3	1.5	0.83	172
Dec-11/Jan-12	25.2	81.8	9.6	0.44	123.8
Jan/Feb-12	20.6	83.2	9.7	0.69	109

Source: Regional Meteorological Centre, Guwahati



Feb-11

Feb/March-11

March/April-11

July-11

April/May-11

May/June-11

Oct/Nov-11

June-1 11

Aug-11

Jan/Feb-12

Sep/Oct-11

Nov/Dec 11

Dec-11/Jan-12

Figure 3.1: Windrose of Guwahati during the entire study period of February 2011 to February 2012.

3.2. Sampling

Samping site locations are shown in Figure 3.2. Five representation sampling locations for bulk deposition, soil and street dust in Guwahati city were selected based on their land use pattern. They included industrial site in Noonmati-Narengi area (S1), commercial site in Machkhowa area (S2), Traffic site in Gauhati University (S3), residential site in Khanapara-Beltola area (S4) and forest site in Basistha area (S5). The S1 site consists of an oil refinery of Indian Oil Corporation Limited and Coal India Limited. S2 site being the commercial hub of the city with the presence of a bus station make this place busiest all the time. S3 location is very near to a traffic junction which is the connecting point to the city from other parts of the country. Therefore, this site has heaviest traffic density in Guwahati. S4 area comprises of many residential apartments together with some major government establishments. S5 is a forest area not so far from the main stream of the city.

Surface water and sediment samples were collected from the Bharalu River passing through the urban stretch of the city. Bharalu originates as Basistha River in Meghalaya hills which finally meets Brahmaputra. Guwahati is situated between the bank of Brahmaputra river and the foothills of shillong plateau. The geographical coordinates in the origin of the river are 26.094301 latitude, 91.78522840000005 longitude. The geographical coordinates of the river in the meeting point to Brahmaputra is 26.1735867 latitude and 91.7313747 longitude.

Samping sites of water and sediment sampling of the Bharalu River are shown in Figure 3.2. Seven representation sampling locations in Bharalu River were selected based on local activities and effluent discharge points. The sites were Bhralumukh (R1), Kumarpara(R2), Athgaon(R3), Rajgarh(R4), Zoo road (R5), Sundarpur (R6) and Dispur(R7). Bharalumukh is the confluence of river Bharalu and Brahmaputra. Kumarpara is mainly a market place with some residential apartments. High traffic density is also observed in this site with mostly 2-3 wheeler light motor vehicles. Athgaon is an important commercial area and large business houses are built up here. Rajgah is a very busy place with thick vehicular traffic. Many commercial complexes are set up in this locality. Zoo road is a mixed commercial and residential area. Assam Industrial development cooperation is also located in this area. This is the heart of the city and it connects to the railway station. Sundarpur is completely a residential place.

Dispur is the capital of Assam and Assam Secretariat House is located here. Lots of vehicle movement is common here with frequent traffic blockage. Dispur is considered as main hub of the city. All the sampling sites with their coordinates and prevailing activities are shown in Table 3.2.

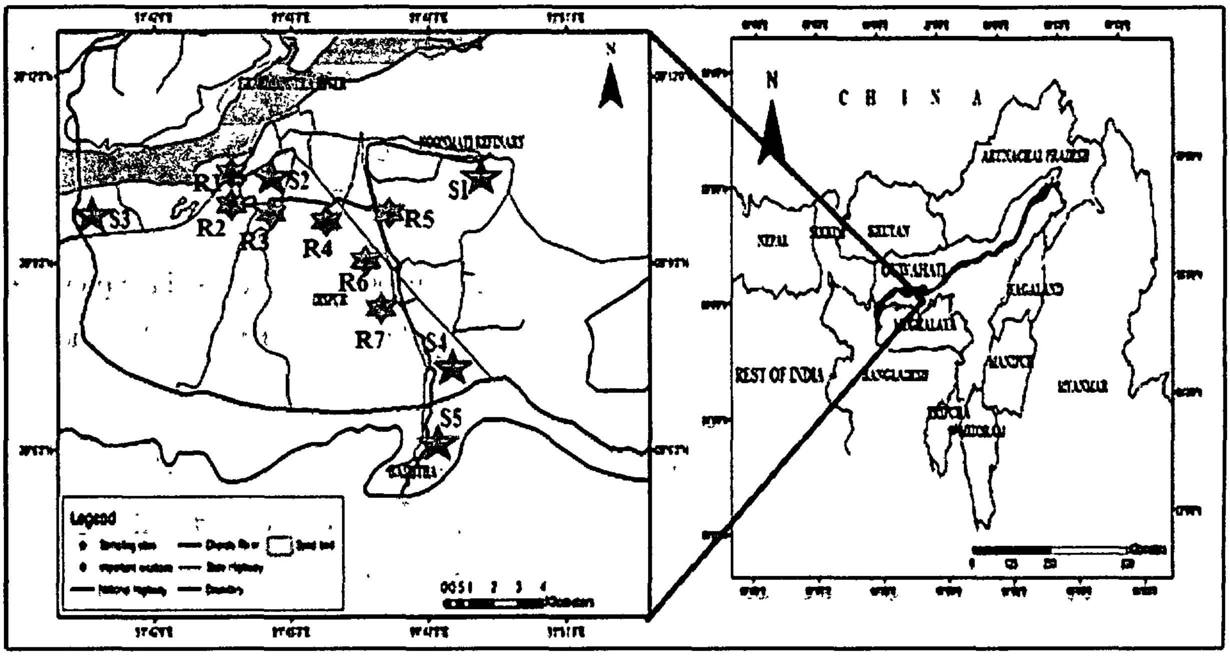


Figure 3.2: Map of Guwahati showing sampling locations and sketch of India where Guwahati has been marked.

Table 3.2 Description of sampling sites in Guwahati.

Sites	Coordinates	Prevailing Activities
S 1: Noonmati-Narengi	91°48′ 12.14″ E 26°11′ 4.78″N	Oil refinery of Indian Oil Corporation Limited and Coal India Limited is located in this area. Considered as industrial site
S 2: Machkhowa	91°44′ 8.275″ E 26°10′ 38.017″N	A commercial hub of the city and the presence of a bus station make this place busiest all the time.
S 3: Gauhati University	91°39′ 45.554″ E 26°9′ 17.845″N	Very near to a traffic junction which is the connecting point to the city from other part of the country. Therefore, this site has heaviest traffic density in Guwahati.
S 4: Khanapara-Beltola	91°48′ 43.523″ E 26°7′ 18.732″N	Comprise of many residential apartments together with some major government establishments.
S 5: Basistha	91°47′ 9.532″ E 26°5′ 42.356″N	A forest area not so far from the main stream of the city.
R 1: Bharalumukh	91°44.798′ E 26°8.49′ N	Confluence of Bharalu to Brahmaputra. A commercial and residential area with heavy traffic.
R 2: Kumarpara	91°73.555′ E 26°14.713′ N	Market place with residential apartments with high traffic density with 2-3 wheeler motor vehicles.

R 3: Athgaon	91°44.345′ E 26°10.27′ N	An important commercial area and large business houses are built here.
R 4: Rajgarh	91°46.231′ E 26°10.48′ N	A place with thick vehicular traffic. Many commercial complexes are set up here.
R 5: Zoo Road	91°46.453′ E 26°10.113′ N	A mixed commercial and residential area and heart of the city.
R 6: Sundarpur	91°46.586′ E 26°9.34′ N	A completely residential area.
R 7: Dispur	91°47.424′ E 26°8.519′ N	The capital region of Assam state, a busy commercial and thickly populated area. The location is surrounded by residential complexes, industrial estates, office buildings, schools, automobile workshops and business houses. Lots of vehicular movement is common here with frequent traffic blockage.

3.2.1 Bulk deposition Sampling

Atmospheric bulk deposition sampling of PAHs was carried out during the period of February 2011 to February 2012 on monthly basis. For bulk deposition the study period was classified into dry and wet seasons seven months of the sampling year had more than 10 rain days, which were considered wet periods.

Bulk deposition was sampled using a passive sampler, which is made of a stainless steel funnel. Samplers, in triplicate, were placed at an average height of 7m and, in addition, a sampler covering with stainless steel sheet was placed as 'field blank' sampler. These passive samplers were kept open for both bulk deposition (mix of dry and wet) for a continuous period of about 4 weeks. Fallouts were collected in a amber colour glass bottle pre-cleaned with Mili-Q water and acetone. Monthly samples of each site were mixed to make composite samples, which was carried to laboratory and stored at 4°C till further analysis. Overflow occurred at 5 instances during the period of May to September 2011of the sampling period. For these samples maximum capacity of collecting bottles were taken into consideration for calculation of results. Schematic diagram of the sampler is shown in Figure 3.3.

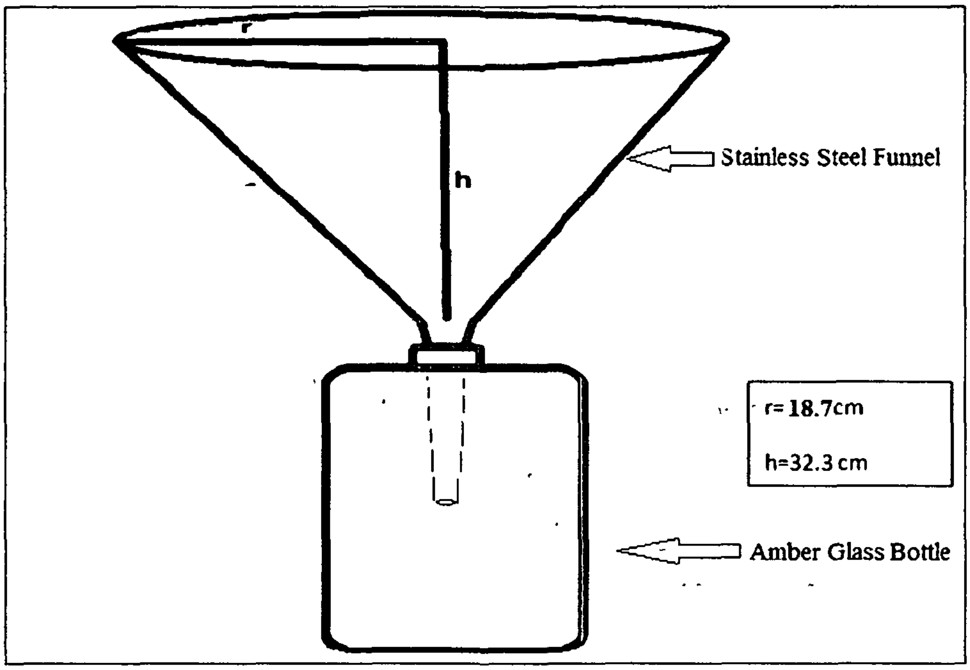


Figure 3.3: Schematic diagram of atmospheric bulk deposition sampler.

3.2.1.1 Bulk Deposition Sampling Artefacts

Possible artefacts related to this type of sampler would be (i) degradation of PAHs at metal surface due to atmospheric radicals, solar radiation etc., (ii) re-volatilization of PAHs due to up-heating of the metal, (iii) particle blow-off due to high wind speed [122]. Moreover, overflow occurred at 5 instances during the period of May-September 2011 might have affected PAH concentration in deposition /total PAH flux.

3.2.2 Soil Sampling

Soil sampling was carried out once in a season for 3 consecutive seasons, viz. monsoon, post-monsoon and pre-monsoon. Top soil samples (0-5cm) were collected with a stainless steel auger. Five samples were collected covering the entire site, pooled and homogenized by coning and quartering to make a composite sample. Samples were air-dried in dark, cleaned from twigs, stones etc, sieved (< 2mm) and stored at 4°C in the laboratory until analysed.

3.2.3 Street dust sampling

Street dust sampling was also carried out once in a season for monsoon, post-monsoon and pre-monsoon. Samples were collected with a stainless steel dust pan. Five samples were collected covering the entire collection area, pooled and homogenized to make a composite sample. All samples were air-dried in a dark place in the laboratory and then twigs, stones etc were removed from them. Then dust samples were sieved through < 2mm steel sieve and characteristic samples were acquired after coning and quartering. Till further processing street dust samples were preserved at 4°C.

3.2.4 Surface water sampling

Surface water samples were collected during the post-monsoon and pre-monsoon season from the seven sampling locations in Bharalu River. The samples were collected with an amber coloured 1liter glass bottle. The bottle was pre-washed with ultra pure water and acetone and dried in oven. After bringing to laboratory all water samples were filtered with Whatman filter paper (no.4) to remove debris and preserved at 4°C till further processing.

3.2.5 River sediment sampling

Sediment samples were collected during the post-monsoon season and pre-monsoon season from the seven sampling locations. Sediment samples were collected from the river bank with a fabricated collector made of bamboo. Three samples were collected from each location within a distance of 1km. All samples were air-dried in dark in the laboratory and then twigs, stones etc were removed from them. Triplicate samples were pooled and homogenised to make a composite sample. Each sediment sample was sieved through < 2mm steel sieve and characteristic samples were acquired after coning and quartering. All sediment samples were preserved at 4°C till further processing.

3.3 Reagents and Materials

Standard mixture of 16 PAHs (specified in EPA method 610) was procured from Sigma-Aldrich (Germany). The four internal standard mixture naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10} and chrysene-d_{12} were obtained from Supelco (Bellefonte, PA, USA). All solvents (acetone, hexane, dichloromethane, toluene, cyclohexane, pentane, acetonitrile, etc.) of HPLC and analytical grade were used for sample processing and analysis. High purity deionised water from Milli-Q system was utilized for analysis.

3.3.1 Preparation of Na_2SO_4 for Column Caping

To dry the extracts, sodium sulfate (Na_2SO_4) was used. Na_2SO_4 of 0.5 gm was capped on the silica gel column. The extracts were transferred to the column and washed with solvent. Although extra pure Na_2SO_4 was procured from company to avoid contamination it was kept for 6hours at 600°C in muffle furnace before use. Dried Na_2SO_4 was then stored in desiccators till use.

3.3.2 *Cleaning of Glassware*

Since PAHs are ubiquitous in our environment, utmost care was taken to reduce contamination. Glassware were rinsed with acetone and cleansed with detergent and chromic acid ($K_2Cr_2O_7$+conc.H_2SO_4) following several washing with tap water and deionised water. The washed glassware was then kept in oven to dry. Clean and dried glassware were wrapped with aluminium foil till use. Aluminium foil was also kept in oven at 600°C before use to avoid contamination.

3.3.3 Instrument and Apparatus

A Waters High performance liquid chromatography (HPLC) equipped with UV detector of 22489 series was used for PAHs analysis. A 4.6mm×250mm, 5µm- particle size Waters C18 column was used for PAHs separation in the entire analysis.

Analytikjena, multi N/C with a series HT1300 (High Temperature solid combustion) was used for carbon analysis. The Instrument is equipped with a NDIR (Non Dispersive Infrared) detector.

Anton Paar, Multiwave with a series of 300, microwave digester was used for sample digestion for heavy metal analysis.

A series of Optima 2100DV Perkin Elmer Inductively Coupled Plasma with Optical Emission Spectrometry (ICP-OES) was used for heavy metal analysis.

3.4 Extraction and pre-concentration techniques used throughout the study

3.4.1 Bulk Deposition

All deposit samples were extracted with liquid-liquid technique. One litre of each sample was extracted three times with a mixture of hexane and dichloromethane (v/v, 85/15) [294]. Before extraction all the samples were spiked with internal standards. Extracts were combined and reduced to about 2ml. Then it was exchanged to cyclohexane for clean up.

3.4.2 Soil

PAHs were extracted from soil by ultrasonic agitation in dichloromethane [295]. Before extraction all the samples were spiked with internal standards. Four grams of each soil sample was extracted for 30 minutes by ultrasonic agitation (Bandelin Sonorex) at a frequency of 20 kHz in 20 ml dichloromethane in triplicates. All three extracts were then mixed and allowed to settle for few minutes. Subsequently extracts were filtered and extracts were then concentrated to 1-2ml in rotary evaporator exchanged to cyclohexane and kept aside for clean-up.

3.4.3 Street Dust

PAHs in street dust samples were extracted by ultrasonic agitation using dichloromethane as solvent [295]. Before extraction all the samples were added with the four internal standards. Four gram of each dust sample was extracted for 30 minutes by ultrasonic agitation (Bandelin Sonorex) with a frequency of 20 kHz in 20 ml dichloromethane for thrice. All the three extracts were then mixed and allowed to settle for few minutes. Subsequently extracts were filtered. The extracts were then concentrated to 1-2ml in rotary evaporator. Then it was exchanged to cyclohexane for clean-up.

3.4.4 Surface Water

Each 1000ml filtered surface water sample was extracted by liquid-liquid extraction in a 2 lit separating funnel according to the method described by APHA [296]. Samples were shaken 3 times and each for 2min, using a mixture of 100ml n-hexane and dichloromethane (1:1 v/v). Extracts were combined and reduced to about 1-2ml using rotary evaporator. Then it was exchanged to cyclohexane for clean-up.

3.4.5 River Sediment

Sediment samples were extracted as developed and recommended by Hong et al. [297] and Zhou et al. [298]. Sediment samples of 5±0.05 gm were extracted thrice by ultra-sonic agitation using 50ml of toluene for 15 min with a frequency of 20 KHz. The extracts were then mixed and concentrated to 1-2ml with rotary evaporator. Then it was exchanged to cyclohexane for clean-up.

3.5 Clean Up

Clean up of samples was conducted as per USEPA 3630C [299]. PAHs in the extracts were separated by a silica gel column of 10mm internal diameter. 10 gm of activated (130° C for 12 hours) silica gel of 100-200 mesh purchased from Merck was made into slurry with dichloromethane. The column was capped with Na_2SO_4 and prewashed with 40ml pentane at the rate of 2ml min^{-1} which was subsequently discarded. The sample was then transferred with 4 ml cyclohexane which was cleaned using 25 ml pentane and again discarded. Finally PAHs in the sample was eluted with 25 ml mixture of dichloromethane and pentane in 2:3 ratio (v/v). This extract was evaporated using rotary evaporator to 0.5-1ml and exchanged to acetonitile.

Schematic diagram of sample preparation for PAHs analysis are illustrated in Figure 3.4.

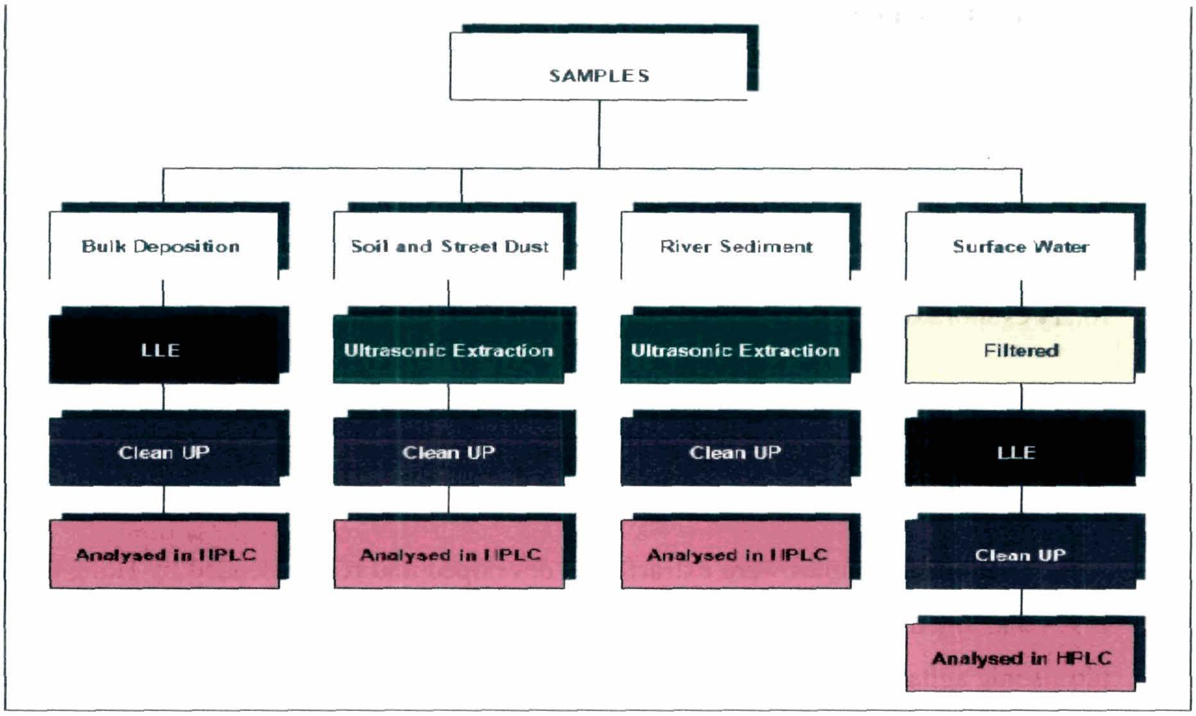


Figure 3.4: Schematic diagram of sample preparation for PAHs analysis extracted from various matrices.

3.6 Analysis

3.6.1 PAHs Analysis

Chemical analysis and quantification of PAHs was done in high performance liquid chromatography (Waters) equipped with UV detector (254 nm) and Waters PAH C18 column (4.6mm×250mm, 5µm- particle size. HPLC grade acetonitrile and degased water in gradient mode (For first 5 min held with 50% acetonitrile; in 5-20 min linear gradient to 100% acetonitrile; till 28 min kept with 100% acetonitrile and from 28 to 32 min linear gradient to 50% acetonitrile; flow rate 1.5 ml/min) was used as mobile phase for 32 minute run time [97].

The quantitative analysis was performed with external and internal calibration method by calculating relative response factor (RRF). Three point average calibrations were applied. Compound concentration was calculated using both peak area response and mean RRF for both internal and external standard.

Measurement with internal standard is considered to be more authenticate than with that of external standards (Garga, 2004). Internal standards were added to samples in equal amounts before extraction and to the calibration standards. The relative response factor (RRF) was calculated as follows

$$RRF = \frac{As \times Cis}{Ais \times Cs}$$

Where,

As = Area (or height) response for the analyte.

Ais = Area (or height) response for the internal standard.

Cs = Concentration of the analyte.

Cis = Concentration of the internal standard.

Thus, RRF for analytes can be estimated by running standard solution containing internal standards. Mean RRF value within ±30% relative standard deviation (according to USEPA method TO-13A) can be used for estimation of analyte concentration in sample applying following equation.

$$Concentration = \frac{As \times Cis \times D}{Ais \times \overline{RRF}}$$

Where, D is the dilution factor [300].

Maximum %RSD of PAHs is shown in Table 3.3.

Table 3.3 Resultant maximum %RSD of PAHs

PAHs	Maximum %RSD
Naph	11.45
Acy	6.38
Acen	16.803
Flu	4.95
Phen	2.32
Anth	2.23
Flan	4.59
Pyr	8.36
BaA	3.75
Chry	30.83
BbF	7.64
BkF	17.72
BaP	4.623
DBA	23.92
BgP	27.469
IP	14.189

3.6.2 Carbon Analysis

Organic carbon (OC) of samples was estimated in TOC analyser (Analytikjena, multi N/C HT1300).

Black carbon (BC) concentration in samples was determined by thermochemical oxidation method (CTO-375) following three steps. (i) Organic fraction of a known amount of dried soil samples were thermally oxidized at 600° C in muffle furnace. (ii) After cooling inorganic carbonates were removed by adding 6M HCl until effervescence stopped. Soil samples were then dried at 60° C. (iii) Finally the residual carbon was quantified as black carbon in TOC analyser (Analytikjena, multi N/C HT1300) [167]. In case of bulk deposit samples BC was estimated in solid particles after filtration.

3.6.3 Heavy Metal Analysis

For heavy metal estimation 0.5gm of each street dust sample was digested in microwave digester (Anton Paar, Multiwave 300) with 9ml of conc. HNO_3, 4ml HF and 1ml concentrated HCl for 35 min following USEPA method 3052. The pressure holds at 40 bars for first 20 minute and maintain till last 15 min in 0.2 bar/sec at 210°C temperature. The analysis of all samples was performed in ICP-OES (Perkin Elmer Optima 2100 DV).

The quantitative analysis was performed with graduated calibration method by using 4 standards of 2.5ppm, 5ppm, 10ppm and 20ppm concentration. Compound concentration was calculated using peak area response and external standard.

3.6.4 Back Trajectory Analysis

Influence of air masses on PAHs bulk deposition from different directions around study area was identified by building air mass trajectories using the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory's Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (available at http://www.arl.noaa.gov/ready/hysplit4.html) [301]. For each sampling, a 120hr (five-day) backward air trajectory was computed at the occurrence UTC (Universal Time Coordinated) time of deposition, at 500, 1000, 1500 m above the ground with 24 hours of time interval.

3.7 Quality Control

3.7.1 Recovery Efficiency

3.7.1.1 Bulk Deposition

All samples and blanks were spiked with the mixture of four internal standards prior to extraction to determine analytical recovery efficiencies. The average recoveries for bulk deposition samples spiked with 40 ppm of internal standard were 52.6±4% for naphthalene-d_8, 78±28% for acenaphthene-d_{10}.

3.7.1.2 Soil and Street Dust

The average recoveries for soil and street dust samples spiked with 40 ppm of internal standard were 68±27% for naphthalene-d_8. 50±0.8% for acenaphthene-d_{10}, 67±1% for phenanthrene-d_{10} and 101±16% for chrysene-d_{12}.

3.7.1.3 Surface water

The average recoveries for water samples spiked with 40 ppm of internal standard were 78±34% for naphthalene-d_8, 82±36% for acenaphthene-d_{10}, 31±6% for phenanthrene-d_{10} and 74±29% for chrysene-d_{12}.

3.7.1.4 River Sediment

The average recoveries for sediment samples spiked with 40 ppm of internal standard were 107±26% for naphthalene-d_8, 68±9%, for acenaphthene-d_{10}, 30±5% for phenanthrene-d_{10} and 37±21% for chrysene-d_{12}.

Chromatogram of external standard and mixture of internal and external standard are shown in Figure 3.5. Retention times of 16 PAHs standard are shown in Table 3.4.

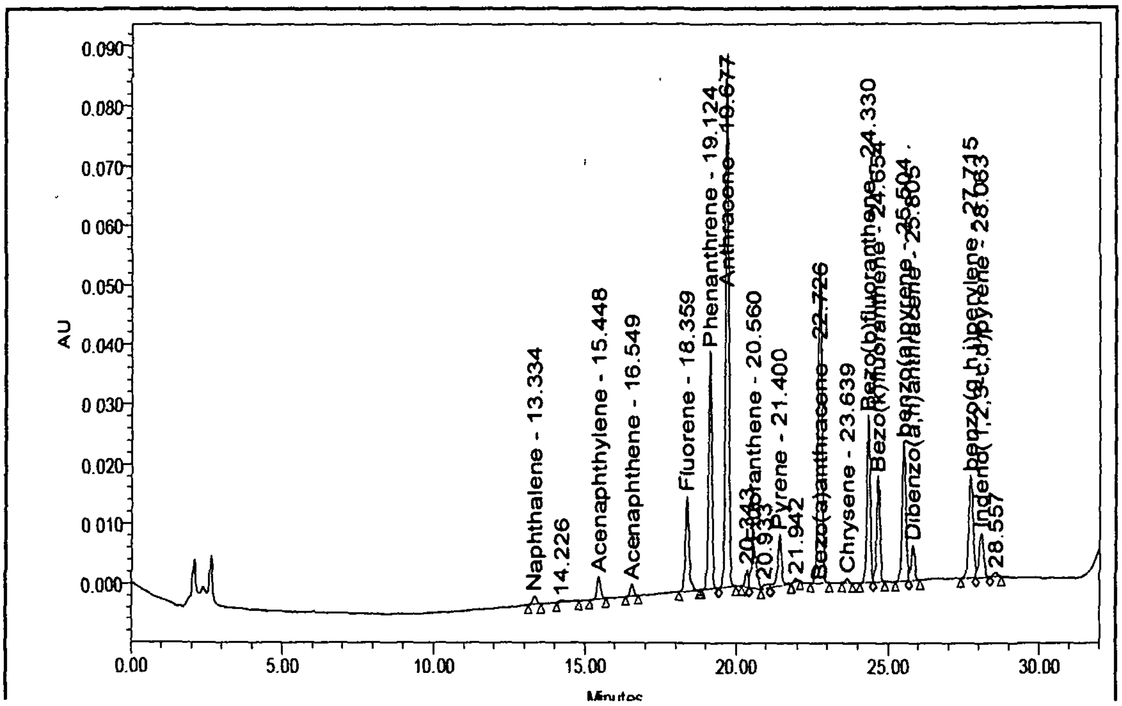


Figure 3.5: Chromatogram of 16 PAHs standard (concentration of Naph=11.4ng/µl, Acy=9.1ng/µl, Acen=10.6ng/µl, Flu=10.1ng/µl, Phen=10.5ng/µl, Anth=8.8ng/µl, Flan=11.7ng/µl, Pyr=11.1ng/µl, BaA=11.6ng/µl, Chry=10.1ng/µl, BbF=10.6ng/µl, BkF=10.8ng/µl, BaP=10.8ng/µl, DBA=11.9ng/µl, BgP=9.9ng/µl, IP=10.9ng/µl).

Table 3.4 Retention time of 16 PAHs standard

Compounds	*Retention time (min)*
Naph	13.334
Acy	15.448
Acen	16.549
Flu	18.359
Phen	19.124
Anth	19.677
Flan	20.560
Pyr	21.400
BaA	22.726
Chry	23.639
BbF	24.330
BkF	24.654
BaP	25.504
DBA	25.805
BgP	27.715
IP	28.063

3.7.2 Limit of Detection of PAHs

The limit of detection (LOD) of HPLC system was found to range between 1.4ppb and 32.9 ppb from Naph to IP (Annexure A). The limit of detection (LOD) was calculated as two times the standard deviation of the replicate analysis of the lowest standard (n=5) [302]. Standard of 0.5 ppm was analysed 5 times and LOD was calculated from it. For statistical analysis of the data set below detection limit (BDL) values were replaced by half of LOD values. Analysis of field blank samples was performed to avoid contamination.

3.7.3 Limit of Detection of Heavy Metals

For statistical analysis of the data set below detection limit (BDL) values were replaced by half of LOD values (Annexure B). LOD values for heavy metals were taken from Standard Operation Procedure, Soil and Plant Analysis Laboratory [303]. Analysis of field blank samples was performed to avoid contamination.

Chapter 4

Results and Discussion

Chapter4: Results and Discussion

4.1 Bulk Deposition of PAHs

4.1.1 Summary Statistics of Bulk Deposition PAHs

Mean concentrations of PAHs in bulk deposits at sampling sites during 2011 - 2012 are shown in Table 4.1. The mean concentration of total PAHs in Guwahati was found to vary from a minimum of 2.2 ng/ml to the maximum of 1035 ng/ml with overall mean value of 71±140ng/ml. BaP concentrations were found to vary from BDL (below detection limit) to 5.6 ng/ml with mean of 0.2±1ng/ml. Moreover, mean percentage contribution of BaP to ∑PAHs was found to be 0 3% Individually, Naph followed by BaA, Chry, Flan and Phen were found to be more abundant in the bulk deposition collected at different locations over Guwahati. Manoli et al. [78] also reported the dominant contribution of Naph in atmospheric bulk deposition samples. They inferred that high water solubility of Naph could be the reason for such high abundance. But water solubility may not be the only reason for the dominance of Naph in bulk samples as despite of their low water solubility, BaA and Chry were found to be the dominant compounds in comparison to Flan and Phen in bulk deposition samples. Zhang et al. [304] reported equal distribution of Naph, BaA and Chry both in gaseous and particulate phase PAHs. Association of these compounds in both the phases in atmosphere could possibly attribute higher concentration of Naph, BaA and Chry in bulk deposition.

In the present study, spatial variations were also investigated on the basis of landuse pattern of the city. The results indicate that the maximum ∑PAHs concentration was observed at industrial site with mean value of 157±277ng/ml followed by residential site of 76±101ng/ml, commercial site of 54±51ng/ml, forest site of 34.8±25ng/ml and traffic site of 34.5±29ng/ml. The pattern for BaP was in the order of industrial site (0.7±2ng/ml)>residential site (0.09±0.1ng/ml)>forest site (0.08±0.1ng/ml)>traffic site (0.06±0.06ng/ml)>commercial site (0.05±0.1ng/ml). However, BaP concentration was observed to be almost in the same range except at industrial site having very high concentration level (0.7±2ng/ml).

Table 4.1 Mean ±SD (min-max) concentrations (ng/ml) of PAHs in bulk deposition

	S1(n=13)	S2 (n=12)	S3 (n=12)	S4 (n=13)	S5 (n=13)	Guwahati(n=63)
Naph	54±73 (BDL-254.6)	32±45 (BDL-148)	24±24 (BDL-72.5)	23.3±28 (BDL-91.2)	21±14 (BDL-48.7)	31±43 (BDL-255)
Acy	4±11 (BDL-33.7)	0.5±1 (BDL-2.1)	0.7±2 (BDL-5.4)	0.5±1 (BDL-2)	1±2 (BDL-4)	1.3±5 (BDL-34)
Acen	4±11 (0.01-41.4)	1.3±2 (0.1-8.6)	0.4±0.4 (0.01-1.3)	2±6 (BDL-20.1)	1±2 (BDL-4)	1.8±6 (BDL-41.4)
Flu	0.6±1 (BDL-3.1)	3.4±10 (BDL-28.7)	0.1±0.1 (BDL-0.4)	1±4 (BDL-13)	0.4±0.2 (BDL-1.6)	1.1±4 (BDL-29)
Phen	9.4±21 (0.02-72.2)	2.6±4 (BDL-13.3)	1.7±3 (0.1-10)	2±4 (BDL-14.8)	2.4±3 (BDL-8)	3.4±11 (BDL-72.2)
Anth	1±2 (BDL-6.7)	0.5±1 (BDL-1.5)	0.1±0.1 (BDL-0.3)	0.4±1 (BDL-2.3)	0.2±0.2 (BDL-0.7)	0.5±1 (BDL-6.7)
Flan	32±67 (BDL-215.5)	2.4±2 (BDL-6.6)	2.5±3 (BDL-6.5)	10.4±26 (BDL-89)	10±4 (BDL-47)	12.8±37 (BDL-215.5)
Pyr	3±8 (BDL-26.4)	0.8±2 (BDL-5.4)	0.2±0.4 (0.02-1.3)	1.5±3 (BDL-11.6)	1.4±1 (BDL-10)	1.4±4 (BDL-26.43)
BaA	40±80 (BDL-251.7)	25.5±20 (BDL-59)	4±3 (BDL-8.8)	16.8±33 (BDL±83)	5±7 (BDL-14)	21±49 (BDL-251.7)
Chry	22±41 (BDL-146.5)	11±15 (BDL-45)	5±7 (0.3-24.1)	36±55 (BDL-153)	4.8±4 (BDL-10.8)	15±33 (BDL-153.1)
BbF	0.1±0.1 (BDL-0.25)	0.1±0.2 (BDL-0.6)	0.03±0.04 (BDL-0.1)	0.1±0.1 (BDL-0.3)	0.1±0.1 (BDL-0.3)	0.08±0.1 (BDL-0.6)
BkF	0.06±0.1 (BDL-0.4)	0.1±0.1 (BDL-0.2)	0.02±0.02 (BDL-0.06)	0.1-0.1 (BDL-0.3)	0.03±0.03 (BDL-0.1)	0.06±0.1 (BDL-0.4)
BaP	0.7±2 (BDL-5.6)	0.05±0.1 (BDL-0.2)	0.06±0.1 (BDL-0.2)	0.09±0.1 (BDL-0.3)	0.08±0.1 (BDL-0.2)	0.2±1 (BDL-5.6)
DBA	0.44±1 (BDL-2.7)	0.26±0.2 (BDL-0.5)	0.1±0.2 (BDL-0.5)	0.1±0.1 (BDL-0.2)	0.12±0.04 (BDL-0.3)	0.2±1 (BDL-2.7)
BgP	0.5±1 (BDL-3.5)	0.1±0.1 (BDL-0.2)	0.1±0.3 (BDL-0.9)	0.1±0.2 (BDL-0.5)	0.05±0.04 (BDL-0.1)	0.2±1 (BDL-3.5)
IP	1.6±3 (BDL-8.3)	1±1 (BDL-1.8)	0.2±0.1 (BDL-0.3)	0.8±1 (BDL-1.9)	0.24±0.2 (BDL-0.5)	0.7±2 (BDL-8.3)
∑PAHs	152±277 (2-1035)	54±51 (2.3-174)	34.5±29 (2.8-85)	76±101 (8.9-371)	34.8±25 (4.2-75.5)	71±140 (2.2-1035)

4.1.2 Temporal Variation of PAHs Concentration

The whole sampling year was segregated into dry and wet season based on the number of rain days. The sampling period with more than 10 rain days was classified as wet season, while the rest of the year was considered as dry season. Thus, the sampling period from March/April-2011 to September/October-2011 were classified as wet season.

Concentrations of PAHs during different sampling period are shown in Table 4.2. Mean concentration of ∑PAHs was found to be maximum (594.3±793ng/ml) during Nov/Dec-11, whereas minimum (38.5±13ng/ml) during Aug-11. Variation of ∑PAHs concentration on the basis of their molecular weight (HMWPAHs and LMWPAHs) during the study period was also examined (Figure 4.1.a). For both LMWPAHs and HMWPAHs maximum concentration peak was observed during Nov/Dec-11 with very high contribution of LMWPAHs to ∑PAHs. In addition to maximum ∑PAHs concentration during Nov/Dec-11 two minor concentration peaks were also detected during the sampling period of May/June-11 and July-11.

Moreover, ∑PAHs concentration in bulk deposition was also found to be varied significantly from dry season to that of wet season during the study period (Table 4.3). During wet season, ∑PAHs concentration in bulk deposition ranged between 14.1ng/ml to 100.2ng/ml with mean value of 43.9±32 ng/ml. However, ∑PAHs concentration varied from 25.5-316.4ng/ml with mean of 93±101ng/ml during dry season. Individually most of the PAH was also observed with an increasing trend during dry season to that of wet season except for BaA which is illustrated in Figure 4.1.b.

The observed pattern in PAHs concentrations could be attributed to prevailing atmospheric conditions during different seasons. From the analysis of the behaviour of air mass from NOAA HYSPLIT model (Figure 4.1.c (a)) and the vertical temperature profile from data (Figure 4.1.c (b)) obtained from Wyoming university atmospheric data repositories, it could be interpreted that prevailing atmospheric condition with low wind activity, subsidence state and inversion condition was the possible cause for high PAHs accumulation during the period of Nov/Dec-11. During the period of May/June-11 and Jul-11, atmospheric dispersion was very less (Figure 4.1.c (c) and (e)) due to the development of inversion state (Figure 4.1.c (d) and (f)) in the lower atmosphere. It could be the possible reason for accumulation of PAHs. The perusal of number the inversion days and mean inversion height during the entire study period, it may be noted that there was an increase in the number of inversion days during dry season in comparison to that of the wet season (Figure 4.1.d). It is pertinent to note that there was a lowering of mean inversion height by approx. 100-200m with the increase in the number of inversion days during dry season that may lead to more accumulation of pollutants during the season.

The wash out of pollutants by heavy rainfall could also be the possible cause of lower concentration during wet season of the year. Moreover, the degradation rate of PAHs is usually faster under high temperature and strong solar radiation during the period. Furthermore, during wet season in India wind from sea also dilute local pollutants in air [305]. Similar temporal trend for bulk deposition PAHs have also been reported by other researchers e.g. Smith and Harrison [306], Ollivon et al. [118], Manoli et al. [78].

Table 4.2 Mean and range of PAHs (ng/ml) during different sampling period in Guwahati

	Naph	Acy	Acen	Flu	Phen	Anth	Flan	Pyr	BaA	Chry
Feb-11	42.6±59	1.6±1	13.8±26	9.9±18	15.1±21	2.2±3	34.8±30	6.5±6	4.8±6	1.6±0.02
	BDL-84.6	0.4-3.3	0.1-52.5	0.2-36.4	1.2-16.0	0.03-6.4	1.2-62.4	1.3-13.6	BDL-9.1	BDL-1.6
Feb/March-11	41.9±18	0.4±0.1	1.6±1	0.1±0.1	0.5±0.4	0.2±0.2	5.5±3	0.2±0.1	0.8±0.00	24±24
	12.9-59.8	BDL-0.5	BDL-2.5	0.1-0.3	0.1-1.1	BDL-0.35	BDL-9.0	BDL-0.3	BDL-0.8	1.9-64
March/April-11	21.6±23	0.5±0 4	0.5±0.4	0.1±0.1	0.8±1	0.4±1	8.4±4	0.1±0.1	4.5±5	26.4±26
	0.4-59.2	BDL-1.2	0.2-1.2	BDL-0.2	0.4-1.5	BDL-0.7	BDL-11.5	0.02-0.1	BDL-10.6	12 6-73.3
April/May-11	47.8±33	0.1±0.1	0.7±1	0.1±0.1	3.6±5	0.4±1	7.8±0.00	1.2±1	23.7±42	14±23.5
	16-90	BDL-0.2	0.2-1.5	0.001-0.2	0.1-13.2	BDL-1.1	BDL-7.8	BDL-3.3	1.5-98.3	0.6-55.9
May/Jun-11	49.9±30	2.3±4	0.5±1	1.8±3	2.5±3	0.7±1	25±43	0.1±0.1	230±0.00	55.6±89
	12.3-84.4	BDL-6 5	BDL-1.0	BDL-5.2	BDL-6.3	BDL-2.2	BDL-74.5	BDL-0.2	BDL-230	0.8-211.9
Jun1-11	25.3±43	0.4±0.2	0.6±1	0.1±0.03	1.2±1	0.1±0.1	3±3	0.4±1	22.3±26	5±4
	0.6-101.6	BDL-0.8	0.1-2.0	0.03-0.1	0.2-2.9	BDL-0.2	0.2-7.2	0.02-1.7	BDL-40.4	BDL-10
Jul-11	BDL	0.1±0.1	0.1±0.1	0.1±0.1	1.1±1	0.2±0.1	0.6±1	0.3±0.2	97±13	55.3±90
	BDL	BDL-0.2	0.01-0.3	BDL-0.2	0.1-1.8	0.1-0.3	BDL-1.3	0.03-0.5	BDL-18.9	2.1-214.3
Aug-11	30.7±12	0.5±0.4	0.3±0.3	0.2±0.1	1.5±1	0.3±0.2	0.7±0.00	0.2±0.2	3.6±0 00	2.7±1
	18.3-45.1	BDL-0.9	BDL-0.7	BDL-0.3	0.4-2.9	0.1-0.5	BDL-0.7	0.004-0.4	BDL-3.6	2-4.3
Sept/Oct-11	39.4±35	1.1±1	0.9±1	0.3±0.2	1.5±1	0.3±0.3	3.7±0.00	0.2±0.3	BDL	1.5±1
	BDL-85.1	0.3-2.0	0.1-2.1	BDL-0.4	0.04-2.3	0.002-0.8	BDL-3.7	0.004-0.7	BDL	BDL-2.6
Oct/Nov-11	34.6±37	2.2±4	1.6±2	1.2±1	4.9±8	0.5±1	1.2±1	1.9±3	6.8±7	8.4±10
	4.9-95.8	0.1-9.7	0.1-5	BDL-1.9	0.2-18	BDL-1.3	BDL-1.6	0.1-8.0	BDL-11	0.6-22
Nov/Dec-11	146.4±195	14.52±27	14.2±14	6.3±1	34.7±57	4.1±5	118.2±173	16.6±20	133.2±198	96.9±108
	13.4-475.2	0.9-62.9	1.5-37.5	0.6-23.7	2.5-135	0.3-12.5	4.1-402.3	0.3-49.3	1.6-469.8	6.8-273.5
Dec-11/Jan-12	103±129	5.99±8	2.4±3	0.7±1	10.7±9	0.3±0.3	3.9±3	2.2±1	22.3±13	24.6±26
	17.2-325.9	BDL-12	0.03-5.8	BDL-1.3	2.2-21.1	BDL-0.6	BDL-5.9	1.0-3.2	9.0-41.3	BDL-53.1
Jan/Feb-12	118.3±103	1.2±1	2.3±2	0.1±0.1	9.7±14	0.2±0.2	1.9±1	1.1±2	21.8±19	6.8±4
	19 3-280.5	BDL-2	0.5-4.5	BDL-0.3	BDL-31	BDL-0.4	BDL-2.8	BDL-3.5	BDL-49.6	BDL-12.4

Contd....

	BbF	BkF	BaP	DBA	BgP	IP	∑16PAHs
Feb-11	0.2±0.00	0.01±0.00	0.03±0.00	0.6±0.00	0.1±0.1	BDL	108.8±106
	BDL-0.2	BDL-0.01	BDL-0.03	BDL-0.6	BDL-0.2		24.6-260.7
Feb/March-11	0.2±0.3	0.2±0.1	0.04±0.00	0.2±0.00	0.9±1	0.5±0.1	74±32
	BDL-0.6	BDL-0.28	BDL-0.04	BDL-0.2	BDL-1.7	BDL-0.6	42.8-119
March/April-11	0.07±0.00	0.03±0.00	BDL	BDL	0.1±0.00	0.7±1	60.8±33
	BDL-0.1	BDL-0.03	BDL	BDL	0.1-0.1	0.4-1.3	23.2-105
April/May-11	0.1±0.04	0.1±0.04	0.1±0.1	0.3±0.2	0.2±0.2	0.7±0.4	93.9±38
	BDL-0.1	BDL-0.1	BDL-0.2	BDL-0.5	BDL-0.3	BDL-1.0	34.3-137
May/Jun-11	0.1±0.1	0.04±0.1	0.1±0.04	0.9±0.00	0.1±0.02	1.2±2	172.5±167
	BDL-0.25	BDL-0.1	BDL-0.1	BDL-0.9	BDL-0.1	BDL-3.4	42-441
Jun1-11	0.03±0.04	0.02±0.03	0.01±0.00	0.2±0.2	0.002±0.0	BDL	44±46
	BDL-0.06	BDL-0.04	BDL-0.01	BDL-0.3	BDL-0.002	BDL	1-119.2
Jul-11	0.1±0.2	0.1±0.1	0.2±0.2	0.4±0.4	0.2±0.2	1.5±1.2	63.3±89
	BDL-0.4	BDL-0.2	0.02-0.4	BDL-1	BDL-0.4	BDL-2.6	6-220.8
Aug-11	0.04±0.02	0.01±0.0	0.2±0.1	0.2±0.00	0.1±0.1	1.5±2	38.5±13
	0.03-0.1	BDL-0.01	BDL-0.3	BDL-0.2	BDL-0.1	BDL-4	27.2-54.6
Sept/Oct-11	0.3±0.3	0.01±0.0	0.04±0.1	0.01±0.01	0.01±0.01	0.3±0.3	38±38
	BDL-0.8	BDL-0.02	BDL-0.1	BDL-0.01	BDL-0.01	BDL0.6	5.0-92.7
Oct/Nov-11	0.4±1	0.1±0.1	0.1±0.2	0.2±0.3	0.1±0.1	0.1±0.04	58.6±69
	BDL-1.4	BDL-0.3	BDL-0.5	0.01-0.8	BDL-0.2	BDL-0.1	6.4-176.1
Nov/Dec-11	0.2±0.2	0.3±0.3	2.2±5	1.1±2	1.7±3	4.9±7	594.3±793
	0.003-0.4	0.02-0.7	0.1-10	0.1-5	BDL-6.5	BDL-15.5	38-1931.9
Dec-11/Jan-12	0.1±0.1	0.1±0.1	0.6±0.4	0.2±0.2	0.04±0.04	0.4±0.3	166.6±132
	BDL-0.2	0.02-0.3	BDL-1.1	BDL-0.3	BDL-0.1	BDL-0.7	55-382.8
Jan/Feb-12	0.1±0.04	0.2±0.2	0.2±0.1	0.4±0.4	0.1±0.1	0.4±0.1	156±101
	BDL-0.1	BDL-0.4	BDL-0.3	BDL-1	BDL-0.3	BDL-0.5	46.7-309.3

Table 4.3 Mean and range of PAHs (ng/ml) in bulk deposition during dry and wet season

	Wet Season		**Dry Season**	
	Mean	Range	Mean	Range
Naph	7.6±21	11.2-28.6	37.9±24	12.4-78
Acy	0.4±1	0.1-1.3	2±3	0.2-7.7
Acen	0.3±0.2	0.1-0.4	3.2±4	0.3-10.9
Flu	0.2±0.4	0.1-1	1.7±3	0.1-7.8
Phen	1.1±1	0.6-2.2	6.1±7	0.3-18.4
Flan	3.9±5	0.3-14.4	14.4±24	0.5-63.3
Anth	0.2±0.1	0.1-0.4	0.7±1	0.1-2.2
Pyr	0.2±0.3	0.1-0.7	2.3±3	0.04-8.8
BaA	34.2±55	1.3-132.7	14.5±25	0.4-71.1
Chry	14.4±17	0.7-39.5	14±17	1.2-51.3
BbF	0.1±0.04	0.02-0.1	0.1±0.1	0.04-0.2
BkF	0.02±0.02	0.002-0.04	0.1±0.1	0.01-0.2
BgP	0.1±0.1	0.002-0.1	0.2±0.3	0.02-0.9
BaP	0.1±0.04	0.004-0.1	0.3±0.5	0.02-1.2
DBA	0.2±0.2	0.005-0.5	0.3±0.2	0.1-0.6
IP	0.6±0.3	0.1-1.1	0.6±1	0.02-2.6
∑PAHs	43.9±32	14.1-100.2	93±101	25.5-316.4

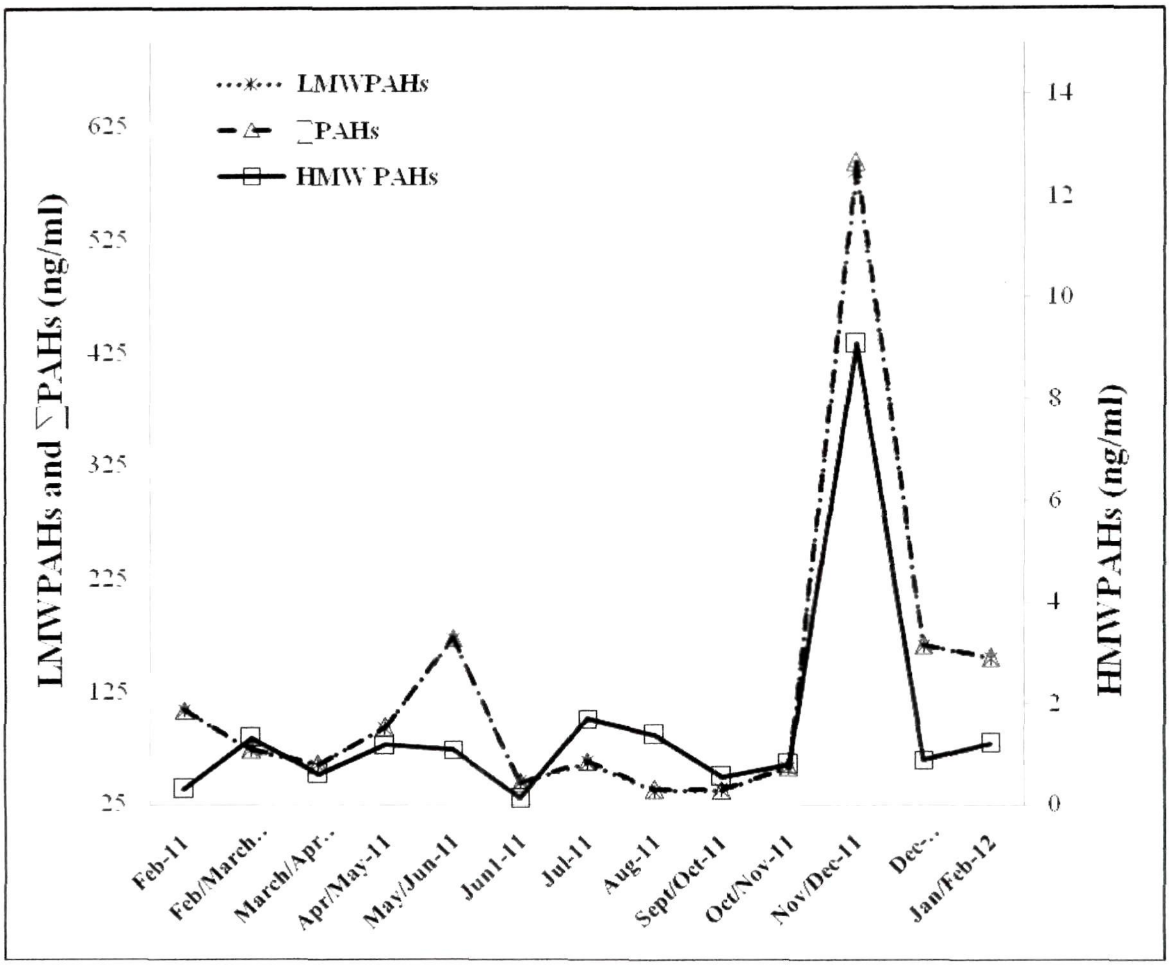


Figure 4.1.a: Monthly variation of LMWPAHs, HMWPAHs and ∑PAHs concentration in bulk deposition samples.

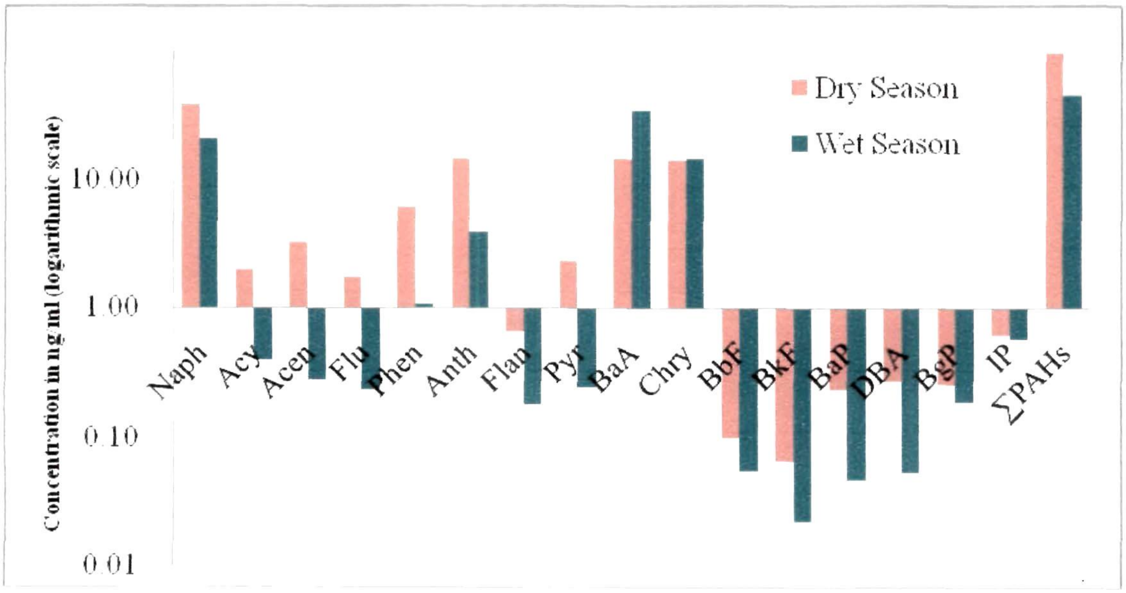
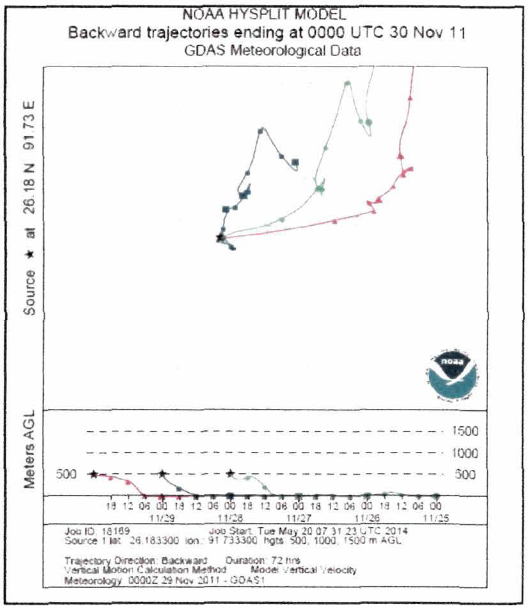
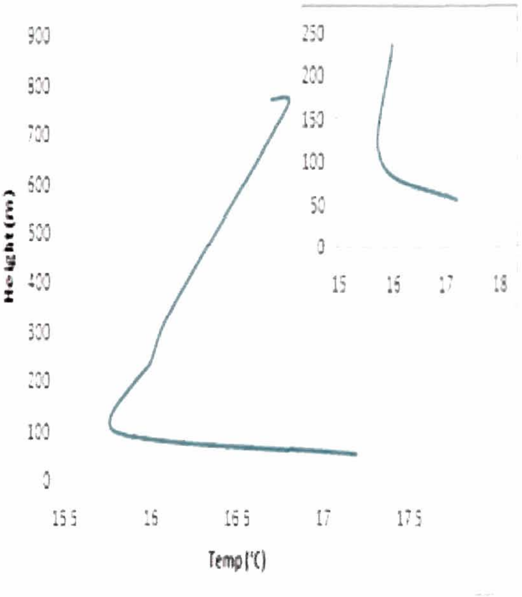


Figure 4.1.b: Comparison of PAH concentration during dry to wet season.


NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 30 Nov 11
GDAS Meteorological Data
Source ★ at 26.18 N 91.73 E
Meters AGL
500
1500
1000
500
18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00
11/29
11/28
11/27
11/26
11/25
Job ID: 18169
Job Start: Tue May 20 07:31:23 UTC 2014
Source 1 lat.: 26.183300 lon.: 91.733300 hgts: 500, 1000, 1500 m AGL
Trajectory Direction: Backward
Duration: 72 hrs
Vertical Motion Calculation Method: Model Vertical Velocity
Meteorology: 0000Z 29 Nov 2011 - GDAS1

(a)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100
50
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15
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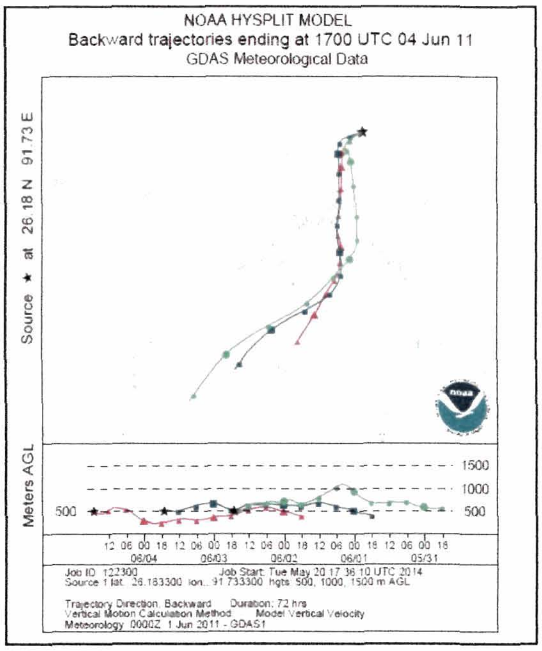
17
18

(b)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Backward trajectories ending at 1700 UTC 04 Jun 11
GDAS Meteorological Data
Source ★ at 26.18 N 91.73 E
Meters AGL
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1500
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12 06 00 18 12 06 00 18 12 06 00 18 12 06 00 18 12 06 00 18
06/04
06/03
06/02
06/01
05/31
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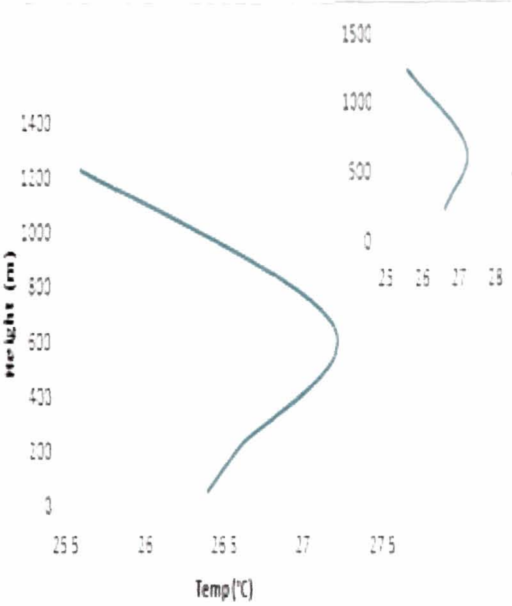
Duration: 72 hrs
Vertical Motion Calculation Method: Model Vertical Velocity
Meteorology: 0000Z 1 Jun 2011 - GDAS1

(c)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200
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Height (m)
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Temp(°C)
1500
1000
500
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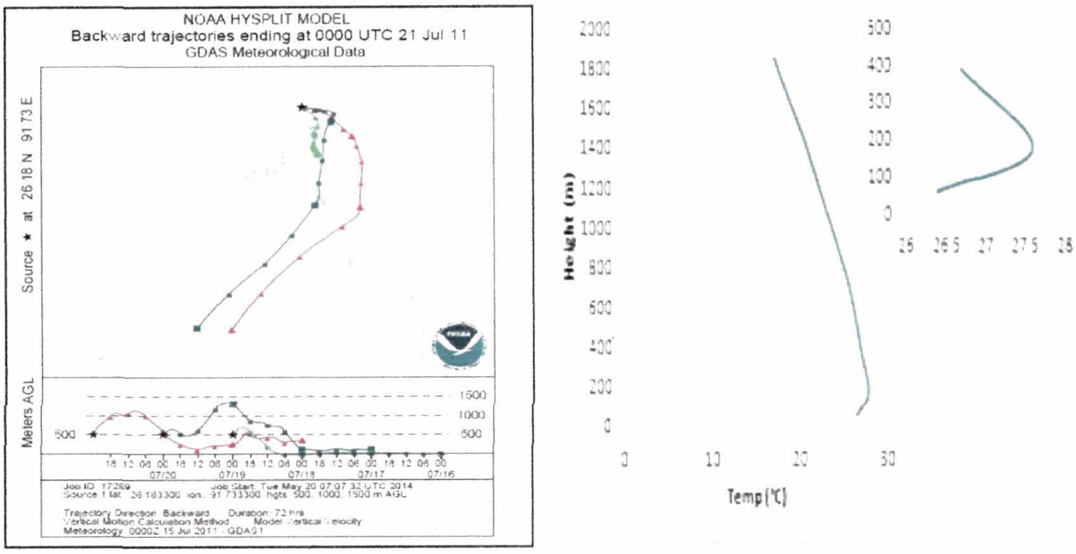
25
26
27
28

(d)

Figure contd...



(e) (f)

Figure 4.1.c: One Twenty hour back-trajectory arriving in Guwahati on (a) 30th November 2011, (c) 4th June 2011 and (e) 21st July 2011 with their respective inversion plot (b) 29th November (d) 4th June and (f) 16th July 2011.

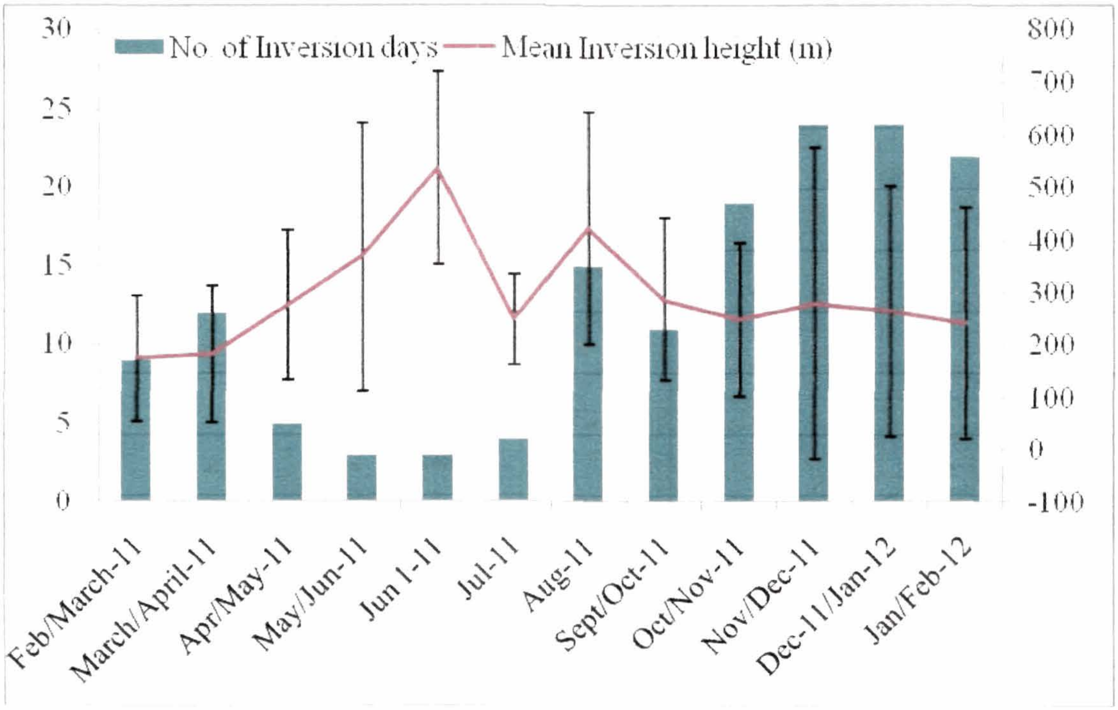


Figure 4.1.d: Mean inversion height (m) Vs number of inversion days during study period.

4.1.3 PAHs Profiles

4.1.3.1 Spatial Variation

In the present study, PAHs in bulk deposition was arranged on the basis of number of rings. It was detected that 2 and 4-ring PAHs were the most dominant compounds observed at all the sites (Figure 4.2a). Percentage contribution of 2-ring PAHs was maximum at site S3 (institutional/traffic site), while 4-ring PAHs was found to be dominant at the site S4 (residential site) (Table 4.4). Three-ring PAHs was observed with maximum percentage contribution at site S2 (Commercial site). On the other hand, occurrence of all 2- to 6-ring PAH compounds were detected only at site S1 (industrial site). Among the HMWPAHs 5-ring PAHs (BbF, BkF, BaP, DBA) were observed only at site S1 and S2. However, 6-ring PAHs (BgP and IP) were found at site S3 and S4 in addition to S1.

Dominance of the PAHs profile by LMWPAHs could be attributed to their higher level of solubility. The 'multi-hop' nature of LMWPAHs made them more susceptible to long range transport and continuous cycle of deposition and re-evaporation [97]. Lower representation of 5 and 6-ring PAHs might be due to their low solubility in wet fraction of deposits. The low molecular weight PAHs found to have significant acute toxicity [96], which is a major concern.

4.1.3.2 Seasonal Variation

Seasonal trend of the representation was also observed in bulk deposition; 4-ring PAHs were mostly abundant in samples of wet season (Figure 4.2.b). During dry season 3-ring PAHs were found to be dominant than that of wet season. However, contribution of 2-ring PAHs was almost similar during both the sampling period.

Table 4.4 Site-wise variation in the percentage composition of three-, four-, five- and six-ring PAHs at five sampling sites in bulk deposition samples

	2-ring	3-ring	4-ring	5-ring	6-ring
S1	33	12	54	1	1
S2	44	13	42	1	0
S3	64	9	26	0	1
S4	28	7	64	0	1
S5	51	12	36	0	0

Figure 4.2.a: Percentage composition of three-, four-, five- and six-ring PAHs at sampling sites (S1-S5 and mean of the five sites as Guwahati) in bulk deposition samples (C1-C13 are sampling events from February 2011 to February 2012).

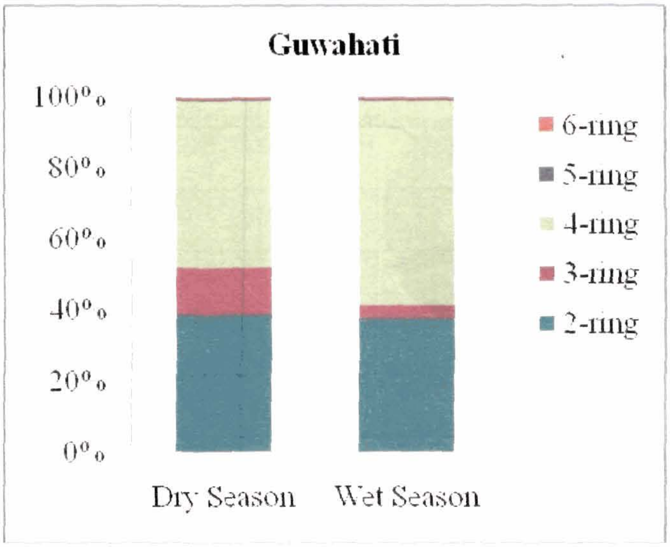
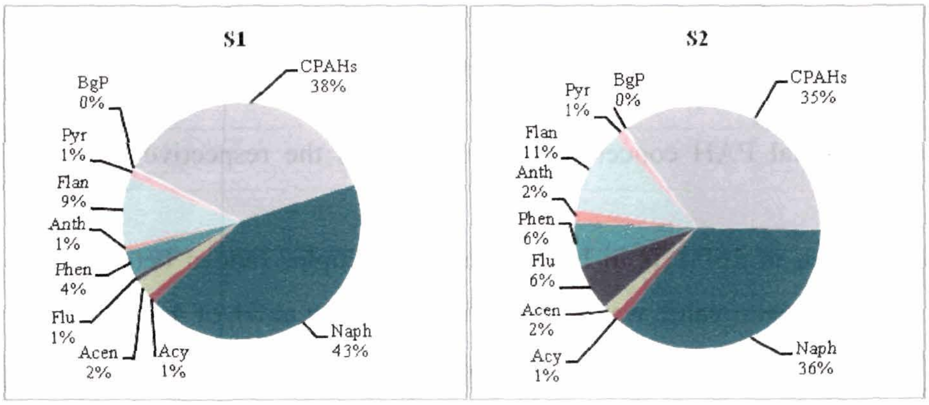


Figure 4.2.b: Percentage composition of three-, four-, five- and six-ring PAHs in Guwahati (mean of the five sites) during dry and wet season in bulk deposition samples

4.1.4 Toxicity

4.1.4.1 Spatial Variation

Percentage distribution on the basis of USEPA recommended 7 carcinogenic PAHs (CPAHs) including BaA, BaP, BbF, BkF, Chry, DBA and IP and non carcinogenic PAHs are shown in Figure 4.3. The maximum fraction of CPAHs was observed at S1 with 38%. In general in Guwahati (mean of S1-S5), CPAHs contribution in bulk deposition was found to be 31%. Among the carcinogenic lot the representation of BaA and Chry were found to be maximum in all sites.



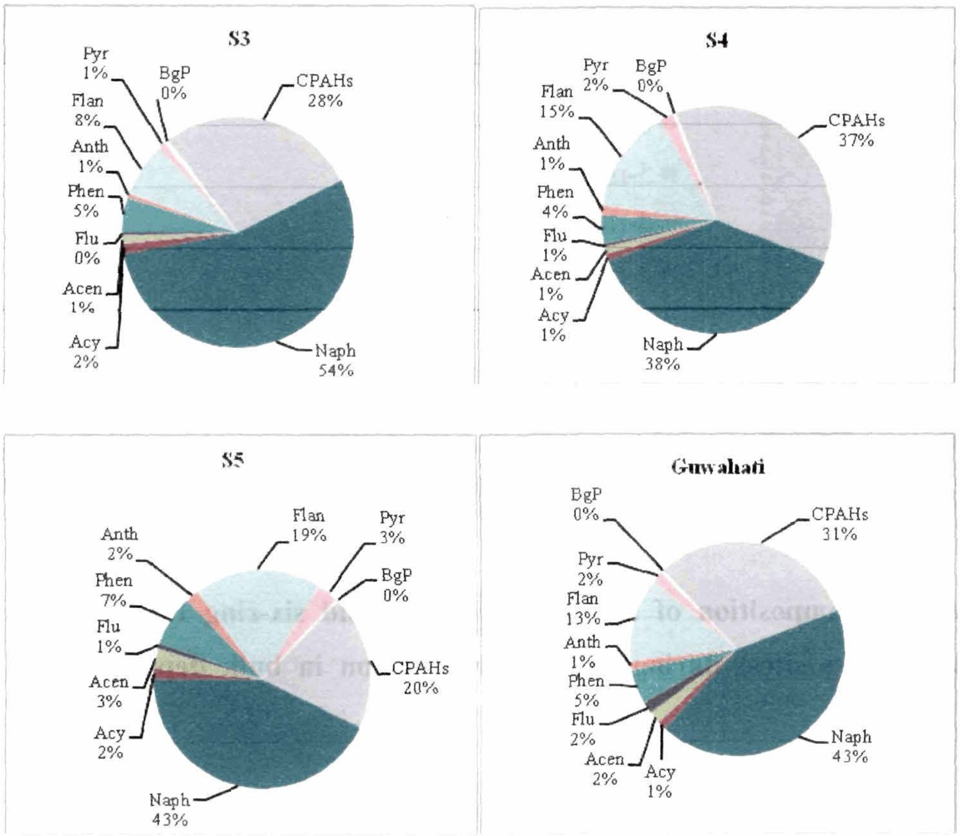


Figure 4.3: Abundance of carcinogenic PAHs (CPAHs) to non carcinogenic PAHs in bulk deposition.

Toxic equivalency factors (TEFs) were employed to estimate carcinogenic potential of individual PAH relative to BaP and to quantify BaP-equivalent concentrations (BaPeq) as per Tsai et al. [307]:

$$Total\ BaPeq = \sum_{i=1}^{n} Ci \times TEFi \qquad \text{-- eq1}$$

Where C_i is the individual PAH concentration and TEF_i is the respective toxic equivalency factor.

Total BaPq concentration of 16PAHs in bulk deposition samples ranged between BDL and 36.5ng BaPq /ml with mean value was found to be maximum at S1 of 4.6±10ng BaPq /ml (Table 4.5a). The mean concentration was observed to be minimum at site S5. If we compare the industrial (S1) and forest (S5) site, the mean ∑PAHs value was ~4 times higher at S1 than S5 but BaPq concentration was ~11.5 times higher in S1 than S5. This is a major concern for the industrial locality with high carcinogenic risk.

Table 4.5.a BaPeq concentrations (ng/ml) of total PAHs at sampling sites (S1-S5)

	S1	S2	S3	S4	S5
Feb-11	0.32	0.56		0.03	0.75
Feb/March-11	0.16	0.37	0.26	0.07	0.18
March/April-11	0.16	0.69	0.50	0.55	0.11
April/May-11	0.84	6.18	0.40	0.65	0.79
May/Jun-11	13.89	0.06	0.55	1.35	0.17
Jun1-11	3.12	0.06	0.41	0.08	0.03
Jul-11	2.24	0.63	0.37	2.23	0.03
Aug-11	0.29		0.14	0.19	0.02
Sept/Oct-11	0.06	0.02	0.06	0.03	0.09
Oct/Nov-11	0.14	0.50	0.05	0.02	0.93
Nov/Dec-11	36.46	2.61	0.26	9.53	0.36
Dec-11/Jan-12	1.34	2.05	0.90	1.01	1.68
Jan/Feb-12	1.02	3.21	1.13	0.61	0.02
Mean	4.6±10	1.4±2	0.42±0.3	1.3±3	0.40±1
Range	(0.06-36.5)	(0.02-6.2)	(BDL-1.1)	(0.02-9.5)	(0.02-1.7)

*for 5 locations (S1 – S5)

4.1.4.2 Seasonal Toxicity

According to Pankow et al. [308], gas/particle partitioning of PAHs which is mostly controlled by meteorological parameters has major influence on human health because the risk of inhaling carcinogenic PAHs depends in which state they enter through our respiratory system. Particulate PAHs deposits in the lungs exert their carcinogenicity over longer period of time. To explore meteorological influence on carcinogenic risk seasonal variation of toxicity was also computed in bulk deposition.

Seasonal mean of total BaPq concentration in bulk deposition samples ranged between 1.0±1ng BaPq/ml during wet season to 2.3±4ng BaPq/ml during dry season (Table 4.5b). Among the individual PAH, BaA and BaP contribute maximum to total PAHs BaPq concentration. Thus, it may be infered that people were more prone to carcinogenic risk during dry season.

Table 4.5.b Seasonal mean toxicity of PAHs in terms of BaPeq concentration (ng/ml) in Guwahati

	Dry Season	Wet Season
Naph	0.04±0.02	0.02±0.01
Acy	0.002±0.003	0.0004±0.001
Acen	0.003±0.004	0.0003±0.0001
Flu	0.002±0.003	0.0002±0.0004
Phen	0.006±0.01	0.001±0.001
Anth	0.14±0.2	0.04±0.1
Flan	0.001±0.001	0.0002±0.0001
Pyr	0.002±0.003	0.0002±0.0002
BaA	1.5±3	1.0±0.7
Chry	0.14±0.2	0.14±0.2
BbF	0.01±0.01	0.01±0.004
BkF	0.01±0.01	0.002±0.002
BaP	0.24±0.3	0.05±0.05
DBA	0.24±0.4	0.05±0.04
BgP	0.002±0.002	0.002±0.002
IP	0.06±0.1	0.05±0 04
∑PAHs	2.3±4	1.0±1.0

4.1.5 Influence of meteorology on PAHs

Table 4.6 illustrates significant correlation of PAHs with various meteorological parameters. It was observed that Naph and Phen showed significant negative correlation with mean temperature, while BbF and DBA displayed significant negative correlation with mean humidity. Naph, Acy, Phen and ∑PAHs exhibited good negative correlation with mean wind speed, while Acy, Acen, BaA, BaP and ∑PAHs showed significant negative correlation with wind direction. Thus LMWPAHs showing negative correlation with mean temperature while HMWPAHs with relative humidity.

Individual PAH compounds behave differentially under different meteorological and climatic conditions depending upon their molecular weight and structure. It has been reported that temperature have significant impact on the dispersion of certain category of PAH compounds having low molecular weight [308]. According to Stronguilo et al. [309] LMWPAHs with higher vapour pressure and higher level of solubility of LMWPAHs become more susceptible to volatilization at room temperature (20°C). Yamasaki et al. [310] and Pankow et al. [308] have also reported that meteorological parameters, especially, temperature and relative humidity play a significant role in dissipation of PAHs. Pankow et al. [308] also observed that gas/particle partitioning process is negatively dependent on relative humidity over the range of 40% ≤ RH ≤ 95%, for some PAHs and groups of PAHs in case of urban particulate matter.

Significant negative relationship of PAHs with wind speed was an indicator of high dispersion of atmospheric PAHs with increasing wind speed. The negative correlation of PAHs with wind direction was an evidence of PAHs deposition mainly through northerly or north-easterly wind, especially during dry season of the year. As the wind direction was shifting towards southerly or south-westerly which was mainly prevalent during wet season of the sampling year, deposition of PAHs was found to be decreased. This phenomenon is also illustrated through the Figure 4.4.

Table 4.6 Correlations of PAHs with various meteorological parameters

	Mean T	Mean_RH	Mean_WS	Mean_WD
Naph	-0.71**	0.33	-0.71**	-0.31
Acy	-0.45	0.21	-0.68**	-.61*
Acen	-0.37	-0.31	-0.49	-.56*
Flu	-0.27	0.19	-0.48	-0.43
Phen	-.60*	0.09	-0.55*	-0.42
Anth	-0.34	-0.13	-0.28	-0.36
Flan	-0.29	0.03	-0.31	-0.37
Pyr	-0.43	0.09	-0.44	-0.41
BaA	-0.25	0.05	-0.55	-.65*
Chry	-0.06	-0.11	-0.32	-0.42
BbF	-0.04	-0.54*	-0.11	-0.22
BkF	-0.25	-0.53	-0.29	-0.39
BaP	-0.33	-0.12	-0.55	-.71**
DBA	-0.13	-.60*	-0.1	-0.35
BgP	-0.28	-0.18	-0.27	-0.3
IP	-0.07	0.13	-0.3	-0.41
∑PAHs	-0.47	0.07	-0.57*	-0.53*

**Correlation is significant at 0.01 level (2-tailed)

*Correlation is significant at 0.05 level (2-tailed)

(T=Temperature, RH=Relative Humidity, WS=Wind Speed, WD=Wind Direction)

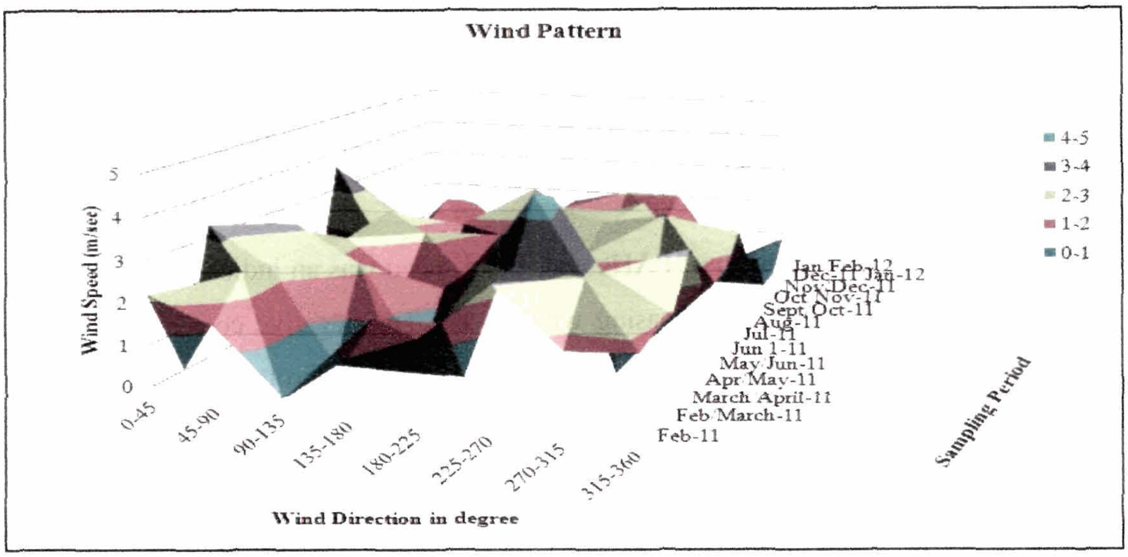


Figure 4.4: Wind pattern during sampling period.

Based on these observations, relationship of PAHs with temperature and relative humidity was tried to establish in this study. Relationship of logarithmic ∑PAHs, ∑LMWPAHs and ∑HMWPAHs with temperature [maximum temperature (T^{max}), mean temperature (T^{mean}) and diurnal temperature range (DTR)] and relative humidity [maximum relative humidity (RH^{max}), mean relative humidity (RH^{mean}) and diurnal relative humidity range (DHR)] is plotted which is shown in Figure 4.4.a, 4.4.b and 4.4.c respectively. ∑PAHs and ∑LMWPAHs showed significant negative relationship with T^{max} (r^2=0.32 and r^2=0.36 respectively) and T^{mean} (r^2=0.4 and r^2=0.4 respectively). However, positive relationship was observed for DTR with r^2 value of 0.36 and 0.24 for ∑PAHs and ∑LMWPAHs respectively. Positive relationship was revealed for both ∑PAHs and ∑LMWPAHs with DHR having r^2 value of 0.3 and 0.32 respectively. However, in case of HMWPAHs no such relationship has been observed with T^{max}, T^{mean}, RH^{max} and RH^{mean}. However, HMWPAHs was found to exhibit positive relationship DTR and DHR with r^2 value of 0.22 and 0.20 respectively.

From the above relationship it is established that LMWPAHs were mostly influenced by temperature, which is not the case for HMWPAHs. At ambient air temperature, LMWPAHs (2- to 4-ring PAHs) mostly occurred in vapour phase while HMWPAHs (5 or more rings) are associated with particulate phase [311] as we have already mentioned that LMWPAHs with high vapour pressure are more prone to volatilization than HMWPAHs [309, 312-313]. Vapour pressure controlling volatilization has been found to be regulated by temperature, humidity and wind speed. PAHs volatilization increases from soil, atmospheric particles, water and vegetation with rise of temperature [81, 101]. Thus, LMWPAHs volatilization is more dependent upon air temperature than HMWPAHs. According to Sofuoglu et al. [81] temperature deviation accounted for gas phase variability of 23-49% in case of Acen and Chry, while only 1-6% for HMWPAHs. Thus, the relationship of LMWPAHs with temperature in the present study could be attributed to temperature dependent scavenging process for the LMWPAHs as documented by Ollivon et al. [118]. Moreover, in the present study, maximum temperature values were found to have more influence on LMWPAHs. Hassan and Khoder [314] in their study, also, reported similar trend of decrease in total PAHs concentration in particulate and gaseous phase with increasing temperature. Tsapakis and Stephanow, [315], Cincinelli et al. [316] also showed similar studies.

Present study also revealed an increase of PAHs concentration with increase of diurnal variation of temperature. The LMWPAHs are often found to be influenced by seasonal and diurnal changes with long range transport and deposition on a surface through continuous air-surface exchange by means of succeeded cycles of deposition and re-evaporation as reported by Yamasaki et al. [310], Hoff and Chan [317], Keller and Bidleman [318]. Higher gas phase percentages were also reported due to increase in temperature in summer than that in winter which increases vapour pressure of LMWPAHs [127, 319]. This could be applicable in case of high diurnal temperature deviations also. Murray et al. [320] showed that for a temperature change of 20 °C there is approximately an order of magnitude change in the vapour pressure of PAHs.

Positive effect of diurnal variation of relative humidity was also found on PAHs concentrations. Relative humidity in the study area was found to rise upto 100%. Thibodeaux et al. [102] reported an increase in absorption of semivolatile organic compounds as relative humidity approaches 100%. Such increase at very high relative humidity is due to partitioning into the liquid or nearly-liquid phase when the gas phase is nearly saturated with water.

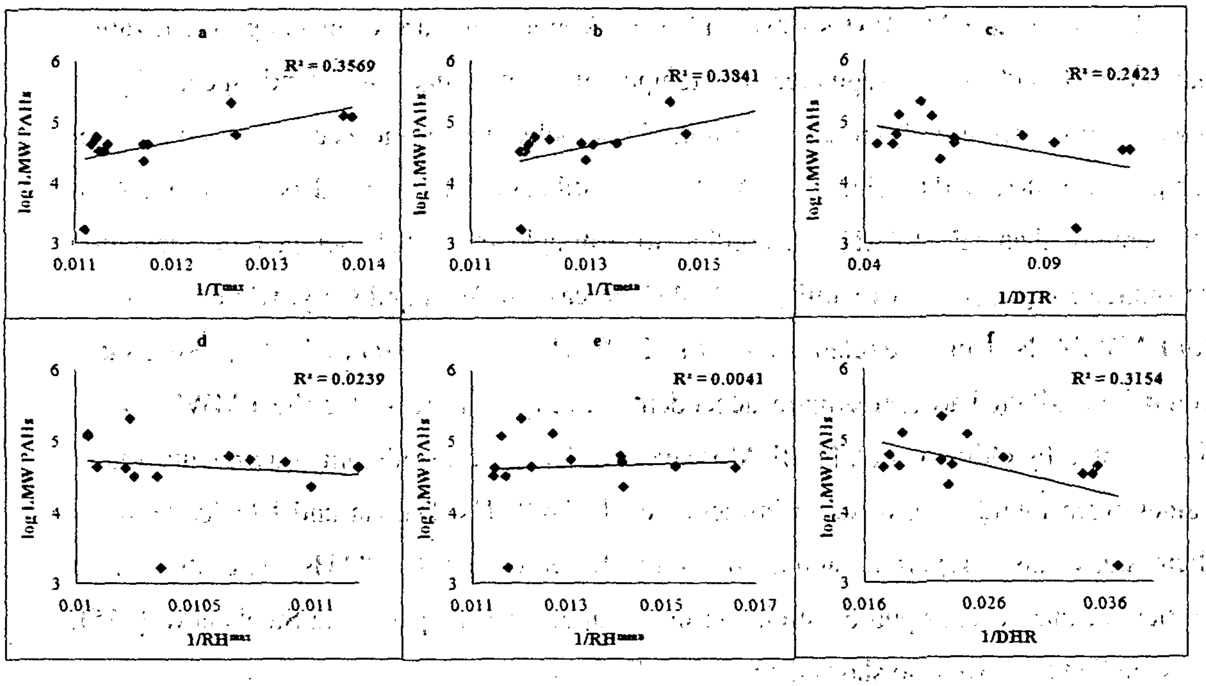


Figure 4.4.a: Regression analysis of LMWPAHs concentrations in bulk deposition with maximum temperature (T^{max}), mean temperature (T^{mean}), diurnal temperature range (DTR), maximum relative humidity (RH^{max}), mean relative humidity (RH^{mean}) and diurnal relative humidity range (DHR).

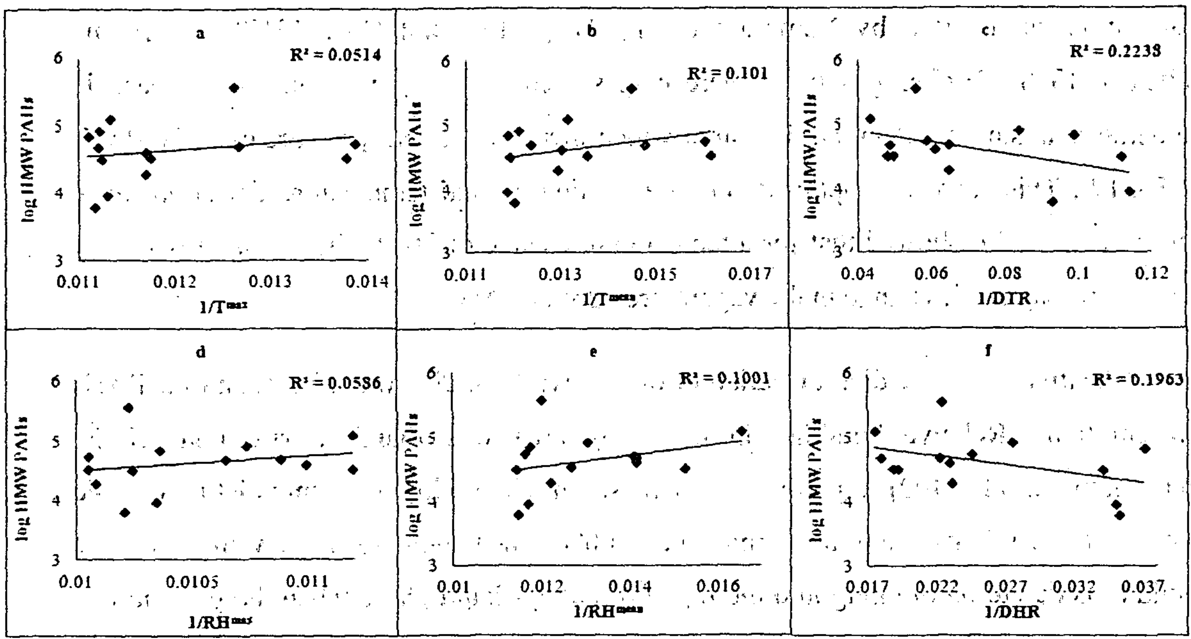


Figure 4.4.b: Regression analysis of HMWPAHs concentrations in bulk deposition with maximum temperature (T^{max}), mean temperature (T^{mean}), diurnal temperature range (DTR), maximum relative humidity (RH^{max}), mean relative humidity (RH^{mean}) and diurnal relative humidity range (DHR).

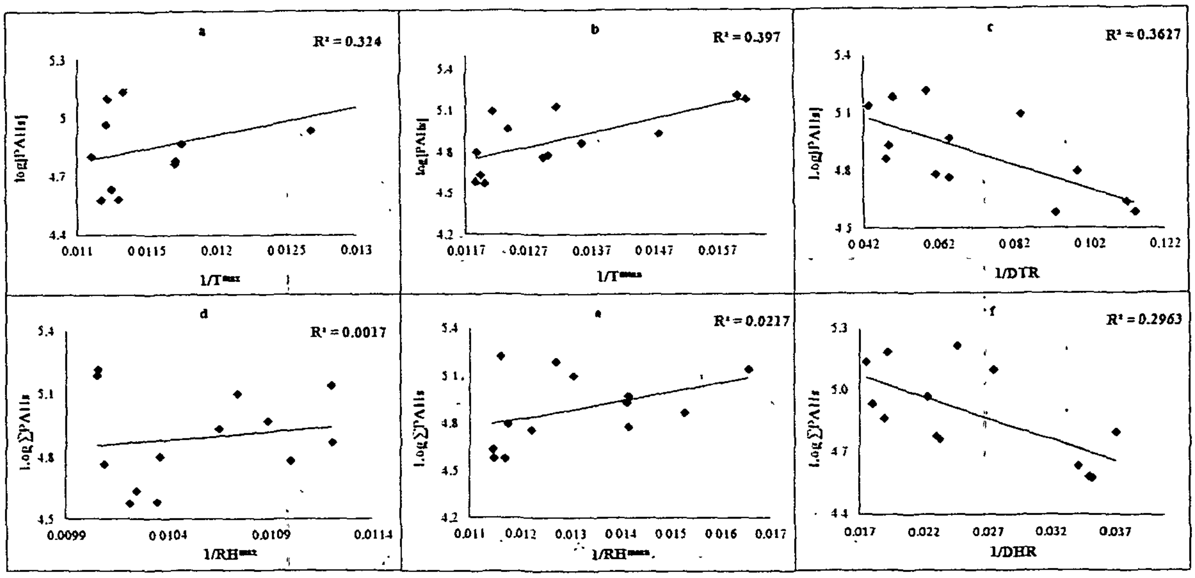


Figure 4.4.c: Regression analysis of ∑PAHs concentrations in bulk deposition with maximum temperature (T^{max}), mean temperature (T^{mean}), diurnal temperature range (DTR), maximum relative humidity (RH^{max}), mean relative humidity (RH^{mean}) and diurnal relative humidity range (DHR).

4.1.6 Bulk Deposition Mass Flux

Site-wise variations of PAHs flux are shown in Table 4.7. Monthly variation of mass flux of ∑PAHs in Guwahati city has been illustrated in Figure 4.5. Variations of 16PAHs flux are also shown in Table 4.8. The flux of ∑PAHs ranged between 63.5µg/m^2 and 10517µg/m^2 (Table 4.8). The mean ∑PAHs flux was found to be maximum at S1 (1802±2685µg/m^2) and minimum at site S3 (880±813 µg/m^2). The deposition rate of BaP ranged from BDL to 11.4µg/m^2 and mean concentration was observed to be maximum at site S3 (traffic site). Moreover, Mean ∑PAHs flux was found to be maximum (4130±3985µg/m^2) during the month of May/Jun-11 and minimum (223±142 µg/m^2) during Jan/Feb-12 (Table 4.8). Site-wise variation of daily PAHs flux is shown in Table 4.9; the value of which was also maximum at S1. Daily flux of 16PAHs is also shown in Table 4.10. Daily ∑PAHs flux varied from 2.1-401.4µg/m^2/day and the same for BaP was BDL-0.24µg/m^2/day (Table 4.10).

The industrial site (S1) witnessed maximum PAHs flux among all the sites. For BaP maximum flux was observed at the traffic site (S3). Furthermore, wet season experienced high mass flux, while minimum was during dry season of the sampling year.

Table 4.7 Mean and range of PAHs flux (μg/m^2) at different sampling sites (S1-S5) of Guwahati city

	S1		S2		S3		S4		S5	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Naph	603±503	BDL-1771	703±635	BDL-1723.6	671±715	BDL-2407.7	516.8±640	BDL-2196.5	876±989	BDL-2411.2
Acy	23±47	BDL-154.6	6±5	BDL-14	10±11	BDL-37.7	10±14	BDL-49.3	43.2±83	BDL-244.9
Acen	37±87	0.2-323.9	15±17	1.4-60	10±17	BDL-61.8	10.7±15	BDL-51.2	26.6±38	BDL-124.8
Flu	13.5±35	BDL-124	43±109	BDL-330.5	3.4±2	BDL-6.8	2.9±3	BDL-8.0	7.9±13	BDL-39.4
Phen	46±74	0.5-283.7	30±28	BDL-88.3	39±42	BDL-149.9	24±20	BDL-56.7	84.8±148	BDL-465.4
Anth	6.7±11	BDL-39.5	9.5±19	BDL-51.8	4.4±5	BDL-13.5	4.9±42	BDL-19.2	8.6±12	BDL-34.9
Flan	270±541	BDL-1776	38±53	BDL-141.1	70.8±80	BDL-180	41.4±43	BDL-132.0	126.8±142	BDL-374.8
Pyr	12±17	BDL-52	9.5±10	BDL-29.3	4.4±3	BDL-10.2	9.1±9	BDL-30.1	32.7±61	BDL-201.1
BaA	671.5±1623	BDL-5484.8	554±1005	BDL-2346.4	48.6±33	BDL-100.2	65.8±91	BDL-244.8	95.9±103	BDL-287.2
Chry	348±456	BDL-1371	291±493	BDL-1614.4	109±91	BDL-285.7	1102±2048	BDL-5243.8	177±199	BDL-552.9
BbF	2±3	BDL-8.6	4.3±11	BDL-32.6	1±1	BDL-3.1	3.2±6	BDL-16	3.2±6	BDL-18.8
BkF	1.2±2	BDL-6.4	1±2	BDL-7.0	0.6±1	BDL-2.4	1.2±2	BDL-5.0	1.2±2	BDL-4.8
BaP	2.3±1	BDL-4	1±2	BDL-4.8	2.5±3	BDL-6.8	2.4±4	BDL-10.9	2.4±5	BDL-11.4
DBA	5±7.2	BDL-22.6	5±6	BDL-18.5	4.4±7	BDL-20.8	1.6±3	BDL-7.3	4.3±6	BDL-12.6
BgP	2±3	BDL-9.3	3±3	BDL-7.4	6±15	BDL-41.9	4.3±8	BDL-22	1.9±2	BDL-4.5
IP	16.4±30	BDL-81.2	31±44	BDL-62.1	6±5	BDL-14.2	23.3±36	BDL-97.5	8.2±7	BDL-20.8
∑PAHs	1802±2685	124.4-10517	1151±1104	63.5-3270.6	880.4±813	116.4-2825.8	1556±1856.4	185.3-5433.3	1173.9±1357	114.4-4431.1

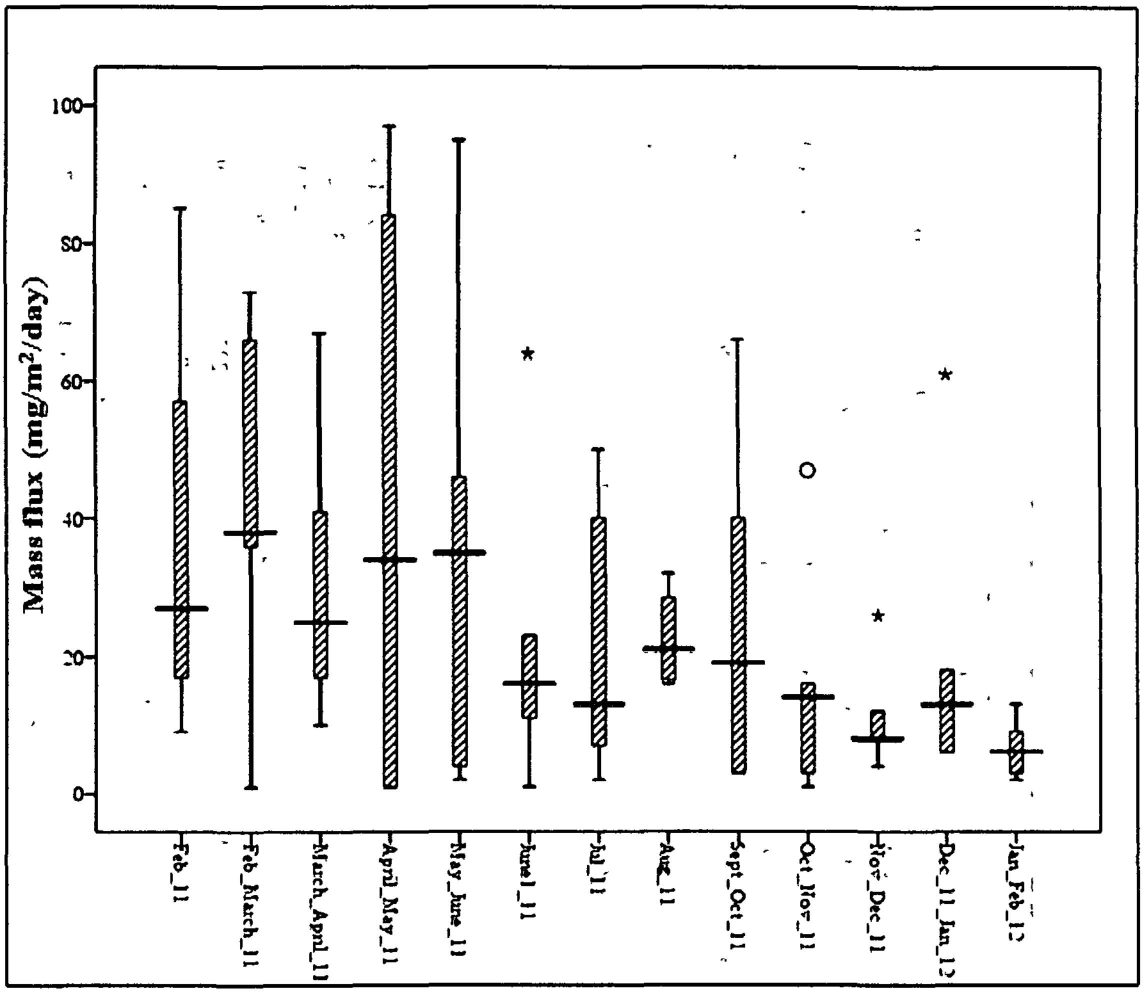


Figure 4.5: Mass flux (mg/m^2/day) of ∑PAHs in Guwahati during sampling periods

Table 4.8 Mean of PAHs flux (µg/m^2) during different sampling periods in Guwahati

	Naph	Acy	Acen	Flu	Phen	Anth	Flan	Pyr	BaA	Chry
Feb-11	263.3±366	11 2±7	86±159	87.3±162	99.4±126	14.8±17	219.2±178	41,7±32	29±36	11.9±3
	BDL-522.1	2.8-19.9	0.9-323.9	1.3-330.5	9.3-283.7	0.2-39.5	10.6-374.8	11,7-81 8	BDL-54.7	BDL-14.3
Feb/March-11	1044.8±457	10.4±2	38.5±24	3.5±2	13.6±10	4.5±4	137.1±77	4.7±3		600.8±600
	319.5-1487	BDL-14	BDL-61.8	1.7-6.3	2.1-26.8	BDL-8.7	BDL-221.9	1.1-8.7	BDL-19.2	48-1614.4
March/April-11	291.2±299	7.1±6	7.6±8	1.3±1	10.3±7	5.1±6	108.3±34	0.9±1	55.2±59	391.2±469
	4.7-762.8	BDL-14	BDL-2.0	0.6-2.4	4.5-19	0.7-9.6	77.3-141.1	0.3-2.3	5.6-130.7	154.4-1230
April/May-11	1151.4±795	3.2±3	15.9±12	2±1	87.3±128	10±14		28.4±31	566.9±998	342.8±578
	393-2196.5	BDL-5.4	4.5-35.5	0.04-3.56	23.4-317	BDL-26.5	BDL-192.3	0.8-78.2	37-2346.4	15-1371
May/Jun-11	1194.3±714	54.1±87	11.7±11	42.4±71	59.2±79	16.8±24	596.1±1022	3.0±1		1340.1±2155
	297.4-2030	0.8-154.6	1-23.5	0.1-124	7.1-149.9	0.9-51.8	0.6-1776.2	BDL-4.4	BDL-5485	19.7-5119.5
Jun1-11	601.3±1019	10.1±6	13.7±20	2.0±1	28.3±27	1.6±2	70.9±62	10,7±17	538.3±620	120.8±86
	15-2407.8	2.6-18 3	1.7-49.3	0.8-2.8	5.7-69.4	0.7±4	4.2-171.6	0.6-40.7	BDL-976.4	BDL-242.7
Jul-11		2.5±2	3.1±3	2.7±1	27.9±22	5.7±3	15.8±15	7.5±5	236.8±321	1350.3±2193
	BDL	0.5-4.5	0.2-6.8	BDL-4.2	3.5-46.4	1.7-8.6	0.6-32.2	0.7-12.7	10.1-463.5	52.3-5243.8
Aug-11	753.3±288	11.7±9	6.9±8	5.8±3	37 3±29	6.8±5		3.7±4		65.7±27
	449-1105.5	3.8-22	0.9-16.2	2.6-8.0	10.1-70.1	2.1-11.1	BDL-17.1	0.1-8.7	BDL-87.4	49.7-106.3
Sept/Oct-11	977.4±893	25.8±22	23.1±27	6.1±5	35.6±21	6.5±8		5.7±7		37.2±27
	BDL-2140	7.5-49.4	2.6-54	1.0-9.5	1.1-56.4	0.1-19.2	BDL-91.1	0.1-16.6	BDL	4.9-62.4
Oct/Nov-11	849.5±928	55.6±106	39.3±54	28.8±24	121±195	11.4±16	29.2±15	47.6±86	169.9±166	206.6±239
	88.8-2411.2	1.5-244.9	1.4-124.8	1.5-45.6	4.1-465.4	0.3-34.9	18.7-39.7	2.4-201.1	52.6-287.2	12-552.9
Nov/Dec-11	94.3±67	8.3±10	12.2±5	3.7±3	22.6±19	2.3±2	60 8±57	8.7±7	57.2±70	63.5±33
	27.6-180.6	1.2-23.9	2.9-16.3	0.9-7.9	1.4-51.2	0.7-5.1	3.9-152.8	0.7-18.7	4.7-178.5	27.5-103.9
Dec-11/Jan-12	465.9±711	18.9±27	9.3±10	2.3±1	36.2±25	1±1	17.3±15	7.8±3	89.2±76	78.4±81
	63.7-1723.6	BDL-38	0.1-19.9	0.7-4	6.5-66.6	0.2-2	BDL-31.1	3.7-10.3	28.8-218.4	4.5-167.6
Jan/Feb-12	174.4±133	1.6±1	3.8±4	0.2±0.2	15 9±27	0.2±0.1	2.7±2	1.9±3	22.2±10	10.2±9
	14.4-374.2	0.1-3.5	0.9-9.6	0.1-0.5	0.5-56.7	0.1-0.3	1.1-5.2	0.2-6.5	11.8-36.9	1.9-23.1

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	BbF	**BkF**	**BaP**	**DBA**	**BgP**	**IP**	**∑16PAHs**
Feb-11					0.7±0.4		713.9±620
	BDL-1.4	BDL-0.1	BDL-0.3	BDL-5.5	BDL-1.2	BDL	185.3-1609
Feb/March-11	4.9±8	4.4±4			23.1±18	13.4±3	1372±1118
	BDL-16	BDL-7.0	BDL-1	BDL-5.3	BDL-41.9	BDL-15.	266-3008
March/April-11						10.7±21	847.6±587
	BDL-0.9	BDL-0.4	BDL	BDL	BDL-1.2	BDL-21	283.6-1759
April/May-11	1.4±1	1.7±1	3.3±2	6.9±4	3.5±4	16.7±9	2264.4±907
	BDL-2.7	BDL-2.6	BDL-4.8	BDl-12.6	BDL-7.4	BDL-23	820-3271
May/Jun-11	1.9±3	1.1±1	1.8±1		1.2±1	28.4±46	4130.3±3985
	0.2-6.1	0.1-2.7	0.6-3	BDL-21	0.8-1.7	0.4-81.2	991.6-10517
Jun1-11	0.8±1	0.5±1		4±5			1050.5±1084
	BDL-1.5	BDL-1.0	BDL-0.1	0.3-7.7	BDL-0.1	BDL	241.3-2825.8
Jul-11	3.4±4	1.4±2	4.1±5	9.9±9	4.5±5	36.1±29	1547.1±2189
	0.9-8.6	0.1-5	0.4-10.9	2.5-22.6	0.2-9.3	BDL-62	149.3-5403.3
Aug-11	1.1±1	0.2±0.02	3.6±2		1.9±2	36.7±53	944.8±304
	0.7-1.9	0.1-0.2	1.6-6.3	BDL-5.4	0.9-3	1.4-97.5	684-1338.3
Sept/Oct-11	6.2±9	0.4±0.1	0.9±1	0.3±0.1	0.2±0.2	8.2±6	941.1±948
	0.4-18.8	0.3-0.4	0.1-2.5	0.1-0.4	BDL-0.4	1.7-14.2	124.4-2333.3
Oct/Nov-11	9.6±15	2.8±3	3.3±5	4.6±8	2.1±2	1.1±1	1444.6±1756.2
	BDL-33	0.01-6.4	0.05-11	0.1-18.5	BDL-4.5	BDL-2	116.4-4431.1
Nov/Dec-11	0.1±0.1	0.2±0.1	1.1±2	0.7±1	0.9±1	2.5±3	339±240
	0.01-0.2	0.1-0.3	0.1-4	0.04-1.9	0.03-2.5	0.3-5.9	114.4-734
Dec-11/Jan-12	0.4±0.3	0.4±1	2±1	0.6±1	0.2±0.2	1.2±1	694.7±761
	0.1-0.7	0.1-1.6	1-3.5	0.3-1	0.03-0.3	0.6-2.2	204.1-2024.4
Jan/Feb-12	0.1±0.1	0.2±0.3	0.2±0.1	0.4±0.3	0.2±0.2	0.6±0.1	223.2±142
	0.02-0.2	0.02-0.7	0.1-0.3	0.1-0.8	0.02-0.4	0.6-0.7	63.5-412.7

Table 4.9 Mean of daily PAHs flux (μg/m^2/day) in sampling sites (S1-S5) of Guwahati city

	S1		S2		S3		S4		S5	
Naph	21.6±18	BDL-67.6	24.4±21	BDL-52.4	25.4±33	BDL-115	17.5±24	BDL-84	28.9±33	BDL-77.3
Acy	0.9±2	BDL-6.0	0.2±0.2	BDL-0.7	0.4±0.4	BDL-1.15	0.3±0.4	BDL-1.4	1.3±2	BDL-7.0
Acen	1.8±5	0.01-17.3	0.5±1	0.05-1.8	0.4±1	0.02-2.1	0.4±0.4	BDL-1.4	0.9±1	BDL-3.6
Flu	0.5±1	BDL-4.7	2.2±6	BDL-17.5	0.1±0.1	BDL-0.2	0.1±0.1	BDL-0.3	0.3±0.4	BDL-1.1
Phen	2±4	0.02-15.2	1.1±1	BDL-4.0	1.3±2	0.1-5.4	0.8±1	BDL-2	3.0±5	BDL-13.4
Anth	0.3±1	BDL-2.1	0.4±1	BDL-2.0	0.2±0.2	BDL-0.5	0.2±0.2	BDL-0.6	0.3±0.4	BDL-1.1
Flan	10.8±21	BDL-67.8	1.5±2	BDL-5.5	2.8±3	BDL-8.2	2±2	BDL-6.6	5.5±7	BDL-18.7
Pyr	0.5±1	BDL-2.8	0.4±0.4	BDL-1.2	0.2±0.1	0.02-0.5	0.4±0.4	BDL-1.2	1.2±2	BDL-5.8
BaA	26.7±62	BDL-209.4	21.5±40	BDL-93.6	2±2	BDL-4.8	2.4±4	BDL-9.4	3.2±3	BDL-8.3
Chry	13.4±18	BDL-54.8	11±18	BDL-55.7	4.1±4	0.25-11	47.5±91	BDL-250.5	6.2±7	BDL-17.1
BbF	0.1±0.1	BDL-0 4	0.1±0.3	BDL-1.0	0.04±0.04	BDL-0.15	0.1±0.2	BDL-0.6	0.1±0.2	BDL-0.54
BkF	0.04±0.1	BDL-0.2	0.1±0.1	BDL-0.2	0.02±0.03	BDL-0.1	0.1±0.1	BDL-0.24	0.04±0.1	BDL-0 14
BaP	0.1±0.1	BDL-0 14	0.04±0.1	BDL-0.2	0.09±0.1	BDL-0.3	0.1±0.2	BDL-0.5	0.1±0.1	BDL-0.3
DBA	0.2±0.4	BDL-1.1	0.2±0.2	BDL-0.6	0.2±0.3	BDL-0.75	0.1±0.2	BDL-0.35	0.2±0.2	BDL-0.5
BgP	0.1±0.1	BDL-0.44	0.1±0.1	BDL-0.3	0.2±1	BDL-1.5	0.2±0.3	BDL-0.8	0.1±0.1	BDL-0.1
IP	0.6±1.1	BDL-3.1	1.5±2	BDL-3.0	0.2±0.2	BDL-0.4	0.8±1	BDL-2.4	0.3±0.3	BDL-0.8
∑PAHs	69.6±103	3.6-401.4	42.6±40	2.1-130.4	33.2±37	3.5-134.9	62±83	6-258	39 9±43	4-127.4

Table 4.10 Mean of daily PAHs flux (µg/m^2/day) during different sampling periods in Guwahati

	Naph	Acy	Acen	Flu	Phen	Anth	Flan	Pyr	BaA	Chry
Feb-11	14.1±20	0.6±0.4	4.6±9	4.6±9	5.3±7	0.8±1	11.3±9	2.1±2	1.5±2	0.6±0.2
	BDL-27.9	0.1-1	0.04-17.3	0.1-17.5	0.5-15.2	0.01-2.1	0.6-19.8	0.6-4.1	BDL-2.7	BDL-0.8
Feb/March-11	36.1±16	0.4±0.1	1.3±1	0.1±0.1	0.5±0.3	0.2±0.2	4.7±3	0.2±0.1		20.7±21
	11.1-51.3	BDL-0.5	BDL-2.1	0.01-0.2	0.1-0.9	BDL-0.3	BDL-7.7	BDL-0.3	BDL-0.7	1.7-55.7
March/April-11	11.2±12	0.3±0.2	0.3±0.3	0.1±0.03	0.4±0.3	0.2±0.2	4.2±1	0.04±0.03	2.1±2	15.1±18
	0.2-29.3	BDL-0.6	0.1-0.8	BDL-0.1	0.2-0.7	BDL-0.4	BDL-5.5	0.01-0.1	BDL-5.1	6.0-47.4
April/May-11	45.5±30	0.1±0.1	0.6±1	0.1±0.1	3.5±5	0.4±1		1.1±1	22.6±40	13.7±23
	15.7-83.9	BDL-0.2	0.2-1.4	0.001-0.1	0.9-12.7	BDL-1.1	BDL-7.7	BDL-3.2	1.5-93.6	0.6-54.8
May/Jun-11	45.3±27	2.1±3	0.5±0.4	1.6±3	2.2±3	0.6±1	22.8±39	0.1±0.04		53±86
	11.9-77.3	BDL-5.9	BDL-0.9	BDL-4.7	BDL-5.4	BDL-2	BDL-67.8	BDL-0.2	BDL-209.4	0.8-204.7
Jun1-11	28.7±49	0.5±0.3	0.7±1	0.1±0.04	1.3±1.3	0.1±0.1	3.4±3	0.5±1	25.7±30	5.8±4
	0.7-115	BDL-0.9	0.1-2.3	0.04-0.13	0.3-3.3	BDL-0.2	0.2-8.2	0.03-1.9	BDL-46.5	BDL-11.5
Jul-11		0.1±0.1	0.2±0.1	0.1±0.1	1.4±1	0.3±0.1	0.8±1	0.4±0.2	11.3±15	64.5±105
	BDL	BDL-0.2	0.01-0.3	BDL-0.2	0.2-2.3	0.1-0.4	BDL-1.6	0.04-0.6	BDL-22.1	2.6-250.5
Aug-11	18.4±7	0.3±0.2	0.2±0.2	0.1±0.1	0.9±1	0.2±0.1		0.1±0.1		1.6±1
	10.9-27	BDL-0.5	BDL-0.4	BDL-0.2	0.3-1.7	0.1-0.3	BDL-0.4	0.003-0.2	BDL-2.1	1.2-2.6
Sept/Oct-11	27.7±25.4	0.7±1	0.7±1	0.2±0.1	1±1	0.2±0.2		0.2±0.2		1.1±1
	BDL-61.2	0.2-1.4	0.1-1.6	BDL-0.3	0.03-1.6	0.001-0.5	BDL-2.5	0.003-0.5	BDL	BDL-1.8
Oct/Nov-11	24.7±27	1.6±3	1.2±2	0.9±1	3.5±6	0.3±1	0.8±0.4	1.4±3	4.9±5	6±7
	2.7-69.3	0.04-7	0.04-4.0	BDL-1.4	0.1-13.4	BDL-1	BDL-1.1	0.1-5.8	BDL-8.3	0.4-16
Nov/Dec-11	3.2±2	0.3±0.3	0.4±0.2	0.1±0.1	0.8±1	0.1±0.1	2.1±2	0.3±0.2	2±3	2.2±1
	1.0-6.5	0.04-0.9	0.1-0.6	0.03-0.3	0.1-1.8	0.02-0.2	0.1-5.5	0.02-0.7	0.2-6.4	1-3.7
Dec-11/Jan-12	14.2±22	0.6±1	0.3±0.3	0.07±0.04	1.1±1	0.03±0.03	0.5±1	0.2±0.1	2.7±2	2.4±3
	1.9-52.3	BDL-1.1	0.003-0.6	BDL-0.1	0.2-2	BDL-0.06	BDL-0.9	0.1-0.3	0.9-6.6	BDL-5.1
Jan/Feb-12	5.6±4.3	0.05±0.1	0.1±0.1	0.01±0.01	0.5±1	0.005±0.004	0.09±0.1	0.06±0.1	0.7±0.4	0.3±0.3
	0.5-12.1	BDL-0.1	0.03-0.3	BDL-0.02	BDL-1.8	BDL-0.01	BDL-0.2	BDL-0.2	BDL-1.2	BDL-0.7

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	BbF	BkF	BaP	DBA	BgP	IP	∑16PAHs
Feb-11					0.04±0.02		37.4±33
	BDL-0.1	BDL	BDL-0.01	BDL-0.3	BDL-0.06	BDL	9.3-85.9
Feb/March-11	0.2±0.3	0.2±0.1			0.8±1	0.5±0.1	63.8±28
	BDL-0.6	BDL-0.2	BDL-0.03	BDL-0.2	BDL-1.5	BDL-0.5	36.8-103.7
March/April-11						0.4±0.4	32.7±23
	BDL-0.03	BDL-0.01	BDL	BDL	BDL-0.1	0.2-0.8	10.9-67.8
April/May-11	0.1±0.04	0.1±0.04	0.1±0.1	0.3±0.2	0.1±0.1	0.7±0.4	90±35
	BDL-0.1	BDL-0.1	BDL-0.2	BDL-0.5	BDL-0.3	BDL-0.9	34.2-130.4
May/Jun-11	0.1±0.1	0.04±0.1	0.1±0.04		0.04±0.02	1.1±2	159.1±153
	BDL-0.2	BDL-0.1	BDL-0.1	BDL-0.8	BDL-0.1	BDL-3.1	35.7-401.4
Jun1-11	0.04±0.1	0.03±0.03		0.2±0.2			50.1±52
	BDL-0.1	BDL-0.05	BDL-0.01	BDL-0.4	BDL-0.003	BDL	11.5-138.9
Jul-11	0.2±0.2	0.1±0.1	0.2±0.2	0.5±0 4	0.2±0.2	1.7±1	74±105
	BDL-0.4	BDL-0 2	0.02-0.5	BDL-1.1	BDL-0.4	BDL-3	7.4-258.1
Aug-11	0.03±0.01	0.004±0.001	0.1±0.1		0.1±0.04	0.9±1	23.1±8
	0.02-0.1	BDL-0.004	BDL-0.2	BDL-0.1	BDL-0.1	BDL-2.4	16.7-32.7
Sept/Oct-11	0.2±0.2	0 01±0.001	0.03±0.04	0.01±0.004	0.01±0 01	0.2±0.2	26.7±27
	BDL-0.5	BDL-0.01	BDL-0.1	BDL-0.01	BDL-0.01	BDL-0.4	3.6-66.7
Oct/Nov-11	0.3±1	0.1±0.1	0.1±0.2	0.1±0.2	0.06±0.1	0.03±0.03	42±51
	BDL-1.0	BDL-0 2	BDL-0.3	0.004-0.6	BDL-0.1	BDL-0.05	3.5-127.4
Nov/Dec-11	0.003±0.003	0.01±0.003	0.04±0.1	0.02±0.03	0.03±0.04	0.01±0.01	11.8±9
	0.0003-0.001	0.003-0.01	0.003-0.1	0.002-0.07	BDL-0.09	BDL-0.2	4.1-26.3
Dec-11/Jan-12	0.01±0.01	0.01±0.02	0.06±0.04	0.02±0.01	0.005±0.01	0.04±0.03	21.2±23
	BDL-0.02	0.002-0.05	BDL-0.1	BDL-0.03	BDL-0.01	BDL-0.07	6.2-61.5
Jan/Feb-12	0.003±0.003	0.01±001	0.01±0.004	0.01±0.01	0.005±0.01	0.02±0.002	7.2±5
	BDL-0.001	BDL-0.02	BDL-0.01	BDL-0.03	BDL-0.01	BDL-0.02	2.1-13.3

4.1.7 PAHs Ratios and Source Identification

To discriminate the origin of PAHs, ratio of the compounds provide accurate and reliable diagnostic tool [202, 321]. Site-wise diagnostic ratios are shown in Table 4.11. Anth/(Anth+Phen) and Flan/(Flan+Pyr) ratios of >0.1 and >0.5 respectively indicate pyrolytic origin of PAHs [193]. Mean Anth/(Anth+Phen) and Flan/(Flan+Pyr) ratios of the present study ranged from 0.14±0.1 to 0.20±0.2 and 0.73±0.2 to 0.82±0.3 respectively indicating pyrogenic origin of PAHs. Moreover, C*PAHs/$\sum$PAHs ~1 (C*PAHs=Flu+Pyr+BaA+Chry+BbF+BkF+BaP+IP+BgP) implies for combustion as the source of PAHs at site S2 [145, 200, 217-220]. C*PAHs/$\sum$PAHs ratio ranged from 0.327±0.2 to 0.532±0.2 indicated combustion origin of PAHs. Therefore, the PAHs in bulk deposition could be mainly from pyrogenic / combustion sources.

The ratio of IP/(IP+BgP) between 0.35 and 0.70 is considered as specific marker for diesel emission [201]. Mean of IP/(IP+BgP) ratio at S1, S2 and S5 site ranged from 0.699±0.3 to 0.713±0.3 indicating that diesel emission as the major source of PAHs. Again, the ratio at S4 of 0.664±0.3 showed signature of wood burning [201]. Phen/(Phen+Anth) ratio of 0.76 is considered as specific marker for coal combustion [322]. Phen/(Phen+Anth) ratio ranged from 0.797±0.2 to 0.860±0.1 respectively indicating coal combustion as one of PAHs source.

Table 4.11 Mean diagnostic ratios of PAHs in bulk deposition in Guwahati city

	IP/(IP+BgP)	Anth/(Anth+Phen)	Flan/(Flan+Pyr)	Phen/(Phen+Anth)	C*PAHs^a/$\sum$PAHs
S1	0.699±0.3	0.153±0.2	0.823±0.3	0.847±0.2	0.410±0.3
S2	0.557±0.3	0.197±0.2	0.734±0.2	0.803±0.2	0.532±0.2
S3	0.713±0.3	0.140±0.1	0.766±0.3	0.860±0.1	0.367±0.3
S4	0.664±0.3	0.203±0.2	0.757±0.3	0.797±0.2	0.426±0.3
S5	0.713±0.2	0.199±0.2	0.784±0.3	0.801±0.2	0.327±0.2

^{a}C*PAHs=Flu+Pyr+BaA+Chry+BbF+BkF+BaP+IP+BgP

To identify seasonal variation in the source of PAHs seasonal mean diagnostic ratios were also studied which is put up in Table 4.12. The recommended ratio for

IP/(IP+BgP) was found to be 0.56±0.3 and 0.70±0.3 during dry and wet season respectively. These ratios clearly indicated that coal combustion was the major source of PAHs emission during dry season [199], while diesel emission was the significant source during wet season [201].

Anth/(Anth+Phen) ratio was found to be higher than 0.1 in Guwahati during both dry (0.56±0.3) and wet season (0.61±0.2) signifying pyrolytic origin of PAHs. Phen/(Phen+Anth) ratio was observed to be less than 0.7 during dry (0.44±0.3) and wet season (0.39±0.2). This implies that biomass burning was a major source of PAHs bulk deposition during both the sampling season [210]. Moreover, Flu/(Flu+Pyr) ratio of 0.38±0.18 and 0.45±0.3 during dry and wet season indicated gasoline engine combustion as another source of PAHs during both the season [207]. It can be concluded that seasonality in source of emission was there in PAHs bulk deposition. Coal burning was observed to be one of the PAHs sources during dry season.

Table 4.12 Seasonal mean diagnostic ratio of PAHs in bulk deposition of Guwahati city

	IP/(Ip+BgP)	Phen/(Phen+Anth)	Anth/(Anth+Phen)	Flu/(Flu+Pyr)
Dry Season	0.56±0.3	0.44±0.3	0.56±0.3	0.38±0.2
Wet Season	0.70±0.3	0.39±0.2	0.61±0.2	0.45±0.3

4.1.8 Source Apportionment

To further demonstrate the sources, Principal Component Analysis (PCA) with varimax rotation was applied to 16 PAHs concentrations. PCA is a multivariate statistical tool to transform the original data set into a smaller one that account for most of the variance of the original data [140]. By extracting the eigenvalues and eigenvectors from the correlation matrix, principal factors with eigenvalues >1 were chosen. The initial eigenvalues extracted were 'cleaned up' by means of Varimax rotation with Keiser Normalization.

The 2 Principal Components (PC), accounting for ~93% of the total variance, along with their eigenvalues are shown in Table 4.13. PC 1, explained ~76% of total variance, had high loading of Naph, Acen, Flu, Phen, Anth, BaA, Chry, BbF, BkF, BaP, DBA, BgP and IP. BbF in addition to BgP, Flan and IP is an indication of diesel-engine vehicle [208, 323]. Also, Anth, Phen, Flan, BaA and Chry, are regarded as specific marker for coal combustion [208, 324] and Phen, Anth and Flan are typical indicator of wood combustion [208]. Thus, PC 1 could be attributed to a mixture of sources of combustion in origin - diesel, coal and wood burning.

PC 2 explained $\sim$16% of the total variance with high loadings of Acy, Flan and Pyr, which are typical markers of vehicular source [325]. Thus, PC2 could be attributed to mobile source like gasoline vehicles. Figure 4.6 shows the components in rotated space, which clearly depicts the two distinct components.

Table 4.13 Principal Component Analysis of PAHs concentration in bulk deposition of Guwahati city (extraction method: Principal Component Analysis (Rotation method: Varimax with Kaiser normalization), loading>0.7 are shown in bold)

Rotated Component Matrix		
	Component	
	1	2
Naph	**0.99**	0.08
Acy	0.10	**0.97**
Ace	**0.87**	0.30
Flu	**0.77**	0.22
Phen	**0.94**	0.33
Anth	**0.97**	0.21
Flan	0.36	**0.91**
Pyr	-0.02	**0.97**
BaA	**0.99**	0.09
Chry	**1.00**	0.07
BbF	**0.99**	0.07
BkF	**1.00**	0.06
BaP	**0.99**	0.14
DBA	**0.99**	0.09
BgP	**0.73**	0.13
IP	**1.00**	0.07
Eigen values	12.20	2.60
% of variance	76.26	16.27
Cumulative %	76.26	92.53

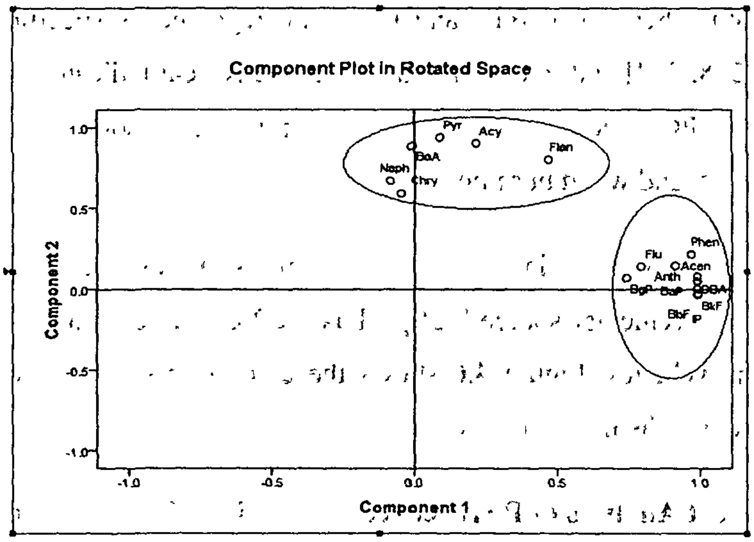


Figure 4.6: Principal Components plotted in the space - 2 components clearly distance from each other.

The principal aim of PCA/MLR is to determine percent contribution of different sources in a given environmental matrix. Multiple linear regression (MLR) analysis from extracted factors was conducted in accordance with Larsen and Baker [71]. For this analysis concentrations were converted into z-scores. Here, PCA factor scores were taken as independent variables and z-score values of sum PAH ($\sum PAH_i$) as dependent variable. In order of their individual simple correlation from maximum to lowest, each independent variable was added into regression stepwise. A default level of significance 0.05 was used.

Factor scores 1 and 2 corresponding source 1 (diesel + coal + wood combustion) and source 2 (gasoline vehicles) respectively, were regressed against the standard normalized deviate (z) of the sum of 16 PAHs. The resulting equations were obtained as

$Z = 0.991FS1 + 0.113FS2$ ($r^2 = 0.995$) --eq5

$\mathit{Mean\ contribution\ of\ source\ i}\ (\%) = 100 \times (\frac{Bi}{\sum Bi})$ --eq6

Where, Bi is the regression coefficient associated with factor score i (FSi).

Thus the mean contribution was ~90% for source 1 and ~10% for source 2 as illustrated in Figure 4.7.

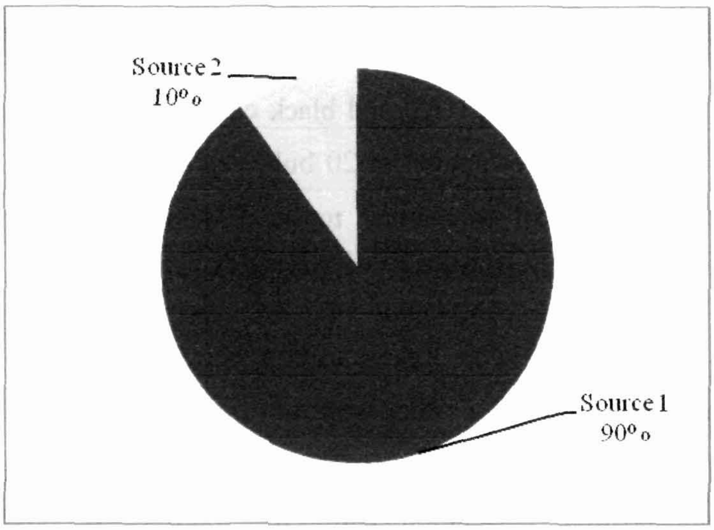


Figure 4.7: Source contribution of PAHs in atmospheric bulk deposition in urban Brahmaputra Valley –Source 1 (diesel, coal and wood combustion by industries, households, agriculture and transport) and Source 2 (gasoline powered vehicles).

In absence of an ordered public transport system in the region there is an exponential growth of 2-wheelers which run on gasoline. Though 2-stroke vehicles which are poor in terms of combustion efficiency have been completely phased out by 4-stroke vehicles, the number of 4-stroke vehicles leads to addition of large volume of PAHs in the atmosphere.

The maximum ∑PAHs concentration at S1 could be attributed to major industrial activities. Occurrence of 2 to 6 rings PAHs at S1 could also be attributed to their industrial location. Moreover, percentage contribution of CPAHs was found to be maximum (38%) at S1 with highest value of carcinogenic potential. The presence of various industrial unit at industrial site may have contributed to the high concentration of PAHs at this location having high carcinogenic potential. The Guwahati Refinery is situated close to the sampling location. Besides, there are coke industries, which produce carbon products, and processing industries in that area that could be possible contributor of PAH in bulk deposition. However, residential site with high concentrations could attribute to highway traffic which is not so far from the sampling area. Similar PAH concentration levels of forest site with that of traffic site is another major concern. However, level of carcinogenic potential at forest site was found to be minimum.

4.1.9 Analysis of Carbon

The mean concentration of organic carbon (OC) and black carbon (BC) in bulk deposition are shown in Table 4.14. BC was estimated in 20 bulk deposition samples. The overall mean value of BC in Guwahati was found to be 7.3±6mg/gm. Mean concentration of OC was found to be maximum (0.04±0.06 %) during Dec-11/Jan-12.

To see the seasonal dependency of PAHs on organic carbon, correlation analysis was carried out (Table 4.15). The results indicate a rather weak or no correlation of any PAH compounds with OC during dry season with the exception of Acen, BbF and IP. Acen and BbF show significant positive correlation with OC, whereas, IP have significant negative correlation with OC. Thus, it may be inferred that, in bulk deposition, only some of the individual PAHs, namely Acy and BbF were found to influence OC content.

Table 4.14 Mean of organic carbon (OC) concentrations (%) and black carbon (BC) concentrations (mg/gm) in Guwahati

	OC	BC
Feb-11	0.005±0.0004	
Feb/March-11	0.012±0.009	
March/Apr-11	0.0012±0.0004	6.6±8
Apr/May-11	0.006±0.003	
May/June-11	0.002±0.001	
Jun1-11	0.005±0.002	
Jul-11	0.002±0.001	
Aug-11	0.003±0.001	
Sept/Oct-11	0.011±0.003	
Oct/Nov-11	0.006±0.003	
Nov/Dec-11	0.008±0.003	7.1±6.1
Dec-11/Jan-12	0.04±0.06	20.1±16
Jan/Feb-12	0.01±0.003	6.7±9
Guwahati	0.01±0.02	7.3±6

Table 4.15 Correlations of organic carbon (OC) with PAHs during dry and wet season

	Dry Season	Wet Season
Naph	0.38	-0.02
Acy	0.22	-0.03
Acen	-0.19	**0.85***
Flu	-0.25	-0.30
Phen	0.03	0.02
Anth	-0.24	-0.20
Flan	-0.19	-0.25
Pyr	-0.11	0.13
BaA	0.00	-0.64
Chry	0.01	-0.64
BbF	-0.26	**0.82***
BkF	0.07	-0.33
BaP	0.04	-0.61
DBA	-0.38	-0.68
BgP	-0.13	-0.50
IP	-0.17	**-0.93***
∑PAHs	0.04	-0.43

*Correlation is significant at 0.05 level (2-tailed)

4.2 PAHs in Soil of Guwahati City

4.2.1 Summary Statistics of Soil PAHs

Soil PAHs were explored to trace if any relationship with PAHs in atmospheric deposition existed. Concentrations of soil PAHs at five locations of Guwahati city during 3 seasons have been put up in Table 4.16. ∑PAHs concentrations ranged between 799.73ng/gm (at S5) and 51299.665ng/gm (at S3). Concentration of BaP varied from BDL (at S5) to 322.4ng/gm (at S1). The details of spatial and seasonal variation have been illustrated in the next section.

4.2.2 Spatial and Seasonal Variation of PAHs

Mean ∑PAHs was found to be maximum at industrial site (S1) (24138±5000ng/gm) and minimum at residential site (S4) (2817±2014ng/gm) (Table 4.16). Spatial variation of the concentrations was quite profound. Dissimilarity in landuse, vehicular density and composition and nearness to major source could be possible determinants of such spatial variations. Mean ∑PAHs concentration at S1 was found to be 9 times higher than the concentration at S4. The maximum concentration at S1 could be attributed to major industrial activities at the site. The minimum concentration of ∑PAHs at S4 could be attributed to low traffic and residential landuse. The decreasing order of mean ∑PAHs concentration was found to be as S1>S3>S5>S2>S4; i.e. industrial > traffic > forest> commercial >residential.

Interestingly, S2 (commercial area) showed lower PAHs concentration than a forest site. Being situated on the bank of the Brahmaputra River, S2 receive cleaner air due to north-easterly wind coming across the river for most time of the day. Despite being a forest site far from major emitting sources, S5 did not show lower concentrations of PAHs. This was probably because forest soils receive atmospheric depositions that remain undisturbed for longer period leading to much accumulation of the compounds.

Among individual PAHs concentrations of Naph, Acy, Acen, Phen, Flan, Pyr, BaA, Chry, BaP and IP were found to be maximum at site S3, S1, S5, S1, S5, S1, S1, S1 and S3 respectively.

Table 4.16 Mean concentrations (ng/gm) and standard deviation (SD) of 16 PAHs in soil of Guwahati city

	Naph	Acy	Acen	Flu	Phen	Anth	Flan	Pyr	BaA	Chry	BbF	BkF	BaP	DBA	BgP	IP	∑PAHs
S1																	
Mean	8454.83	680.95	6.83	7.9	601.54	73.04	278.59	114.13	9109.8	4704.62	43.42	9.01	164.21	21.57	27.73	70.92	24137.54
StdDev	6676	879		3	132	27	247	83	7187	1960	30	5	149	14	13	58	5000
S2																	
Mean	3534.64	33.49	26.97	4.79	116.21	18.67	61.51	20.84	224.09	208.78	32.24	1.6	14.98	2.98	4.69	12.58	4318.51
StdDev	1438	42	11	2	43	15	48	13	201	206	50	1	19	2	5	5	1853
S3																	
Mean	17178.1	22.21	132.49	6.51	193.57	15.9	169.59	86.89	750.38	537.14	3.78	8.45	77.43	6.73	12.52	141.29	19261
StdDev	28366	1	83	0.6	166	20	53	56	467	370	2	4	47		1	97	27746
S4																	
Mean	784.64	31.42	24.44	15.17	58.44	12.24	192.96	39.03	1035.89	566.28	7.21	9.53	51.48	6.05	15.05	53.87	2817.06
StdDev	566		32	14		10	106	59	1624	565	2	12	77	4	18	25	2014
S5																	
Mean	4025.75	39.96	54.8	13.03	144.27	6.13	370.51	50.82	221.49	1554.84	7.63	9.52	13.24		4.6	77.96	5991.02
StdDev	6404	55	73	8	5	2	292	62	185	1912	8	9	6		0.3	66	8274

Table 4.17 Mean PAH concentrations (ng/gm) and mean BaPq equivalents in soil of Guwahati during various seasons

	Monsoon-11			Post- monsoon-11			Pre-monsoon-12		
	Mean	Range	BaPq mean	Mean	Range	BaPq mean	Mean	Range	BaPq mean
Naph	1792.4±1562	(260.2-4376)	1.8±2	16443.7±19693	(420.5-49931.4)	16.4±20	2150 7±2273	(396.4-4829.3)	2.2±2
Acy	7.5±6	(BDL-11.7)	0.01±0.01	378±617	(BDL-1302.5)	0.4±1	26.2±21	(5.9-59.4)	0.03±0.02
Acen	74.5±96	(3.3-217)	0.1±0.1	52.7±60	(BDL-138.6)	0.1±0.1	47.4±56	(BDL-129.3)	0.05±0.1
Flu	8.5±3	(4.9-12.4)	0.01±0.003	13.2±10	(5.9-25.4)	0.01±0.01	4.6±2	(BDL-6.9)	0.004±0.002
Phen	155.4±204	(BDL-461.3)	0.2±0.2	293.5±289	(BDL_725.4)	0.3±0.3	321.4±221	(BDL-618)	0.3±0.2
Anth	22.1±22	(4.5-47.7)	0.2±0.2	20.2±32	(BDL-68.6)	0.2±0.3	39.3±37	(7.6-102.8)	0.4±0.4
Flan	213.7±169	(6.5-385.3)	0.2±0.2	128±58	(70.9-207.3)	0.1±0.1	311±275	(99.9-655.3)	0.3±0.3
Pyr	46±57	(1.1-121.8)	0 05±0.1	77.4±78	(8.7-193.1)	0.1±0.1	63.6±56	(13.7-139.8)	0.01±0.1
BaA	2333±4456	(12.4-10252)	233.3±446	501.7±524	(168.1-1419.2)	50.2±52	3970.3±6625	(116.7-15658.1)	397±663
Chry	1094.9±1820	(BDL-3823.9)	11±18	1403±15827	(48.7-3338.9)	14±16	1953.1±2822	(202.6-6951)	19.5±28
BbF	12.2±9	(BDL-23)	1.2±1	9.6±13	(BDL-28.5)	1±1	37±44	(0.7-90.9)	3.7±4
BkF	1.8±1	(BDL-2.6)	0.2±0.1	11.5±9	(0.6-23.5)	1.1±1	7.9±5	(BDL-7.9)	0.8±1
BaP	66.8±75	(BDL-144.4)	66.8±75	17±9	(3-25.8)	17±9	119.7±124	(8.3-322.4)	119 7±124
DBA	6.6±0.7	(BDL-6.6)	6.6±0.7	13.2±20	(BDL-36.2)	13.2±20	9.9±8	(BDL-21.4)	9.9±8
BgP	9±13	(BDL-28.2)	0.1±0.1	8±6	(BDL-14.2)	0.1±0.1	23.3±14	(BDL-40.8)	0.2±0.1
IP	86.9±98	(BDL-231.1)	8.7±10	79±62	(6.5-155.5)	7.9±6	49.8±50	(16.1-138.6)	5±5
∑PAHs	5570.7±7830	(799.7-19492)	308.6±525	19292.1±19932	(1271.4-51299.7)	116.4±93	9052.3±11508	(1639.7-29492.3)	557±828

Seasonal variations of ∑PAHs are shown in Table 4.17 and also illustrated in Figure 4.8. The maximum concentration of ∑PAHs was observed at S3 during post-monsoon period. S3 experience very heavy traffic all through the day.

The mean concentration of ∑PAHs (19292.1±19932 ng/gm) was found to be maximum during post-monsoon period. During post-monsoon less rainfall and low average temperature enhance higher rate of scavenging of PAHs that leads to higher deposition on soil surface. Low disintegration rate and less wash out might have triggered such high concentration levels. The post-monsoon concentration was followed by values of pre-monsoon (9052.3±11508 ng/gm) and monsoon (5570.7±7830ng/gm) seasons. Heavy rainfall received during the monsoon might wash-away top soil carrying PAHs along, which could be the possible reason for such lower concentrations. Individually, mean PAH concentrations were found in the order of Naph>BaA> Chry> >Phen>Flan.

Mean concentrations of LMWPAHs, naphthalene to chrysene, were found to be abundant during post-monsoon and HMWPAHs including BaP were abundant during pre-monsoon. Temperature dependent scavenging of LMWPAHs and their subsequent deposition could be attributed to such variability in PAHs. The LMWPAHs are often found to be influenced by seasonality with variation of temperature. This lead to long range transport and deposition of PAHs on a surface through continuous air-surface exchange by means of succeeded cycles of deposition and re-evaporation as reported by Yamasaki et al. [310].

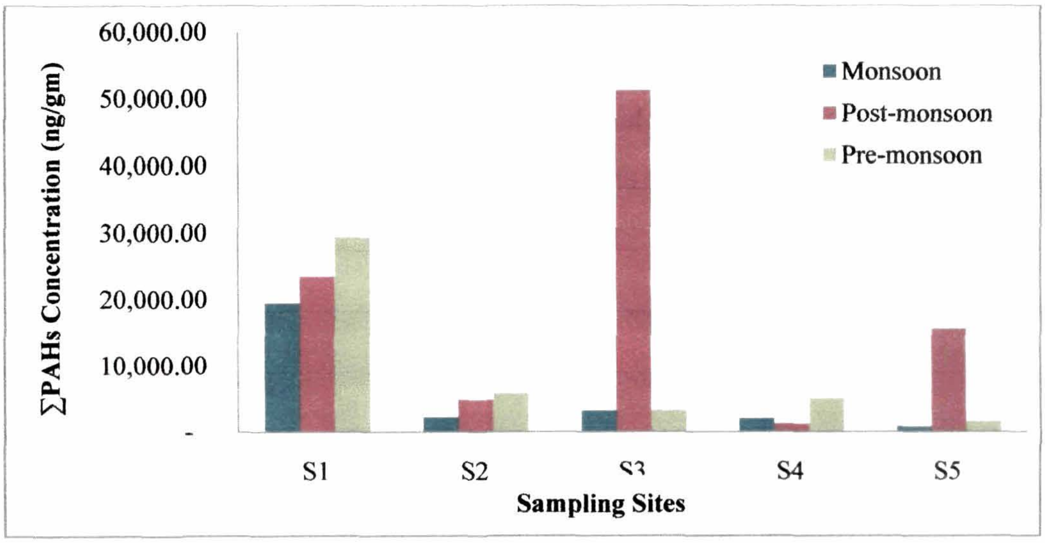


Figure 4.8: ∑PAHs in soil of Guwahati during monsoon, post-monsoon and pre-monsoon seasons.

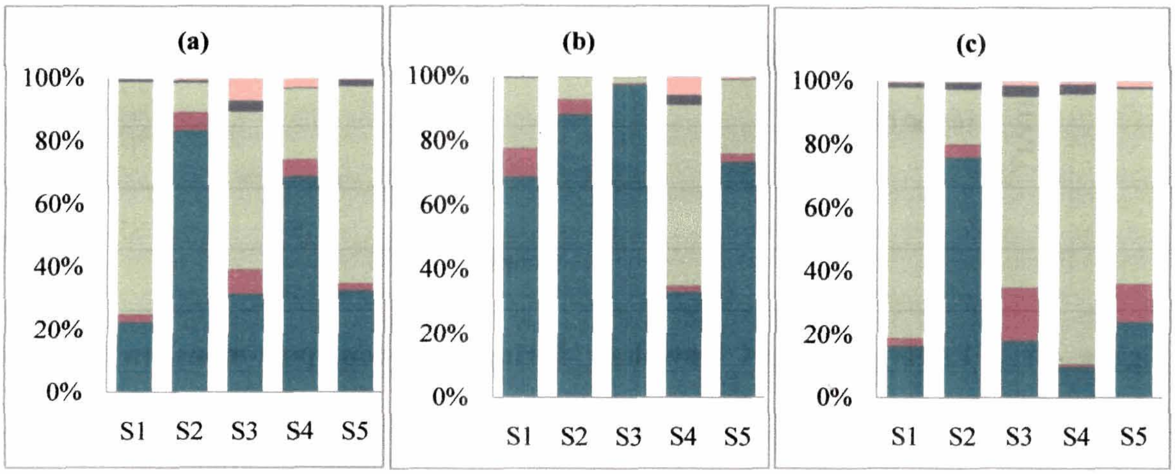
4.2.3 PAHs Profiles

The composition profiles of PAHs by ring number have been illustrated in Figure 4.9. Two-ring PAHs were prevalent during monsoon at S2 and S4 representing 83% and 69%, respectively of ∑PAHs. During monsoon 4-ring PAHs were found to be dominant at S1, S3 and S5. The highest representation of 4-ring PAHs was found to be at S1; contributing 74% to ∑PAHs. However, Dominance of 2-ring PAHs was observed almost at all the sites during post-monsoon season. During pre-monsoon predominance of 4-ring PAHs was observed at all sites barring S2. At S2, 2-ring PAHs dominated in all the three seasons.

In general, in Guwahati PAHs profile was found to be dominated by 2- and 4-ring PAHs during monsoon and pre-monsoon season, while high abundance of 2-ring PAHs was noticed *during* post-monsoon season. Similarly, contribution of 2 and 4-ring PAHs was also observed by Choi [326] in South Korea soil.

The observed pattern could be explained in terms of physicochemical properties of PAHs and varied local environmental conditions. Moreover, 'Multi-hop' nature of LMWPAHs allows long range transport and so is more susceptible to continuous deposition and re-evaporation [97]. The change in concentration of 2-ring polycyclic aromatic hydrocarbon in post-monsoon and pre-monsoon may be attributed to various atmospheric and meteorological factors. The prevailing atmospheric condition with low wind activity, subsidence state and inversion condition might be the possible cause for such variation during pre-monsoon season.

LMWPAHs are known to have significant acute toxicity [96] and it is worthy to note that Naph, BaA, Chry, Flan, Phen and Pyr are predominating PAHs in soils of Guwahati.



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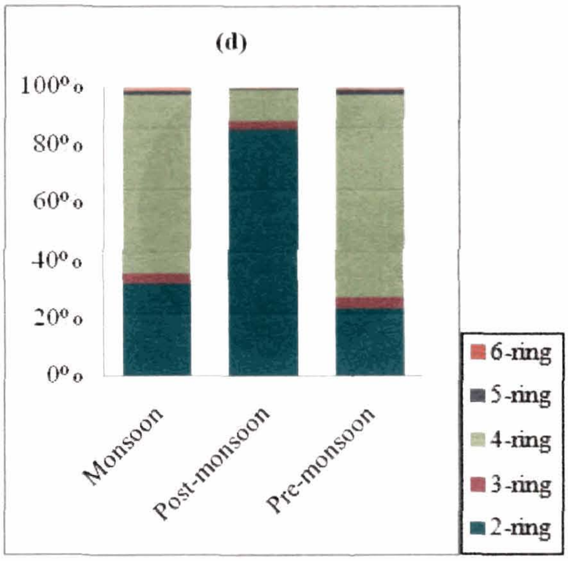


Figure 4.9: Percent composition of three-, four-, five- and six-ring PAHs at five sampling sites during (a) monsoon, (b) post-monsoon (c) pre-monsoon season and (d) Guwahati (mean of all the sites, S1-S5).

4.2.4 Toxicity

Representation of site-wise carcinogenic PAHs (CPAHs) with rest of the PAHs has been illustrated in Figure 4.10. The percentage contribution of CPAHs was ≥ 50% at S1, S4 and S5, and the highest contribution was found to be at S1 with 57% contribution. In general in Guwahati CPAHs contribution was revealed as 42%.

CPAHs contribution was also illustrated seasonally in Figure 4.11. CPAHs percentage was found to be 40%, 28% and 56% during monsoon, post-monsoon and pre-monsoon season respectively. Thus carcinogenic PAHs contribution was observed as maximum during pre-monsoon season. Rise in heating activities during pre-monsoon season could probably trigger such high percentage in that season.

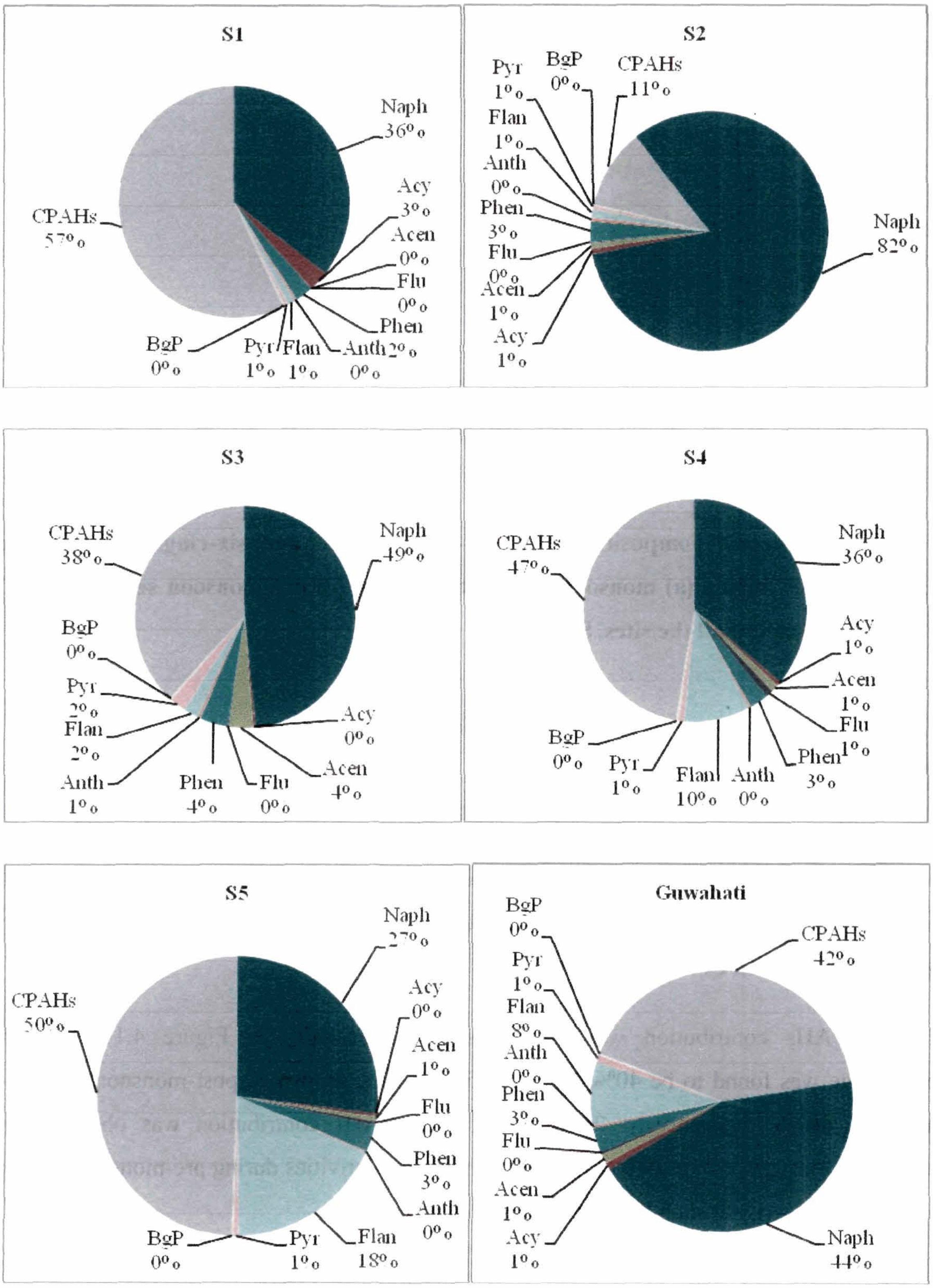


Figure 4.10: Abundance of carcinogenic PAHs (CPAHs) to non-carcinogenic PAHs at sampling sites (S1-S5) and in Guwahati (mean of five sampling sites, S1-S5).

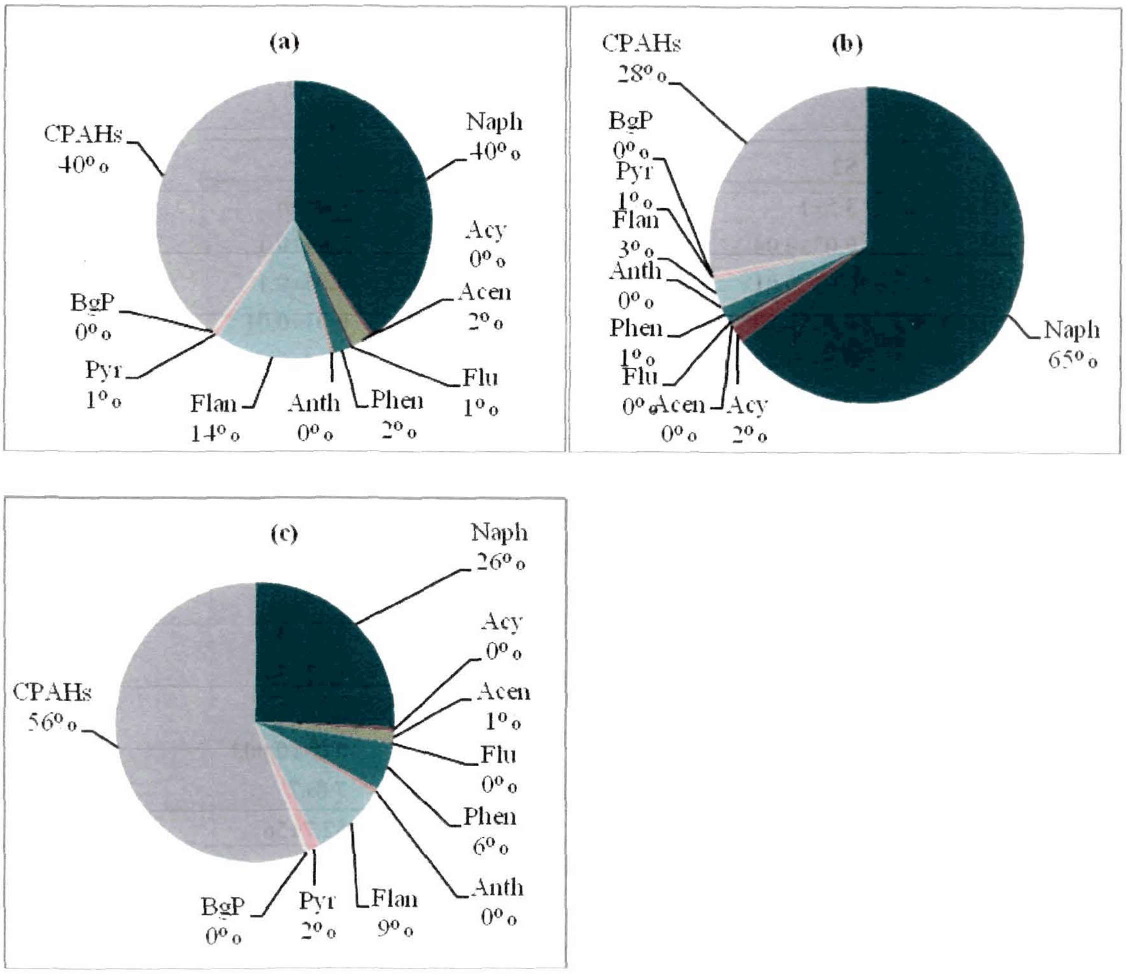


Figure 4.11: Abundance of carcinogenic (CPAHs) to non-carcinogenic PAHs during (a) monsoon, (b) post-monsoon and (c) pre-monsoon in soil of Guwahati.

Mean BaPq of ∑PAHs in soil ranged between 51.1±46 (at S2) and 1167±874 (at S1) ngBaPq/gm (Table 4.18). If we compare the industrial site (S1) and forest site (S5), although the total mean PAHs at S1 was 4 times higher than S5, BaPq was as high as 22 times. BaPq of industrial soil of Guwahati was higher than traffic soil of Delhi 1009 ng BaPq/gm [97], soil of Shanghai, China 892 ngBaPq/gm [276], soil of petrochemical region of Portugal of 162.02 ng BaPq/gm [327], soil of San Nicolas, central Mexico of 140 ng BaPq/gm [328]. Thus, the exposure risk of PAHs for Guwahati soil was found to be high.

Total mean BaPq values were found to be 308.6±525ng/gm, 116.4±93ng/gm and 557±828ng BaPq/gm during monsoon, post-monsoon and pre-monsoon seasons respectively (Table 4.17). Thus, PAHs exposure risk from soil was found to be maximum during pre-monsoon season, when the emission rate of PAH was maximum triggered by favourable meteorological conditions.

Table 4.18 Site-wise mean BaPeq concentrations (ng/gm) of PAHs

	S1	S2	S3	S4	S5
Naph	8.5±7	3.5±1	17.2±28	0.8±1	4.01±6
Acy	0.7±1	0.03±0.04	0.02±0.001	0.03±0.0	0.04±0.1
Acen	0.01±0.0	0.03±0.01	0.13±0.1	0.02±0.03	0.05±0.1
Flu	0.01±0.003	0.005±0.003	0.01±0.001	0.02±0.01	0.01±0.01
Phen	0.6±0.1	0.1±0.04	0.2±0.2	0.06±0.0	0.14±0.01
Anth	0.7±0.3	0.2±0.2	0.16±0.2	0.12±0.1	0.06±0.02
Flan	0.3±0.3	0.06±0.1	0.17±0.1	0.19±0.1	0.37±0.3
Pyr	0.1±0.1	0.02±0.01	0.1±0.1	0.04±0.1	0.05±0.1
BaA	911±719	22.4±20	75.04±47	103.6±162.4	22.15±19
Chry	47.1±20	2.1±2	5.4±4	5.7±6	15.6±19
BbF	4.3±3	3.2±5	0.4±0.3	0.7±0.2	0.8±1
BkF	0.9±1	0.2±0.1	0.8±1	0.95±1	0.95±1
BaP	164.2±149	15±19	77.4±48	51.5±77	13.2±7
DBA	21.6±15	3.0±3	6.7±0.0	6.1±4	BDL
BgP	0.3±0.1	0.05±0.1	0.13±0.01	0.15±0.2	0.05±0.003
IP	7.1±6	1.3±1	14.1±10	5.4±3	7.8±7
∑PAHs	1167±874	51.1±47	192.9±72	172.8±247	52.7±56

4.2.5 PAHs Ratios and Source Identification

The diagnostic ratios found in the present study were indicative of pyrogenic origin of PAHs (Table 4.19).

Anth/(Anth+Phen) ratios were found to be 0.14±0.1, 0.1±0.1 and 0.14±0.1 during monsoon, post-monsoon and pre-monsoon respectively. Similarly, Flan/(Flan+Pyr) ratios were 0.71±0.3, 061±0.3 and 0.74±0.2 during monsoon, post-monsoon and pre-monsoon respectively, which inferred pyrogenic input of PAHs in all three seasons. BaA/Chry ratio of 1.11 is considered as specific marker for coal combustion [208, 322]. BaA/Chry ratios were found to be 0.92±1and 1.4±1 during post-monsoon and pre-monsoon seasons respectively could explain coal combustion during these two seasons only. Phen/(Phen+Anth) ratio greater than 0.7 is an indicative of fossil fuel emissions according to Kavouras et al. [210]. Phen/(Phen+Anth) mean ratio was greater than 0.7 in three seasons indicate source emission from fossil fuels in soil PAHs. The ratio of IP/(IP+BgP) between 0.35 and 0.70 is considered as specific marker for diesel emission [201] and BgP is often considered as a vehicular marker. Mean IP/(IP+BgP) ratio was 0.71±0.2 only during pre-monsoon, while 0.77±0.3 and 0.85±0.1 in monsoon and post-monsoon respectively. This indicated that diesel emission was an important source of soils PAHs during pre-monsoon only. Thus, seasonality of source strengths of PAHs was vividly displayed by the source diagnostic ratios.

Table 4.19 Seasonal mean diagnostic ratios of PAHs in soil of Guwahati city

	Monsoon-11		Post- monsoon-11		Pre-monsoon-12	
	Mean	Range	Mean	Range	Mean	Range
Anth/(Anth+Phen)	0.14±0.1	(0.07-0.23)	0.1±0.1	(0.01-0.3)	0.14±0.1	(0.05-0.3)
Flan/(Flan+Pyr)	0.71±0.3	(0.35-1)	0.61±0.3	(0.4-0.95)	0.74±0.2	(0.49-0.96)
IP/(IP+BgP)	0.77±0.3	(0.42-0.99)	0.85±0.1	(0.7-0.99)	0.71±0.2	(0.47-0.94)
Phen/(Phen+Anth)	0.85±0.1	(0.77-0.93)	0.87±0.1	(0.7-0.99)	0.85±0.1	(0.7-0.95)
BaA/Chry	2.01±1.8	(0.1-4.4)	0.92±1	(0.15-3.45)	1.4±1	(0.6-2.4)

4.2.6 Source Apportionment

Five factors explaining 86% of variance were obtained for soil PAHs using PCA (Table 4.20). Factor 1 explained 39.8% of variance and had high loadings of Phen, Anth, Flan, BaA, Chry, BbF, BaP, DBA, BgP, and IP. BbF in addition to BgP and Flan is an indication of diesel-engine exhaust [324]. However, Anth, Phen, Flan, BaA and Chry, are regarded as specific marker for coal combustion [208, 329] and also Phen, Anth and Flan are typical indicators of wood combustion [208]. Thus, factor 1 could be attributed to mixture of diesel, coal and wood combustion.

Factor 2 explained 16% of variance with high loadings of Acy, Phen, Anth, Pyr and DBA. This factor could explain coal combustion [208]. Factor 3 had high loading of Acen, Pyr and IP explaining 13% of variance and they are considered as typical marker for mobile sources (traffic) [329]. Factor 4 explained 10 % of variance with high loading of Flu, Chry and BkF indicating for vehicular sources. Factor 5 explained 7% of total variance with significant loading of Naph and IP. This factor is marked for diesel powered vehicle. Thus, the sources could be broadly divided into two major categories of pyrogenic origin – factors 1 and 2 representing stationary sources and factors 3, 4 and 5 representing mobile sources.

Table 4.20 Principal Component Analysis (PCA) of soils PAHs of Guwahati city (extraction method: Principal Component Analysis; Rotation method: Varimax with Kaiser normalization)

	Components				
	1	2	3	4	5
Naph	-0.083	0.137	0.114	-0.034	**0.896**
Acy	0.038	**0.888**	-0.220	0.028	**0.251**
Acen	-0.211	0.051	**0.925**	-0.024	-0.053
Flu	-0.199	-0.066	0.033	**0.942**	-0.115
Phen	**0.675**	**0.629**	-0.134	-0.017	**0.212**
Anth	**0.888**	**0.386**	-0.161	-0.050	0.018
Flan	**0.410**	-0.453	-0.221	-0.088	**0.253**
Pyr	0.138	**0.840**	**0.344**	0.113	-0.135
BaA	**0.960**	-0.057	0.000	0.057	-0.024
Chry	**0.888**	0.273	0.014	**0.240**	0.088
BbF	**0.676**	0.014	-0.214	-0.230	-0.010
BkF	0.157	**0.213**	0.052	**0.885**	0.087
BaP	**0.934**	-0.059	**0.251**	-0.004	-0.103
DBA	**0.524**	**0.746**	-0.247	0.049	0.141
BgP	**0.896**	0.138	-0.027	-0.040	-0.014
IP	0.218	-0.153	**0.787**	0.181	**0.445**
Eigen Value.	6.369	2.572	2.119	1.562	1.109
% of Variance	39.809	16.076	13.245	9.761	6.929
Cummulative %	39.809	55.885	69.130	78.890	85.820
Identified Sources	diesel + coal + wood combustion	diesel + coal combustion	traffic	vehicular	diesel engine / vehicular emission
	Stationary sources		**Mobile sources**		
Source Contribution (%)	25.452	11.454	6.966	1.407	54.722
	~37%		**~63%**		

PCA Factor scores 1-5 corresponding diesel+Coal+Wood combustion, diesel + coal combustion, traffic, vehicular, diesel engine/vehicular emission, were taken as independent variable and z-score values of sum PAH ($\sum PAH_i$) as dependent variable. In order of their individual simple correlation from highest to lowest, each independent variable was added into stepwise regression. The resulting equation 7 was obtained after computed for PCA/MLR.

$$Z = 0.38FS1 + 0.171FS2 + 0.104FS3 + 0.021FS4 + 0.817FS5 \quad \text{--- [eq7]}$$

Thus the mean contributions were found to be 25.452%, 11.454%, 6.966, 1.407 %, and 54.722 % for factors 1 to 5 respectively. So, vehicular emission (factor 4) dominated the source of PAHs in soil.

4.2.7 Seasonal Association of Carbon with PAHs

Mean and range of OC, BC and BC/OC have been presented in Table 4.21. From the table it was observed that for OC maximum mean was observed during monsoon season with mean concentration of 26.9±13mg/gm and maximum mean concentration of BC 25.5±6mg/gm was found during post-monsoon season. However, BC/OC ratio was almost equal during post-monsoon and pre-monsoon season of 1.4±0.7 and 1.4±0.8 respectively.

Table 4.21 Mean and ranges (mg/gm) for organic carbon (OC), black carbon (BC) and BC/OC in soils of Guwahati (n=15)

	Monsoon-11		Post-monsoon-11		Pre-monsoon-12	
	Mean	Range	Mean	Range	Mean	Range
OC	26.9±13	(16.2-48.2)	22.7±14	(13.1-47)	23.2±13	(1.2-4.5)
BC	19.8±8	(10-29.2)	25.5±6	(18.7-32.8)	25.3±4	(20.5-31.6)
BC/OC	1.3±1	(0.2-3)	1.4±0.7	(0.4-2.1)	1.4±0.8	(0.6-2.7)

Pearson's correlations were built between carbon and PAHs for the 3 seasons (Table 4.22). During monsoon, greater number of members showed association with OC, however, during pre- and post-monsoon season association was more pronounced with BC and BC/OC.

During monsoon Acen, Pyr, BaA, BkF, BaP, IP and ∑PAHs were showing significant correlations with OC. While only Flu, Flan and BbF were found to represent significant correlations with BC and BC/OC. During post-monsoon Naph, Acen, Flan, BaP, BgP, IP and ∑PAHs were observed to show significant correlations with OC. While Acy, Phen, Anth, Pyr, BaA, Chry, BbF, DBA and BgP showed good correlations with both BC and BC/OC during post-monsoon season. During pre-monsoon, only Acen, Flu, Pyr and

BkF showed significant correlation with OC, however, most of the individual PAH were found to show significant correlations with BC and BC/OC.

Pre-monsoon is a much drier period of the year. During pre-monsoon period there are intense biomass burning practices in the region like festive meji burning, forest fires for management, clearing agricultural land for jhum cultivation and for crop rotation prevail in the region. As dry biomass combustion emits more BC than that of wet biomass which released more OC into the environment [330], during the long spell of dry period of pre-monsoon biomass burning could add more of BC and PAHs.

Coal fired brick kilns, another important source of PAHs and BC, are also active during dry periods of post- and pre-monsoon. Activities in the brick kilns become most productive during pre-monsoon as the operations are to be closed before the onset of the monsoon that carries high and prolonged rainfall.

Pre-monsoon season is also the period when financial year ends in India. Since the northeast Indian region receives major supplies from India's mainland; supply and transport activities multiply many folds to meet demand before the financial year ending. This could also explain for more co-emission of PAHs with BC.

Table 4.22 Correlations of PAHs with organic carbon (OC) and black carbon (BC), BC/OC in soil during three sampling periods

Monsoon	Naph	Acy	Acen	Flu	Phen	Anth	Flan	Pyr	BaA	Chry	BbF	BkF	BaP	DBA	BgP	IP	∑PAHs
OC	0.06	0.14	**0.88***	-0.21	0.06	0.09	-0.08	0.71	0.21	0.15	-0.13	0.49	0.74	-0.22	0.09	**0.96***	0.20
BC	-0.15	-0.85	-0.70	0.82	0.09	0.05	0.54	-0.32	0.06	0.07	0.66	-0.12	-0.28	-0.08	0.20	-0.70	0.01
BC/OC	-0.36	-0.71	-0.65	0.66	-0.16	-0.17	0.48	-0.53	-0.20	-0.18	0.43	-0.11	-0.50	-0.16	-0.06	-0.71	-0.24
Post-monsoon																	
OC	**0.98****	-0.21	0.21	-0.37	-0.03	-0.24	0.74	-0.23	-0.12	-0.20	-0.22	-0.31	0.58	-0.20	0.55	0.78	**0.94***
BC	-0.31	0.71	0.16	-0.29	0.69	0.68	-0.77	0.87	0.69	0.75	0.73	-0.20	0.05	0.62	0.31	-0.51	-0.19
BC/OC	-0.76	0.38	-0.19	-0.09	0.27	0.39	-0.85	0.40	0.28	0.27	0.38	-0.15	-0.55	0.32	-0.29	**0.88***	-0.71
Pre-Monsoon																	
OC	-0.68	-0.28	**0.89***	0.51	-0.56	-0.43	-0.38	0.86	-0.49	-0.43	-0.67	0.33	-0.33	-0.29	-0.35	-0.37	-0.53
BC	0.23	**0.94***	-0.18	0.40	0.83	0.77	0.55	0.26	**0.89***	**0.90***	0.07	0.77	**0.88***	**0.89***	0.75	**0.94***	0.82
BC/OC	0.79	0.74	-0.63	-0.28	0.66	**0.88***	0.51	-0.64	**0.91***	**0.90***	0.70	0.33	0.79	0.78	0.71	0.86	**0.94***

*Correlation is significant at the 0.05 level (2-tailed)

**Correlation is significant at the 0.01 level (2-tailed)

To better understand the effect of BC on dispersion of soil PAHs, dependencies of logPAHs on BC/OC ratios were examined (Figure 4.12). Negative slopes were obtained for monsoon and post-monsoon period when log∑PAHs were regressed over BC/OCs; however, a positive slope with high coefficient of determination (r^2=0.75) was found during pre-monsoon period (Figure 4.12c). Similar trends were also found when log∑LMWPAHs and log∑HMWPAHs were regressed over BC/OC; positive slopes (with coefficient of determinations r^2 = 0.76 and 0.44, respectively) were found during pre-monsoon period (Figure 4.12f,i). The relationship was found to be relatively weak in case of HMWPAHs. However, HMWPAHs was observed with stronger negative relationship with OC than that of LMWPAHs and ∑PAHs during monsoon season.

In soil, this kind of reversal of PAHs-BC relationship is unusual because soil receives continuous deposition for very long period and, therefore, a characteristic pattern is established over a period of time. The observed relationship could be very unique for regions that receive high rainfall during one season of the year; like the heavy monsoon shower received by the Brahmaputra valley.

The region represented in the study receives very heavy rainfall during monsoon. Torrential rains during monsoon loosen the top soil and probably wash away the deposited particles with the storm water. This could remove the PAHs signature of the past. Then after the monsoon, a long spell of dry days - post- and the pre-monsoon periods follow separated by a short spell of winter. After monsoon, fresh depositions build up. It could be so that during monsoon and post-monsoon period BC contributions are not sufficient enough to control the association of soil PAHs with OC. During pre-monsoon, however, sufficient deposition of BC on to soil could create a situation where BC starts interfering with OC. Agarwal and Bucheli [151] reported that BC could be a better predictor for PAHs distribution in Indian soil than OC. They, in fact, reported data from a very dry region of India. In the high rainfall regions of Indian subcontinent, however, seasonal trend of PAHs – BC relationship is likely, as found in the present study. So, it could be relevant to say that BC played significant role in soil PAHs dispersion during dry pre-monsoon season.

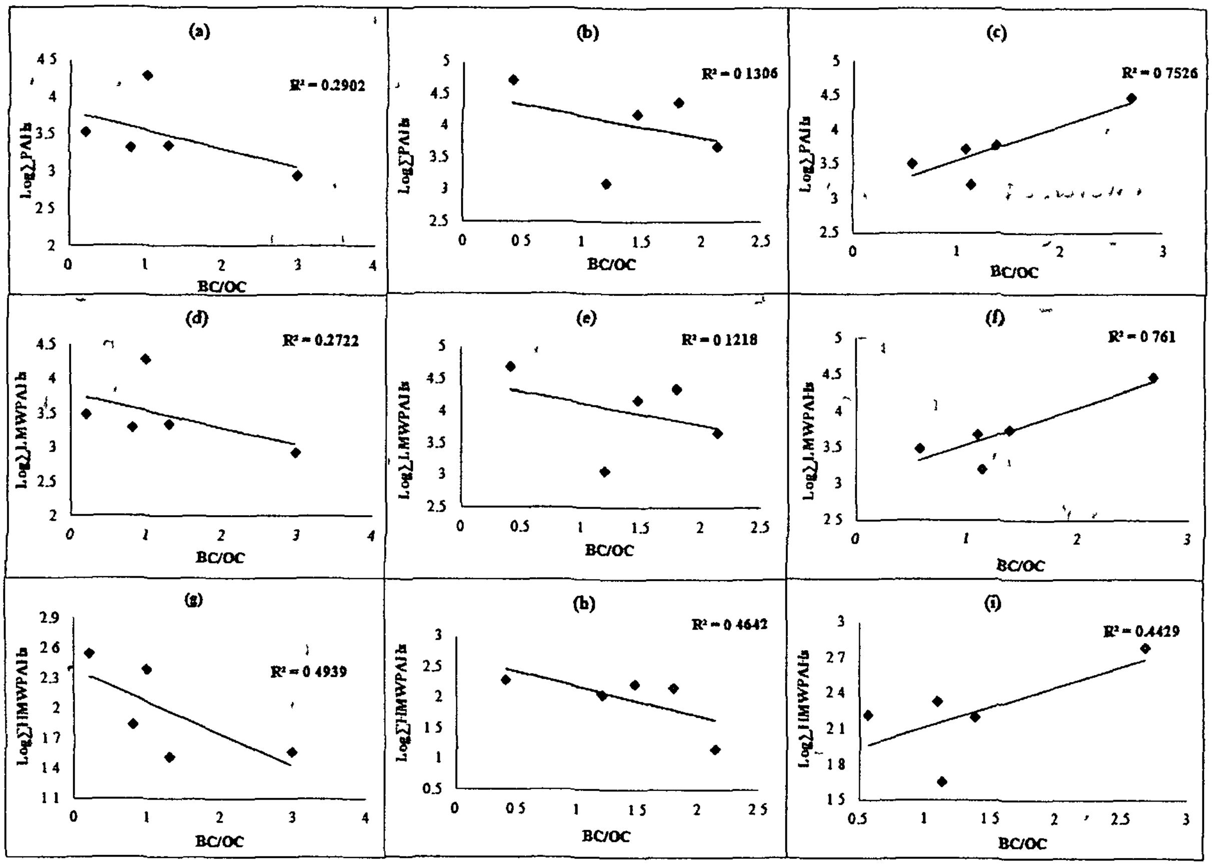


Figure 4.12: Dependency of log∑PAHs on BC/OC ratios: (a) log∑PAHs on BC/OC during monsoon, (b) log∑PAHs on BC/OC during post-monsoon, (c) log∑PAHs on BC/OC during pre-monsoon, (d) log∑LMWPAHs on BC/OC during monsoon, (e) log∑LMWPAHs on BC/OC during post monsoon, (f) log∑LMWPAHs on BC/OC during pre-monsoon, (g) log∑HMWPAHs on BC/OC during monsoon, (h) log∑HMWPAHs on BC/OC during post-monsoon and (i) log∑HMWPAHs on BC/OC in pre-monsoon.

4.2.8 Heavy metals in Soil

The concentration of eight heavy metals viz. Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were estimated in five locations of Guwahati during three seasons. Seasonal variations of heavy metals are illustrated in Table 4.23. Mean concentration of Cd (0.25±0.1 µg/gm), Cr (26.29±7 µg/gm), Cu (12.48±2 µg/gm), Fe (16314.63±2269 µg/gm), Mn (363.32±111 µg/gm), Ni (12.79±3 µg/gm) and Pb (8.67±7 µg/gm) were found to be maximum during monsoon season. However, mean concentration of Zn (127.76±178.88 µg/gm) was maximum during pre-monsoon season.

Table 4.23 Seasonal mean and range of heavy metal concentration (μg/gm) in soil of Guwahati

	Monsoon		Post-monsoon		Pre-monsoon	
Cd	0 25±0.1	BDL-0.33	0.17±0.1	0.06-0.25	0.14±0.1	0.004-0.35
Cr	26.29±7	BDL-36.83	21.28±6	13.86-25.94	21.63±12	8.45-35.08
Cu	12.48±2	BDL-15.03	12.13±7	5.06-20.92	9.81±4	4.10-13.44
Fe	16314.63±2269	BDL-18605.4	12960.32±2390	9878.2-16051.8	12858.37±4703	6994.41-18603.81
Mn	363.32±111	BDL-522.65	269.58±38	209.92-313.92	253.79±78	168.51-366.25
Ni	12.79±3	BDL-17.26	10.26±4	5.04-13.60	10.48±6	4 49-17.56
Pb	8.67±7	0.42-14.48	7.91±6	3.56-17.25	4.14±4	0.61-11.59
Zn	72.59±21	BDL-112.99	103.64±125	37.01-326.74	127.76±179	20.14-445.95

Pearson's correlations were built between heavy metals and PAHs for the three sampling seasons (Table 4.24). The results showed that during monsoon season Cd, Mn and Zn exhibited significant positive correlation with Flan while Pb showed significant negative correlation with DBA. On the other hand during post-monsoon season, negative correlation was observed for Cr and Ni with Flu while, Pb with BaP. Most of the heavy metals during pre-monsoon exhibited significant positive relationship with some individual PAHs such as Cd with BbF, Cr with Phen and BkF, Mn with Phen and Anth, Ni with Phen and Pb with Pyr.

Relationships of PAHs with heavy metals were more pronounced during pre-monsoon season than monsoon and post-monsoon season. Atmospheric condition and anthropogenic activities during pre-monsoon season could possibly attribute such relationship of PAHs with heavy metals. Moreover, from the relationship of signature PAH such a Phen, Anth and Pyr with that of Cr and Ni were an indicator of coal combustion source. Relationship of BaP, BbF and BkF with Pb and Cd revealed vehicular emission as another source.

Table 4.24 Correlations of PAHs with heavy metals during monsoon, post-monsoon and pre-monsoon season

Monsoon	Naph	Acy	Acen	Flu	Phen	Anth	Flan	Pyr	BaA	Chry	BbF	BkF	BaP	DBA	BgP	IP	∑PAHs
Cd	-0.56	0.20	0.20	0.17	-0.35	-0.46	**0.95***	-0.17	-0.26	-0.29	0.17	-0.28	-0.09	-0.88	-0.23	0.24	-0.31
Cr	-0.14	0.58	0.62	0.06	-	-0.05	0.53	0.48	0.16	0.10	0.17	0.11	0.55	-0.58	-0.10	0.73	0.12
Cu	-0.22	0.19	0.15	0.43	0.03	-0.07	0.86	0.19	0.14	0.10	0.49	-0.12	0.28	-0.63	0.17	0.26	0.08
Fe	-0.26	0.41	0.36	0.21	-0.06	-0.16	0.79	0.23	0.06	0.02	0.30	-0.11	0.31	-0.70	0.06	0.46	0.02
Mn	-0.37	-0.04	0.09	0.54	-0.09	-0.17	**0.88***	0.06	0.02	-0.02	0.49	-0.03	0.15	-0.67	0.07	0.16	-0.05
Ni	-0.10	0.53	0.58	0.14	0.05	-	0.53	0.51	0.21	0.15	0.24	0.14	0.58	-0.54	0.16	0.70	0.17
Pb	-0.75	0.26	0.35	-0.11	-0.61	-0.70	0.86	-0.35	-0.53	-0.56	-0.15	-0.30	-0.26	**-0.98****	-0.52	0.34	-0.57
Zn	-0.39	-0.13	-0.09	0.56	-0.11	-0.20	**0.94***	-0.09	-0.03	-0.05	0.52	-0.17	-	-0.66	0.04	-0.03	-0.09
Post-monsoon	**Naph**	**Acy**	**Acen**	**Flu**	**Phen**	**Anth**	**Flan**	**Pyr**	**BaA**	**Chry**	**BbF**	**BkF**	**BaP**	**DBA**	**BgP**	**IP**	**∑PAHs**
Cd	-0.10	0.61	-0.78	-0.71	0.59	0.63	-0.05	0.24	0.47	-0.06	0.56	-0.51	-0.13	0.60	0.30	-0.79	-0.06
Cr	0.52	0.42	-0.37	**-1****	0.55	0.40	0.15	0.20	0.36	-0.07	0.38	-0.86	0.15	0.37	0.62	-0.26	0.54
Cu	0.06	0.75	-0.43	-0.82	0.79	0.74	-0.25	0.56	0.67	0.28	0.73	-0.61	0.08	0.70	0.54	-0.64	0.13
Fe	0.17	0.71	-0.69	-0.82	0.74	0.72	0.11	0.36	0.61	0.07	0.66	-0.54	0.15	0.70	0.57	-0.58	0.22
Mn	0.16	0.07	0.26	-0.68	0.18	0.03	-0.53	0.23	0.05	0.07	0.08	-0.86	-0.26	-0.05	0.15	-0.24	0.17
Ni	0.44	0.47	-0.33	**-0.99****	0.59	0.45	0.02	0.28	0.41	0.01	0.44	-0.86	0.11	0.41	0.60	-0.34	0.46
Pb	-0.38	-0.40	0.04	-0.21	-0.40	-0.40	-0.63	-0.30	-0.49	-0.40	-0.40	-0.58	**-0.88***	-0.47	-0.59	-0.48	-0.44
Zn	-0.29	-0.17	-0.30	-0.48	-0.17	-0.17	-0.45	-0.26	-0.31	-0.46	-0.20	-0.72	-0.80	-0.23	-0.39	-0.66	-0.35

Pre-monsoon	Naph	Acy	Acen	Flu	Phen	Anth	Flan	Pyr	BaA	Chry	BbF	BkF	BaP	DBA	BgP	IP	∑PAHs
Cd	0.81	-0.13	-0.10	-0.75	0.08	0.36	-0.44	-0.45	0.11	0.12	**0.89***	-0.08	0.08	0.06	0.14	0.01	0.25
Cr	0.57	0.51	0.41	-0.11	**0.88***	0.79	-0.06	0.09	0.59	0.66	0.50	**0.89***	0.62	0.65	0.49	0.65	0.65
Cu	0.68	0.38	0.34	-0.25	0.70	0.73	-0.32	0.05	0.49	0.54	0.66	0.72	0.54	0.56	0.49	0.49	0.57
Fe	0.67	0.56	0.28	-0.16	0.86	0.85	-0.10	0.02	0.65	0.71	0.61	0.84	0.68	0.70	0.59	0.68	0.72
Mn	0.74	0.59	0.14	-0.30	**0.94***	**0.90***	0.23	-0.25	0.74	0.79	0.65	0.78	0.68	0.71	0.51	0.81	0.81
Ni	0.49	0.57	0.42	-0.01	**0.92***	0.79	0.01	0.14	0.62	0.69	0.41	**0.94***	0.66	0.69	0.52	0.70	0.66
Pb	-0.51	0.03	0.84	0.61	0.19	-0.13	-0.40	**0.91***	-0.19	-0.13	-0.53	0.59	0.01	0.04	-0.02	-0.09	-0.24
Zn	0.61	-0.48	0.01	-0.85	-0.19	0.03	-0.46	-0.47	-0.23	-0.23	0.73	-0.35	-0.30	-0.31	-0.23	-0.31	-0.09

**Correlation is significant at 0.01 level (2-tailed)

*Correlation is significant at 0.05 level (2-tailed)

4.3 PAHs in Street Dust of Guwahati City

4.3.1 Summary Statistics of Street Dust PAHs

PAHs concentrations in street dust varied significantly in monsoon to non-monsoon (post-monsoon and pre-monsoon) season. All the samples exhibited an increase in ∑PAHs concentration during non-monsoon seasons. In general, ∑PAHs concentrations in monsoon samples ranged from 2248.8-13550ng/gm with mean value of 8500.8±4608ng/gm, whereas they varied from 1394.7-43789.0 ng/gm during post-monsoon with mean value of 23294.7±15164 ng/gm and during pre-monsoon season the concentration ranged from 5153.5-28796.3 ng/gm with mean value of 14770.5±9900 ng/gm (Table 4.25). BaP concentration was ranged between BDL-273.78ng/gm with maximum mean concentration 74.9±111.8ng/gm observed during pre-monsoon.

Table 4.25 Mean± standard deviation (SD) and range of PAHs (ng/gm), Organic Carbon (OC) (%), Black Carbon (BC) (mg/gm) and heavy metals (µg/gm) during monsoon, post-monsoon and pre-monsoon

	Monsoon		Post-monsoon		Pre-monsoon	
	Mean	Range	Mean	Range	Mean	Range
Naph	5409.5±2953	BDL-7668.9	18209.7±11666	688.4-30581.8	3077 7±2008	826.2-5333
Acy	223.5±312	BDL-583.2	637±1219	BDL-2465.0	42.2±39	0.8-105.0
Acen	44.1±12	BDL-55.5	48.1±37	BDL-88.2	114.7±178	BDL-380.5
Flu	15.5±13	BDL-30.6	8.3±5	3.0-14.2	25.3±25	0.9-67.1
Phen	60.4±50	BDL-132.9	373.1±372	1.6-953.3	1827.9±2540	212.8-6183 0
Anth	23.0±38	BDL-79.9	37.4±24	5.7-63.5	63.1±101	BDL-212.6
Flan	287.9±226	65.1-578.0	322.7±483	13.0-1172.2	1110.3±1925	28.5-4515.3
Pyr	29.0±13	BDL-38.2	133.1±114	5.9-298.1	331.0±583	7.4-1365.7
BaA	2447.2±2863	242.8-5714.2	911.0±1093	79.4-2770	3951.9±4006	140.1-9577.4
Chry	567.6±270	BDL-878.5	2552.9±2716	116 3-6199.6	3988.0±3656	312.5-8918.8
BbF	51 4±83	BDL-147.6	16.9±13	BDL-35.9	45.0±51	1.0-119.1
BkF	3.4±0.0	BDL-3.4	13.9±19	BDL-42.6	47.7±45	BDL-101.5
BaP	29.3±35	BDL-54.2	29.0±21	BDL-50.4	74.9±112	10.9-273.8
DBA		BDL	28.5±31	BDL-73.7	9.9±9	2.1-20.1
BgP		BDL	37.0±37	BDL-85.8	44.7±67	4.1-161.0
IP	847.3±1380	BDL-2906	107.6±99	12.8-261.9	61.2±49	9.5-127.1
∑PAHs	8500.8±4608	2248.8-13550	23294.7±15164	1394.7-43789.0	14770.5±9900	5153.5-28796
OC	0.4±0.3	0.08-0.83	1.2±0.9	0.2-2.6	1.6±1	0.4-2.6
BC	19.3±1	17.99-20.11	22.1±3.6	18.4-26.5	25.5±4	19.7-29.0

Cd	0 0001±0 0	0 0001-0 0002	0 0002±0 00	0 0001-0 0003	0 0001±0 0001	0 0001-0 0003
Cr	0 01±0 003	0 01-0 02	0 01±0 003	0 01-0 02	0 01±0 004	0 01-0 02
Cu	0 01±0 002	0 003-0 01	0 01±0 01	0 001-0 02	0.006±0 004	0 002-0 012
Fe	10 8±3	8 04-15 50	11 9±1	9 9-13 2	10 06±3	5 1-14 2
Mn	0 3±0 2	0 16-0 53	0 4±0 3	0 18-0 98	0 2±0 1	0 1-0 4
Ni	0 01±0 001	0 004-0 007	0 005±0 001	0 003-0 01	0 01±0 002	0 002-0 01
Pb	0 01±0 004	0 003-0 01	0 01±0 01	0 001-0 03	0 003±0 001	0 001-0 005
Zn	0 03±0 01	0 02-0 04	0 03±0 01	0 02-0 05	0 03±0 02	0 01-0 06

4.3.2 Spatial and Seasonal Variation of PAHs

Apparent variation in ∑PAHs mean levels was observed in street dust of different landuse sites (Figure 4.13). The site wise variation in ∑PAHs level was in the order of industrial>commercial>institutional>residential>forest with mean concentration of 24,944.719±21036ng/gm, 17,312.102±4792ng/gm, 15,357.360±11217ng/gm, 11,387.941±9057ng/gm and 8607.815±8086ng/gm respectively.

Seasonal variation of street dust PAHs concentrations are illustrated in Figure 4.14. All the sites experienced a decrease in ∑PAHs concentration during monsoon season. ∑PAHs concentration reached maximum level at all the sites during post-monsoon season except at S5 during pre-monsoon.

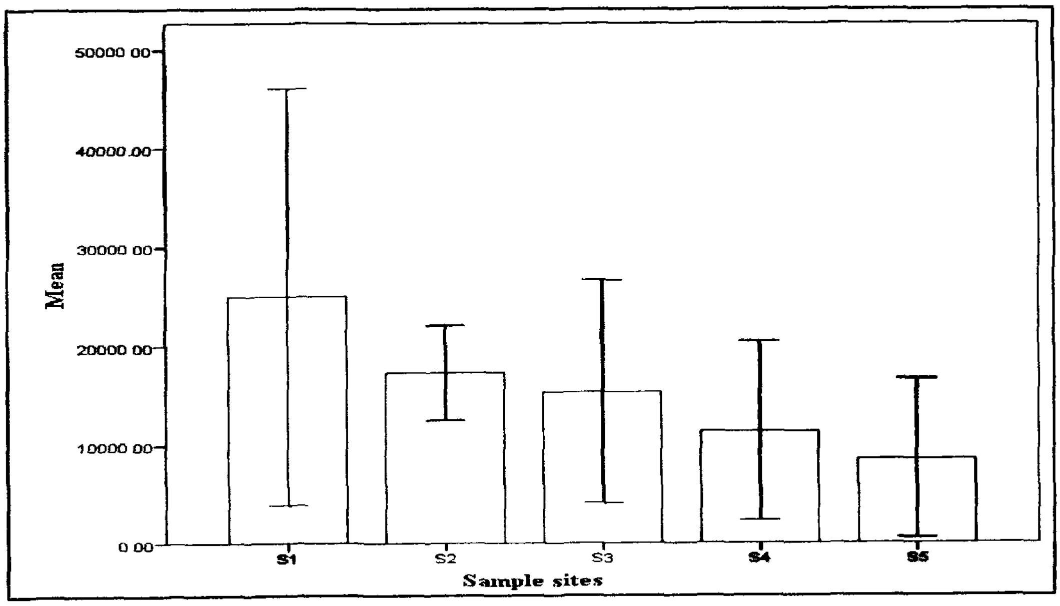


Figure 4.13: Mean with standard deviation of ∑PAHs concentrations (ng/gm) in sampling sites (S1-S5).

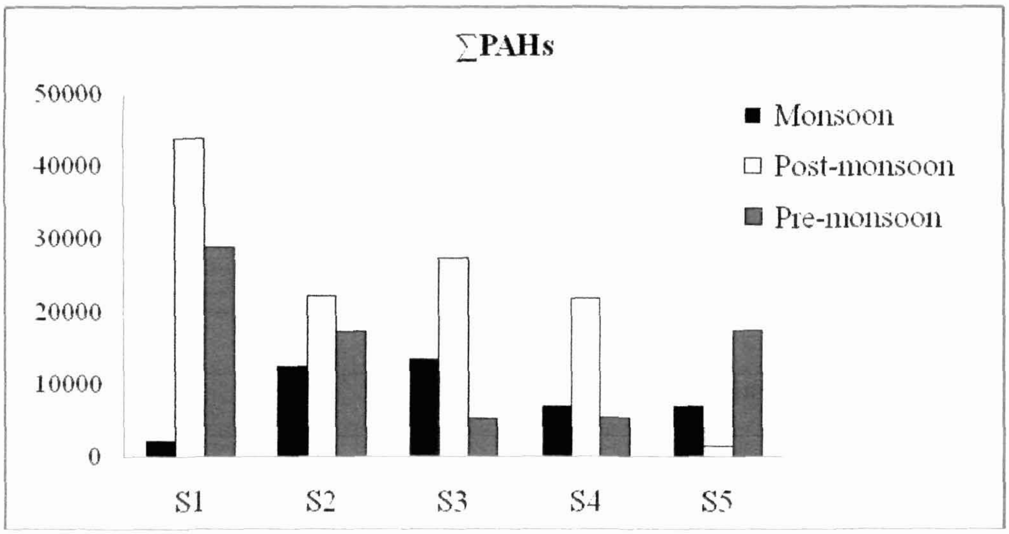


Figure 4.14: ∑PAHs concentrations in street dust of Guwahati during monsoon, post-monsoon and pre-monsoon.

The differential seasonal concentrations could be attributed to variation in meteorological conditions and human activities during monsoon and non-monsoon seasons, the effect of which could be directly observed in street dust. Heavy rainfall along with clean wind during monsoon results into less accumulation of pollutants. Moreover, degradation of PAHs gets enhanced under high temperature and strong sunlight during monsoon. On the other hand, during post-monsoon and pre-monsoon season both outdoor and indoor heating activities added more PAHs along with wind carrying contaminants [234]. The favourable atmospheric condition with lower mixing height might favour more atmospheric deposition of PAHs in street dust near to source during pre-monsoon. Pereira Netto et al. [233] point out possibilities of seasonal variation of ∑PAHs and carcinogenic PAHs concentration as they observe high ∑PAHs and carcinogenic PAHs concentration with decrease of temperature in street dust.

The maximum ∑PAHs concentration at S1 could be attributed to major industrial activities. Site S5 with minimum ∑PAHs level was due to its landuse type with vegetation cover.

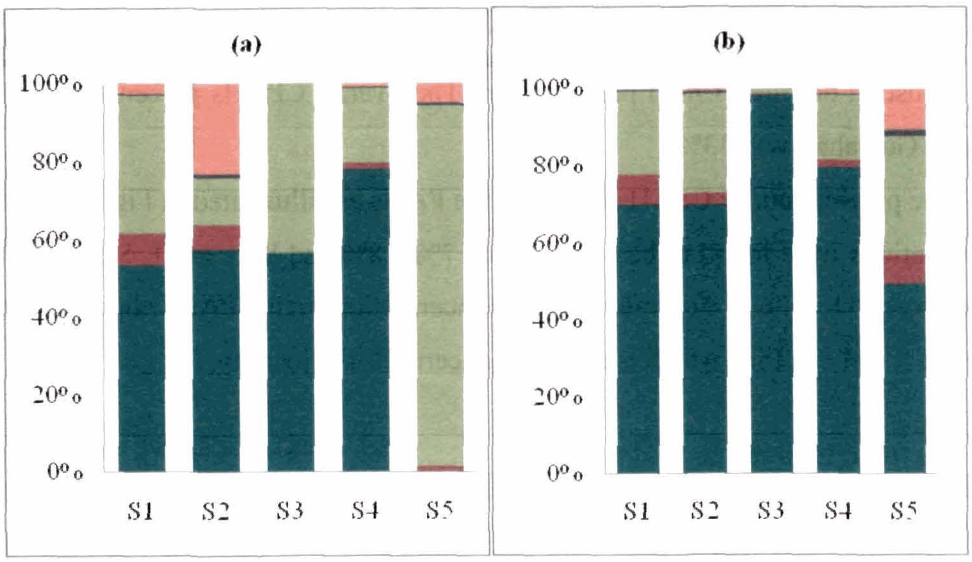
Individual PAH homologues concentration varied from BDL to 7669ng/gm in monsoon, BDL to 30582ng/gm in post-monsoon and BDL to 9577ng/gm in pre-monsoon (Table 4.25). Prominent increase in the PAHs levels was observed during post-monsoon and pre-monsoon season. However, PAHs distribution characteristics in all the three seasons revealed uniformity with throughout dominance of LMWPAHs in street dust.

The present study indicated abundance of Naph, Chry, BaA, Flan and Pyr in street dust samples. High percentage of naphthalene is mainly characteristic of exhaust from several diesel engines [331]. These compounds emitted from incomplete combustion adsorbed to particles suspended in air and deposited on soil and dust near roadside [160]. Among HMWPAHs mainly IP, BaP and BgP found to have high contribution to total PAHs.

4.3.3 PAHs Profiles

The composition profile of PAHs by ring number during three sampling seasons is represented in Figure 4.15. During monsoon and post-monsoon season 2-ring PAHs contributed more than 50%. Four-ring PAHs were found to be most dominated during pre-monsoon in street dust samples. Thus, in general in Guwahati, PAHs profile was found to be dominated by 2-ring PAHs during monsoon and post-monsoon, while by 4-ring PAHs during pre-monsoon season.

This profile pattern was relevant to source and physicochemical characteristics of PAHs. Similar to soil the 'multi-hop' nature of LMWPAHs might have resulted into their predominance during all three seasons in street dust also. Long continuous dry spell during pre-monsoon period could have assisted local source influence, which could be inferred from the prevalence of 4- ring PAHs during that period.



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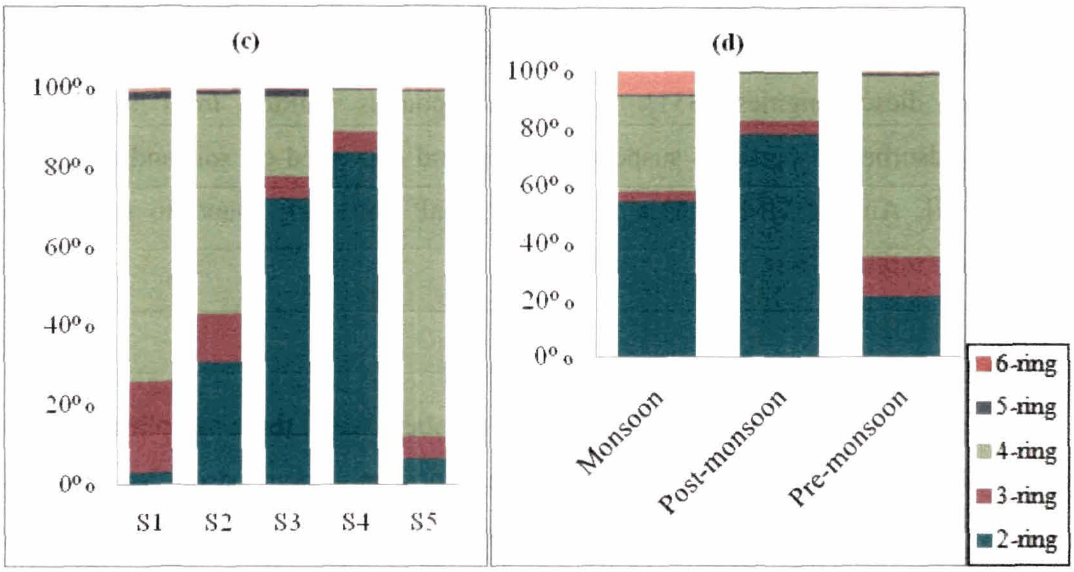


Figure 4.15: Percentage composition of three-, four-, five- and six-ring PAHs during (a) monsoon, (b) post-monsoon (c) pre-monsoon and (d) Guwahati (mean of five sampling sites, S1-S5) in street dust.

4.3.4 Toxicity

Percentage distribution of CPAHs to other studied PAHs is represented in Figure 4.16. CPAHs contribution in monsoon, post-monsoon and pre-monsoon was 39%, 16% and 55% respectively. There was noticeable rise in carcinogenic PAHs percentage during pre-monsoon season. Thus the maximum exposure risk was observed in pre-monsoon season. It was also found that during monsoon CPAHs percentage was much higher than that of post-monsoon despite of high precipitation. The overall CPAHs percentage load in street dust of Guwahati was 33%.

Site-wise pie diagram of CPAHs to rest of the PAHs are illustrated in Figure 4.17. CPAHs contributions were found to be 40%, 37%, 17%, 18% and 83% at S1, S2, S3, S4 and S5 respectively. Despite of minimum PAHs concentration high CPAHs contribution was observed at forest site (S5) which is a major concern for the locality.

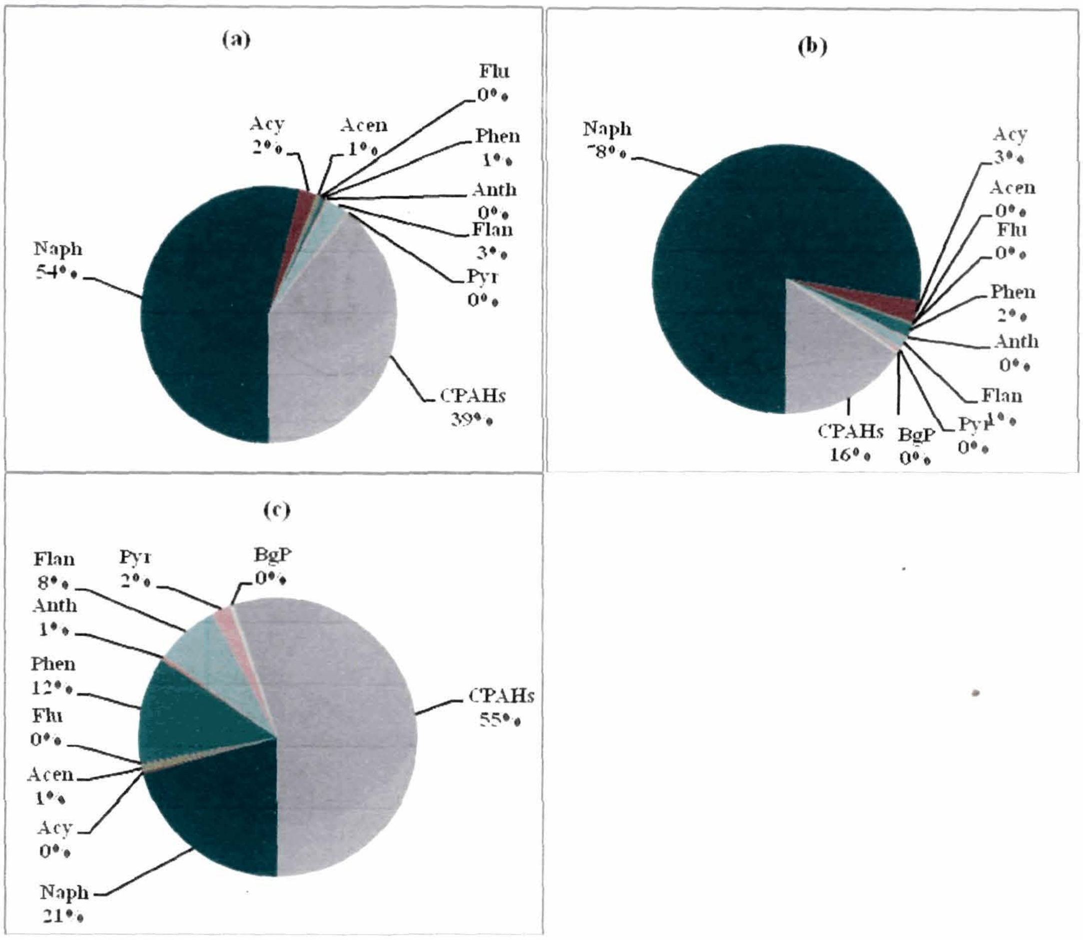


Figure 4.16: Abundance of carcinogenic PAHs (CPAHs) in street dust during- (a) monsoon, (b) post-monsoon and (c) pre-monsoon.

Seasonal mean BaPq level for ∑PAHs was 337±282ngBaPq/gm, 194.4±159ng BaPq/gm and 541.7±550ngBaPq/gm during monsoon, post-monsoon and pre-monsoon season respectively (Table 4.26). Great rise in toxicity was observed during pre-monsoon season. Meanwhile, individual PAH had a common contribution to total BaPq concentration during all the three seasons. Thus street dust of Guwahati possesses high exposure risk to people mainly during pre-monsoon season.

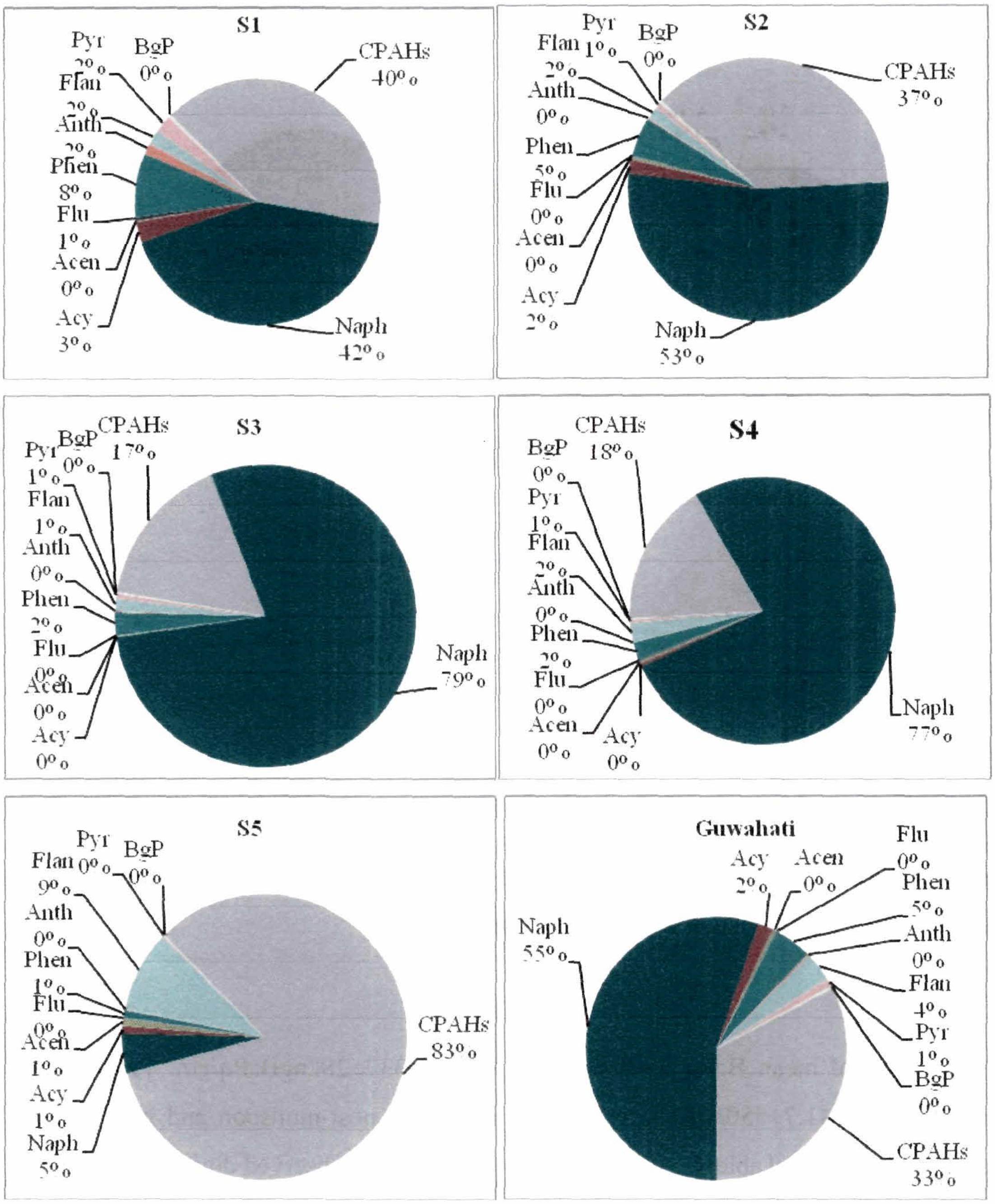


Figure 4.17 Abundance of carcinogenic PAHs (CPAHs) in street dust in all the sampling sites and Guwahati (mean of five sampling sites, S1-S5).

Table 4.26 Mean BaPeq concentrations (ng/gm) of 16 PAHs in street dust of Guwahati during monsoon, post-monsoon and pre-monsoon

	Monsoon	Post-monsoon	Pre-monsoon
Naph	5.4±3.0	16.5±10	3.1±2
Acy	0.2±0.3	0.6±1	0.04±0.04
Acen	0.04±0.01	0.05±0.03	0.09±0.2
Flu	0.02±0.01	0.01±0.04	0.03±0.02
Phen	0.1±0.1	0.4±0.4	1.8±3
Anth	0.2±0.4	0.4±0.2	0.6±1
Flan	0.3±0.2	0.3±1	1.1±2
Pyr	0.03±0.01	0.1±0.1	0.3±1
BaA	244.7±286	91.1±109	395.2±401
Chry	5.7±3	25.5±27	39.9±37
BbF	5.1±8	1.7±1	4.5±5
BbK	0.34±0.0	1.4±2	4.8±5
BaP	29.3±35	29±11	74.9±112
DBA		28.5±31	9.9±9
BgP		0.4±0.4	0.4±1
IP	84.7±138	10.8±10	6.1±5
∑PAHs	337±282	194.4±159	541.7±550

4.3.5 PAHs Ratios and Source Identification

PAHs ratios in street dust are shown in Table 4.27. The IP/(IP+BgP) ratio of 0.62 is a specified marker for wood burning [201]. Mean IP/(IP+BgP) ratio 0.74±0.3 during post-monsoon indicated diesel emission as the major source of PAHs in street dust while, the value of 0.67±0.2 during pre-monsoon specify wood combustion as primary source. The ratio of Pyr/ BaP ~10 and ~1 represent diesel and gasoline engine emission respectively [215]. The ratio of Pyr/BaP in the present study was 3.04±4, 4.42±4 and 3.41±2 during monsoon, post-monsoon and pre-monsoon respectively indicating diesel and gasoline engine combustion were the mixed sources of PAHs emission.

In all three season Flan/(Flan+Pyr) ratio ranged was >0.5 indicating pyrolytic origin of PAHs in street dust of Guwahati. Phen/(Phen+Anth) ratio of >0.7 is designated to fossil fuel combustion source [210]. The mean Phen/(Phen+Anth) ratio in Guwahati street dust was greater >0.7 during all the seasons inferred fossil fuel combustion as one of the sources of PAHs.

Furthermore, BaA/Chry ratio can be employed to estimate distance of potential sources. BaA is photodegraded faster during transporation than its isomer Chry [332]. Thus, BaA/Chry can be used as a marker for degree of photodegradation and source discrimination [142]. In the present study BaA/Chry ratio were found to be 0.55±0.1, 0.52±0.4 and 0.89±0.4 during monsoon, post-monsoon and pre-monsoon season respectively. The high value of BaA/Chry ratio during pre-monsoon clearly revealed that sources of PAHs during that season were exclusively local.

Table 4.27 Mean diagnostic ratios of PAHs in street dust during three seasons in Guwahati city

	IP/(IP+BgP)	Pyr/BaP	Flan/(Flan+Pyr)	Phen/(Phen+Anth)	BaA/Chry
Monsoon	0 92±0.1	3 04±4	0.83±0.2	0.77±0.3	0.55±0.1
Post-monsoon	0.74±0.3	4.42±3	0.58±0.3	0.75±0.4	0.52±0 4
Pre-monsoon	0.67±0.2	3.14±2	0.62±0.3	0.97±0.02	0.89±0.4

4.3.6 Source Apportionment

The four factors were identified using PCA accounting for about 83.9% of the total variance along with their eigen values are depicted in Table 4.28. Factor 1, explained 45.5% of total variance, had high loading of Phen, Anth, Pyr, BaA, Chry, BbF, BkF, BaP, BgP. BbF in addition to BgP and Pyr is an indication of diesel-engine vehicle [324]. However, Anth, Chry, BaA, BbF, BkF and BaP are regarded as specific marker for coal combustion [208]. Moreover, Phen, Anth, Pyr, BaA and Chry are typical indicator of wood combustion [208]. So, the 1st factor is selected as the combination of diesel engine, coal and wood combustion.

Factor 2 explained 17.864% to the total variance had high loading with Acen, Flu and Flan. Acen, Flu and Flan are considered to be from vehicular combustion [325]. Thus the 2nd factor reflected as mobile emission source.

Factor 3 had high loading of Naph, BbF and IP contributing 12.8% of total variance. These compounds are identified as typical tracer for diesel powered vehicle [324]. This factor is thus selected for diesel engine vehicle.

Factor 4 explained 7.7 % of total variance with high contribution from Acy, Chry and DBA. Acy, Chry and DBA are considered as specific marker for automobile exhaust [333]. This factor is considered as traffic source.

Table 4.28 Principal Component Analysis of PAHs in street dust of Guwahati city (extraction method: Principal Component Analysis (Rotation method: Varimax with Kaiser normalization), loading>0.5 are shown in bold)

	1	2	3	4
Naph	-0.292	-0.216	**0.612**	-0.105
Acy	0.049	-0.015	0.333	**0.636**
Acen	0.000	**0.965**	-0.058	0.115
Flu	0.142	**0.907**	0.115	-0.067
Phen	**0.989**	0.025	0.025	0.034
Anth	**0.910**	0.029	-0.102	0.043
Flan	0.033	**0.967**	-0.125	-0.062
Pyr	**0.981**	-0.027	0.012	0.096
BaA	**0.715**	0.419	-0.072	-0.159
Chry	**0.771**	0.260	-0.063	**0.519**
BbF	**0.478**	0.055	**0.791**	0.054
BkF	**0.906**	0.087	0.034	0.167
BaP	**0.984**	0.021	-0.011	0.025
DBA	0.202	-0.060	-0.324	**0.771**
BgP	**0.890**	-0.010	-0.110	0.382
IP	-0.113	0.051	**0.885**	0.042
Eigen Value	7.275	2.858	2.048	1.245
% of Variance	45.467	17.864	12.799	7.779
Cummulative %	45.467	63.330	76.129	83.908

4.3.7 Seasonal Association of Carbon with PAHs

Range of OC, BC, BC/OC in Guwahati street dust samples were 0.08-2.63%, 17.99-29 mg/gm and 1-22.8 respectively (Table 4.29). For both OC (1.6±0.9 mg/gm) and BC (25.5±4.0 mg/gm) maximum mean value was exhibited during pre-monsoon season. Correlation analysis was also performed to explore the relationship of PAHs with OC, BC and BC/OC in street dust. Correlation coefficient of PAHs with OC, BC and BC/OC for the entire study period are put up in Table 4.30. Significant correlation was observed for OC with DBA only while, BC showed significant correlation with Chry and DBA. But no significant correlation was observed in case of BC/OC with any PAH.

Table 4.29 Correlation matrix of PAHs with organic carbon (OC), black carbon (BC), BC/OC and heavy metals in street dust in Guwahati

	Naph	Acy	Acen	Flu	Phen	Anth	Flan	Pyr	BaA	Chry	BbF	BkF	BaP	DBA	BgP	IP	∑PAHs
Cd	-0.2	-0.5	-0.3	-0.2	0.0	0.0	-0.3	-0.1	-0.1	0.3	0.0	0.3	-0.1	0.2	0.0	0.2	-0.2
Cr	-0.1	0.0	-0.1	-0.1	0.3	0.4	0.0	0.3	0.3	0.3	0.0	0.3	0.3	0.2	0.3	0.1	0.0
Cu	0.1	0.0	0.3	0.2	0.3	0.3	0.1	0.3	0.2	**0.6***	0.2	0.4	0.3	**0.8****	**0.6***	0.1	0.2
Fe	-0.1	0.0	-0.2	-0.1	0.3	0.4	0.0	0.3	0.2	0.1	-0.1	0.2	0.3	0.0	0.2	-0.1	0.0
Mn	0.0	**0.9****	-0.1	0.1	0.2	0.4	-0.1	0.3	0.2	0.4	0.1	0.4	0.2	0.1	0.3	-0.1	0.1
Ni	-0.2	0.2	-0.2	0.0	0.2	0.4	-0.1	0.2	0.2	0.2	0.1	0.3	0.2	0.2	0.3	0.3	-0.1
Pb	-0.1	-0.2	0.0	-0.2	-0.2	-0.1	-0.1	-0.1	-0.1	0.0	0.0	-0.2	-0.1	**0.7****	0.2	0.2	-0.1
Zn	-0.1	-0.1	-0.1	-0.1	0.3	0.2	-0.1	0.2	0.2	0.4	0.0	0.4	0.2	**0.5***	0.4	0.2	-0.1
OC	-0.2	0.0	-0.2	-0.3	0.1	0.0	-0.3	0.1	-0.2	0.3	0.0	0.2	0.1	**0.5***	0.3	-0.1	-0.2
BC	0.3	0.1	0.4	0.2	0.3	0.1	0.4	0.2	0.2	**0.6***	-0.2	0.4	0.2	**0.5**	0.4	-0.2	0.4
BC/OC	0.1	-0.2	0.1	0.1	-0.2	-0.2	0.1	-0.2	-0.1	-0.2	-0.3	-0.2	-0.2	-0.2	-0.3	-0.1	0.0

**Correlation is significant at 0.01 level (2-tailed)

*Correlation is significant at 0.05 level (2-tailed)

Correlation was also computed on seasonal basis (Table 4.30). Good positive correlation was observed for PAH with OC during monsoon (Naph, Acy, Phen, BbF, IP and ∑PAHs) and post-monsoon (Acen, BaP, DBA, BgP and IP) season while the relationship was significantly negative during pre-monsoon season (Naph, Acen, Flu, Flan, BaA, IP and ∑PAHs).

Considering BC, no significant relationship was revealed during monsoon and pre-monsoon. However, street dust samples in post-monsoon showed good positive correlation with BC (Acen, Phen, Pyr, BaA, Chry, BkF, BaP, DBA and BgP). However, street dust PAHs (Naph, Acen, Flu, Flan and ∑PAHs) recorded strong significant correlations with BC/OC only during pre-monsoon.

Table 4.30 Correlation matrix of PAHs with organic carbon (OC), black carbon (BC), BC/OC and heavy metals in street dust of Guwahati during monsoon, post-monsoon and pre-monsoon

Monsoon	Naph	Acy	Acen	Flu	Phen	Anth	Flan	Pyr	BaA	Chry	BbF	BkF	BaP	DBA	BgP	IP	∑PAHs
Cd	0.1	**0.9***	0.4	0.5	0.7	0.0	0.2	0.1	-0.3	0.1	**0.9***	-0.2	0.1	-0.2	-0.2	**0.9***	0.3
Cr	0.7	0.1	-0.4	0.0	0.4	0.0	0.3	-0.6	0.3	-0.6	0.1	**−0.9***	-0.4	-0.5	-0.5	0.1	0.7
Cu	0.4	0.9	0.5	0.7	0.8	0.1	-0.5	0.6	-0.8	0.6	0.9	-0.1	-0.5	-0.2	-0.2	0.8	0.2
Fe	0.5	-0.1	-0.7	0.1	0.2	0.3	0.1	-0.5	0.3	-0.6	-0.1	-0.8	-0.4	-0.8	-0.8	-0.2	0.4
Mn	-0.4	-0.1	-0.7	0.8	-0.3	**1.0****	-0.4	0.3	-0.3	-0.2	-0.2	0.2	-0.2	-0.9	-0.9	-0.2	-0.6
Ni	0.6	0.4	-0.4	0.5	0.6	0.3	-0.1	-0.2	-0.1	-0.3	0.4	-0.8	-0.6	-0.8	-0.8	0.3	0.5
Pb	0.6	0.5	0.0	-0.1	0.7	-0.4	0.6	-0.6	0.4	-0.5	0.6	**−0.9***	0.0	-0.3	-0.3	0.5	0.9
Zn	0.7	0.7	0.2	0.0	0.8	-0.5	0.4	-0.4	0.2	-0.2	0.7	-0.9	-0.1	-0.1	-0.1	0.7	**0.9***
OC	0.7	0.7	0.1	0.1	0.8	-0.3	0.4	-0.4	0.2	-0.3	0.7	**−0.9***	-0.1	-0.3	-0.3	0.7	0.9
BC	-0.2	-0.2	-0.7	0.0	-0.2	0.3	0.6	-0.7	0.7	-0.9	-0.2	-0.6	0.4	-0.6	-0.6	-0.2	0.2
BC/OC	*-0.2*	*-0.5*	*0.2*	*-0.1*	*-0.4*	*0.0*	*-0.6*	*0.6*	*-0.4*	*0.7*	*-0.5*	0.8	-0.3	0.5	0.5	-0.5	-0.5
Post-monsoon	Naph	Acy	Acen	Flu	Phen	Anth	Flan	Pyr	BaA	Chry	BbF	BkF	BaP	DBA	BgP	IP	∑PAHs
Cd	0.6	**0.9***	0.4	0.6	0.9	0.7	-0.2	**0.9***	**0.9***	0.9	**0.9***	**1.0***	0.9	0.1	0.5	-0.4	**0.9***
Cr	0.1	0.1	0.3	0.4	0.1	0.8	0.1	0.3	0.2	0.2	-0.1	0.1	0.4	0.3	0.2	-0.4	0.2
Cu	-0.4	0.0	**1.0****	-0.3	0.3	0.2	-0.1	0.4	0.2	0.6	0.0	0.1	0.6	1.0	**0.9***	-0.4	-0.1
Fe	0.3	-0.2	**−0.9***	0.4	-0.5	0.0	0.2	-0.5	-0.4	-0.8	-0.3	-0.3	-0.7	-0.8	**−1.0***	0.3	-0.1
Mn	0.7	1.0	0.1	**0.7**	**0.9***	0.5	-0.1	0.8	**1.0****	0.7	**1.0****	**1.0****	0.7	-0.1	0.2	-0.1	**1.0****
Ni	0.2	0.3	0.5	0.4	0.3	0.9	0.0	0.5	0.4	0.5	0.1	0.4	0.6	0.4	0.4	-0.5	0.4
Pb	-0.6	-0.4	0.8	-0.6	-0.1	0.1	-0.2	0.0	-0.2	0.3	-0.4	-0.3	0.3	0.9	0.8	-0.5	-0.4
Zn	-0.6	-0.4	0.7	-0.3	-0.1	0.3	0.1	0.1	-0.2	0.2	-0.5	-0.3	0.3	0.8	0.6	-0.3	-0.4
OC	-0.2	-0.1	0.8	-0.4	0.1	0.4	-0.4	0.1	0.0	0.4	-0.1	-0.1	0.5	0.8	0.8	-0.7	-0.1
BC	-0.3	0.4	**0.9***	0.2	0.7	0.2	0.3	0.8	0.6	0.9	0.4	0.5	0.9	0.9	**0.9***	0.0	0.2
BC/OC	-0.4	-0.2	-0.4	0.4	0.0	-0.5	**0.9***	0.1	0.0	-0.2	-0.1	-0.1	-0.3	-0.2	-0.4	**1.0***	-0.3

Pre-monsoon	Naph	Acy	Acen	Flu	Phen	Anth	Flan	Pyr	BaA	Chry	BbF	BkF	BaP	DBA	BgP	IP	∑PAHs
Cd	-0.3	0.1	-0.4	-0.2	0.0	-0.1	-0.3	-0.1	-0.1	0.3	-0.4	0.4	-0.1	**0.6**	0.0	0.2	-0.3
Cr	-0.1	0.3	-0.1	-0.2	0.6	0.5	0.0	0.5	0.5	0.6	-0.1	0.6	0.5	0.5	0.5	0.5	0.0
Cu	0.1	0.5	0.1	0.2	0.5	0.4	0.2	0.3	0.5	0.8	-0.1	0.7	0.3	0.8	0.4	0.7	0.2
Fe	-0.1	0.4	0.0	-0.1	0.7	0.7	0.0	0.7	0.6	0.6	0.1	0.6	0.7	0.4	0.7	0.6	0.0
Mn	0.0	0.8	0.1	0.1	**0.9***	**1.0***	0.1	**0.9***	**0.9***	**0.9***	**0.5**	**0.9**	**0.9***	**0.7**	**0.9***	**0.9***	0.1
Ni	-0.2	0.4	-0.2	-0.2	0.6	0.5	-0.1	0.5	0.4	0.6	-0.2	0.7	0.4	0.6	0.5	0.5	-0.1
Pb	-0.1	0.0	-0.1	-0.1	0.0	-0.1	-0.1	-0.1	0.0	0.3	-0.6	0.3	-0.2	0.5	0.0	0.2	-0.1
Zn	-0.2	0.3	-0.3	-0.2	0.4	0.2	-0.2	0.2	0.2	0.6	-0.3	0.6	0.2	0.7	0.3	0.5	-0.2
OC	-0.7	-0.3	-0.8	**− 0.9***	-0.2	-0.3	-0.8	-0.2	-0.7	-0.4	-0.4	-0.1	-0.3	0.0	-0.3	-0.5	-0.8
BC	0.3	-0.3	0.2	0.1	-0.2	-0.2	0.2	-0.2	0.0	0.1	-0.8	0.0	-0.3	0.1	-0.2	0.1	0.3
BC/OC	**1.0****	-0.1	**1.0****	**1.0****	-0.1	-0.0	**1.0****	-0.1	0.4	-0.2	-0.2	-0.1	-0.1	-0.2	-0.1	0.3	**1.0****

**Correlation is significant at 0.01 level (2-tailed)

*Correlation is significant at 0.05 level (2-tailed)

To better understand the effect of BC on street dust PAHs dispersions, dependencies of log PAHs on BC/OC ratios were examined (Figure 4.18). Negative slopes were obtained for monsoon and post-monsoon period when log∑HMWPAHs, log∑LMWPAHs and log∑PAHs were regressed over BC/OCs with coefficient of determination r^2=0.43, r^2=0.04 and r^2=0.28 during monsoon and r^2=0.002, r^2=0.12 and r^2=0.08 during post-monsoon respectively. However, a positive slope with high coefficient of determination r^2=0.23, r^2=0.98 and r^2=0.99 for log∑HMWPAHs, log∑LMWPAHs and log∑PAHs respectively was found during pre-monsoon period (Figure 4.18 c). In case of OC, log∑HMWPAHs, log∑LMWPAHs and log∑PAHs showed positive slope with co-efficient of determination r^2=0.29, r^2=0.48 and r^2=0.72 respectively during monsoon (Figure 4.19). While negative slope was observed during pre-monsoon with co-efficient of determination r^2=0.41, r^2=0.58 and r^2=0.52 for log∑HMWPAHs, log∑LMWPAHs and log∑PAHs respectively.

This relationship of PAHs with carbon in street dust was found to be almost similar to that of soil. The possible reason for such association is already well explained in 'soil' section.

Thus in street dust of Guwahati, PAHs dissipation is controlled by both BC and OC. This relationship also indicated that the PAHs were mostly from combustion derived i.e. anthropogenic activities. However, more detailed study is required to make some definite conclusion regarding PAH-BC relationship.

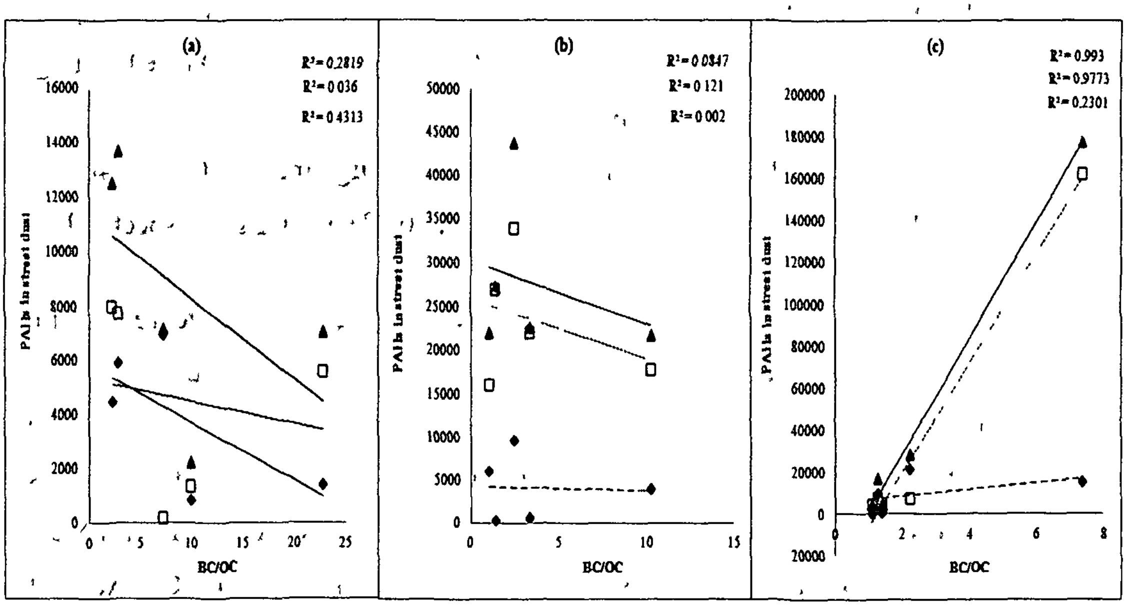


Fig.4.18: Relationships of HMWPAHs (◆), LMWPAHs (□) and ΣPAHs (▲) with BC/OC during-(a) monsoon, (b) post-monsoon and (c) pre-monsoon season.

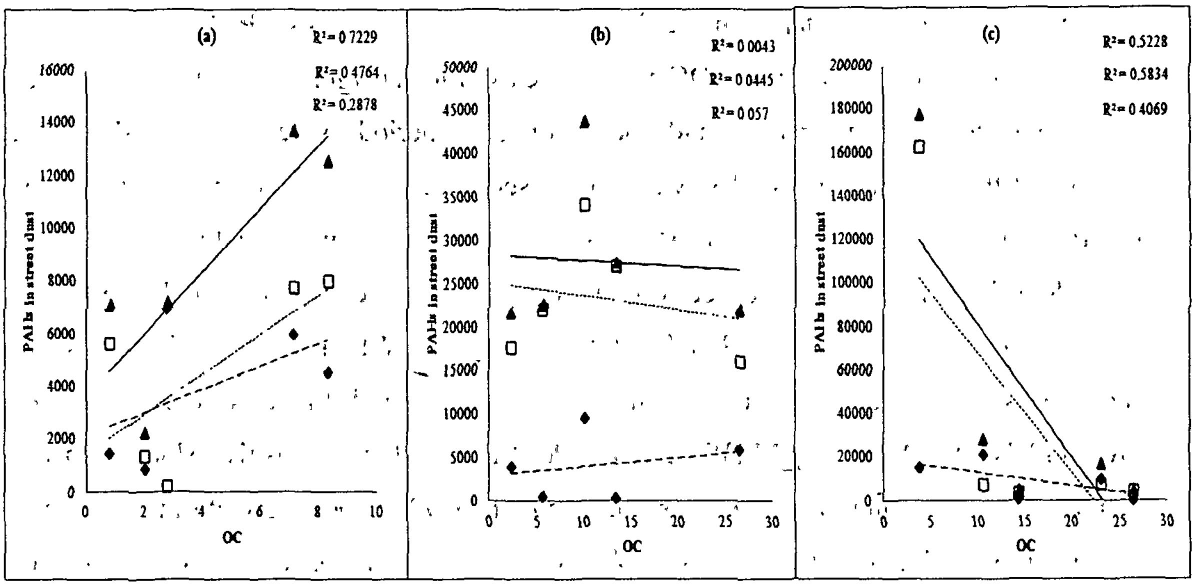


Fig.4.19 Relationships of HMWPAHs (◆), LMWPAHs (□) and ΣPAHs (▲) with OC during- (a) *monsoon*, (b) *post-monsoon and* (c) *pre-monsoon season.*

4.3.8 Heavy metals in Street Dust

Seasonal mean and range of heavy metals Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were shown in Table 4.25. The mean value of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn, during monsoon were 0.0001±0.0µg/gm, 0.01±0.003µg/gm, 0.01±0.002µg/gm, 10.8±3.1µg/gm, 0.3±0.15µg/gm, 0.01±0.001µg/gm, 0.01±0.004µg/gm and 0.03±0.01µg/gm respectively, during post-monsoon values were 0.0002±0.000µg/gm, 0.01±0.0030µg/gm, 0.01±0.010µg/gm, 11.9±1µg/gm, 0.4±0.30µg/gm, 0.005±0.001µg/gm, 0.01±0.01µg/gm and 0.03±0.01µg/gm respectively and during pre-monsoon the values were 0.0001±0.0001µg/gm, 0.01±0.004µg/gm, 0.006±0.004µg/gm, 10.06±3.4µg/gm, 0.2±0.1µg/gm, 0.01±0.002µg/gm, 0.003±0.001µg/gm and 0.03±0.02µg/gm respectively.

Combinations of many source identification methods are often considered as more efficient than one single method to increase resolution of dataset Masclet et al. [334], Dickhut et al. [322]. Therefore, in addition to diagnostic ratio and PCA correlation study of street dust PAHs with heavy metals like Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn was also employed (Table 4.30). The overall correlation of PAHs with heavy metal did not revealed very significant relationship. Only Acy with Cd; Chry, DBA and BgP with Cu; Acy with Mn DBA with Pb and Zn was observed. However, seasonality was observed in the association of heavy metals with PAHs (Table 4.31). Cd showed significant association with various PAHs during monsoon and post-monsoon season. Cu showed significant relationship with individual PAHs during post-monsoon. Moreover, very strong correlation was observed for Mn with PAHs during pre-monsoon season.

Cd and Pb are found to be emitted from Gasoline vehicle [335].Fuel oil and coal combustion used to release heavy metals such as Cd, Cr, Cu, Mn, Ni and Zn [336, 337]. Thus, estimation of the heavy metals and their relationship with PAHs further confirmed the diesel, wood and coal combustion as the sources of street dust PAHs in Guwahati.

4.4 PAHs in River Water of Guwahati City

4.4.1 Summary Statistics of River Water PAHs

Concentration of PAHs with their mean and range values are shown in Table 4.31. The concentration of total detected PAHs in Bharalu River ranged from 3.351-72.893 ng/ml with mean value of 29.8±22. The BaP concentrations were found to be between BDL and 2.608 ng/ml with mean of 0.4±1.

Table 4.31 Mean concentrations (ng/ml) with range of individual PAHs, ∑PAHs and their mean BaPeq concentration in Bharalu River

Compound	Mean (Range)	BaPeq mean
Naph	2 0±2 (BDL-6 6)	0 002±0 002
Acy	1 2±2 (BDL-7 2)	0 001±0 002
Acen	0 5±1 (BDL-1 8)	0 0004±0 001
Flu	1±1 (BDL-3 9)	0 001±0 001
Phen	8 0±4 (BDL-13 7)	0 008±0 004
Anth	1 1±2 (BDL-4 9)	0 011±0 02
Flan	1 9±2 (BDL-5 6)	0 002±0 002
Pyr	7 1±7 9 (BDL-16 9)	0 007±0 01
BaA	0 40±1 (BDL 1 2)	0 036±0 02
Chry	3 2±2 (BDL-8 3)	0 032±0 02
BbF	8 3±15	0 827±2

	(BDL-44.5)	
BkF	2.8±5 (BDL-14.6)	0.283±1
BaP	0.4±1 (BDL-2.6)	0.372±1
DBA	1.9±3 (BDL-7.7)	1.903±3
BgP	0.1±0.1 (BDL-0.1)	0.0006±0.001
IP	5.9±10 (BDL-23.9)	0.591±1
∑PAHs	29.8±22 (3.4-72.9)	2.274±3

4.4.2 Seasonal and Spatial Variation of PAHs

Site wise ∑PAHs is shown in Table 4.32 and illustrated in Figure 4.20 and 4.21 for post-monsoon and pre-monsoon season respectively. On spatial basis, the maximum concentration was observed at R5 during pre-monsoon season. The river channel receives input from the catchment of the industrial belt of the city at this site where the refinery and many industries are located. The industrial area around the refinery hosts few coke industries also which would have deposited large volumes of PAHs that are drained to the Bharalu River. The minimum concentration was found at site R7 during post-monsoon season.

Almost all the sites showed an increase in ∑PAHs concentrations with high standard deviation during pre-monsoon compared to post-monsoon periods. Such results can be attributed to difference in the discharge regime of the river between the seasons. High runoff together prevailing atmospheric condition might have triggered PAHs dissipation and decomposition that in turn resulted into lower PAHs levels during post-monsoon [338]. On the other hand, atmospheric conditions like higher emission rates from various sources, lower inversion height, and lower intensity of sunshine with less efficient photochemical decomposition might favour more atmospheric deposition of PAHs during pre-monsoon time [339].

Table 4.32 Concentrations (ng/ml) of 16 PAHs and their sums in water of river Bharalu during post-monsoon and pre-monsoon season

	Naph	Acy	Acen	Flu	Phen	Anth	Flan	Pyr	BaA	Chry	BbF	BkF	BaP	DBA	BgP	IP	∑PAHs
Post monsoon																	
R1	0 95	0 29	BDL	0 06	1 56	0 08	1 24	16 94	BDL	5 32	0 66	0 05	0 04	BDL	BDL	0 44	27 6
R2	6 55	0 05	0 38	0 10	2 89	0 82	0 42	BDL	0 02	1 96	1 13	BDL	0 02	BDL	BDL	BDL	14 3
R3	3 64	BDL	BDL	2 60	BDL	BDL	0 57	BDL	0 00	2 11	44 46	14 57	BDL	BDL	BDL	BDL	68 0
R4	0 36	BDL	BDL	BDL	BDL	4 87	0 22	BDL	0 29	3 41	0 13	0 01	0 01	0 02	BDL	BDL	9 3
R5	4 77	BDL	0 41	0 03	10 54	1 43	2 03	1 18	BDL	5 49	BDL	BDL	0 07	BDL	0 02	BDL	26 0
R6	2 40	0 08	BDL	BDL	BDL	0 02	1 35	BDL	BDL	BDL	1 08	0 05	0 07	BDL	0 13	0 45	5 6
R7	1 87	0 90	BDL	0 33	BDL	BDL	BDL	BDL	BDL	BDL	0 25	BDL	BDL	BDL	BDL	BDL	3 4
Pre monsoon																	
R1	BDL	BDL	0 25	1 06	13 73	BDL	2 61	BDL	0 07	2 89	1 09	0 03	0 47	BDL	BDL	0 15	22 3
R2	0 41	0 05	0 33	0 91	9 79	0 12	4 10	BDL	0 09	2 62	2 90	1 10	0 26	BDL	BDL	BDL	22 7
R3	0 07	1 09	0 31	1 16	8 31	1 04	1 26	0 30	1 14	1 90	10 78	1 23	0 39	7 67	0 03	4 63	41 3
R4	2 18	0 13	0 08	0 17	9 65	0 06	2 49	BDL	1 21	1 95	2 29	0 06	0 14	0 49	BDL	23 88	44 8
R5	0 39	7 19	1 82	3 91	11 24	0 19	0 54	BDL	BDL	1 92	39 82	2 60	2 61	0 67	BDL	BDL	72 9
R6	BDL	0 98	0 31	BDL	2 34	2 02	5 56	10 05	0 62	8 34	1 57	11 12	0 20	0 67	BDL	BDL	43 8
R7	0 09	BDL	0 10	0 14	10 41	BDL	2 03	BDL	0 17	0 96	1 33	0 30	0 20	BDL	BDL	BDL	15 73

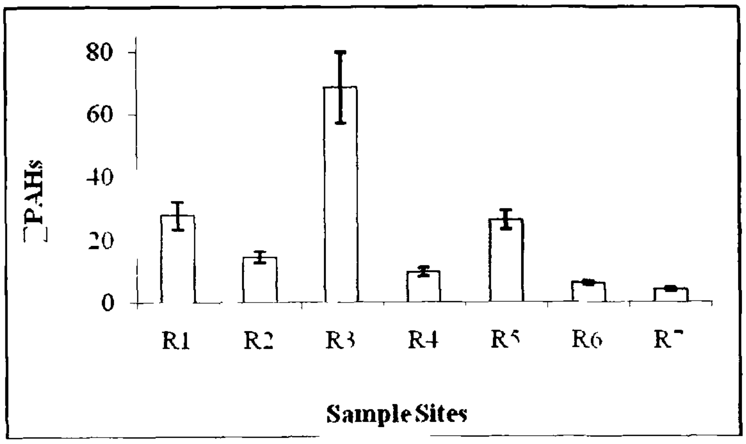


Figure 4.20: ∑PAHs (±SD) of Bharalu River water at seven sites during post-monsoon.

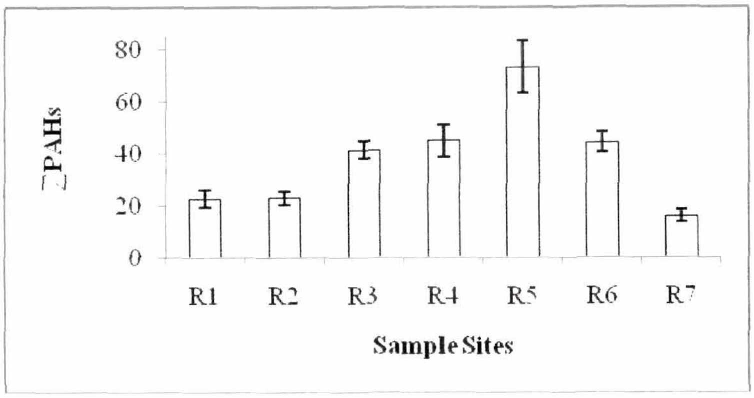


Figure 4.21: ∑PAHs (±SD) of Bharalu River water at seven sites during pre-monsoon.

4.4.3 PAHs profiles

PAHs profile was dominated mainly by 2, 3, and 4-ring PAHs during post-monsoon season (Figure 4.22). In samples during pre-monsoon predominance of 3-5 ring PAHs prevails in almost all the sites. Prominent meteorological condition and differential behaviour of PAH with different molecular weight could be the possible reason for such PAHs profile in river water. Dominance of 5-ring PAHs at site R3 during post-monsoon and 6-ring PAHs at site R5 during pre-monsoon was also observed.

Presence of 2-ring PAHs during post-monsoon time and its drastic decrease during pre-monsoon time directly indicated their high solubility in water. However, the prevalence of HMWPAHs in water despite of their low solubility could be due to continuous discharge of waste material into the river.

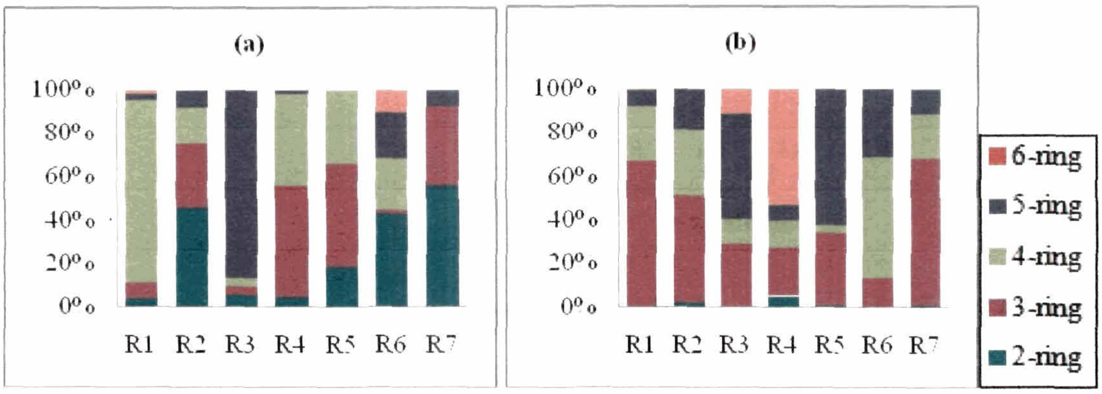


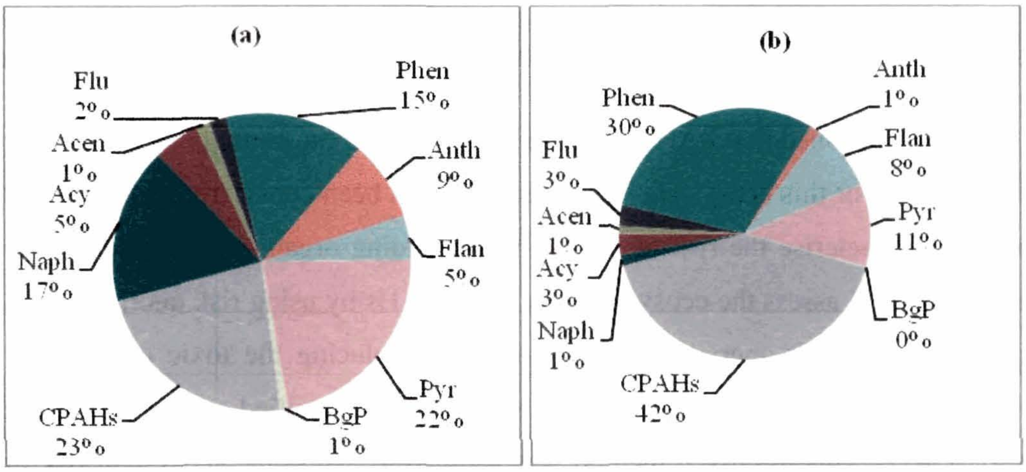
Figure 4.22: Percentage composition of three-, four-, five- and six-ring PAHs at seven sampling sites in Bharalu River water during (a) post-monsoon and (b) pre-monsoon seasons.

4.4.4 Toxicity

Percentage of CPAHs to rest of the PAHs was almost same in both the sampling seasons with contribution of 53% and 54% during post-monsoon and during pre-monsoon season respectively (Figure 4.23). Individually, concentration of seasonal mean of individual PAH were found to be in the order - Naph>BbF>Chry>Phen>Pyr>Anth and Phen>>BbF>IP>Flan>Chry during post- and pre-monsoon seasons respectively. High abundance of Naph and Phen could be due to their high solubility in water (Appendix A).

The similar contribution of CPAHs during both the sampling seasons showed a continuous input of carcinogenic PAHs from same type of sources in water. This is a matter of concern for the river system.

BaPq concentration of ∑PAHs ranged from 0.03-9.89ngBaPq/ml (Table 4.33). Mean BaPeq concentration of ∑PAHs was found to be maximum during pre-monsoon season (3.6±4ngBaPq/ml) and minimum during post-monsoon season (1.0±2ngBaPq/ml). The maximum concentration was observed at site R3 during pre-monsoon and minimum at R7 during post-monsoon season. Thus the risk is comparatively high during pre-monsoon period. There is no regulation of PAHs concentrations in aquatic environment so far in India. More so in the Northeast India no systematic PAHs study is taken up so far.



Figur 4.23: Abundance of carcinogenic PAHs (CPAHs) in Bharalu River during- (a) post-monsoon and (b) pre-monsoon season.

Table 4.33 BaPeq concentrations of ∑PAHs (ng/ml) with their seasonal mean in Bharalu River Water

PoM	∑PAHs (Total BaPeq)
R1	0.23
R2	0.17
R3	5.93
R4	0.15
R5	0.15
R6	0.24
R7	0.03
	1.0±2
PrM	
R1	0.64
R2	0.71
R3	9.89
R4	3.40
R5	7.56
R6	2.32
R7	0.40
Mean	3.6±4

4.4.5 Ecosystem Risk

It is fully established that PAHs in aquatic environment can cause potential risk for aquatic ecosystems. For this ecosystem risk assessment has been considered to be a useful tool in order to characterise the risk of PAHs to surrounding organisms and ecosystems [340]. Kalf et al. [341] assess the ecosystem risk of 10 PAHs by using risk quotient (RQ). However, Cao et al. 2010 upgraded the method by introducing the toxic equivalency factors for all the USEPA listed 16 priority PAHs which was verified as more authentic and scientific [342]. This improved method was adopted to assess the ecosystem risk of PAHs in water and sediment of Bharalu River system.

Risk quotients (RQ) value indicated the levels of risk posed by certain PAHs which were calculated using following equation:

$RQ = C_{PAHs} / C_{QV}$

Where C_{PAHs} is the concentration of certain PAHs in the medium, C_{QV} was the corresponding quality values of certain PAHs in the same medium [341]. In place of quality values the negligible concentration (NCs) and the maximum permissible concentrations (MPCs) in the medium as recommended by Kalf et al. [341] were used in the present study. The RQ_{NCs} and RQ_{MPCs} were represented as follows:

$RQ_{NCs} = C_{PAHs} / C_{QV(NCs)}$

$RQ_{MPCs} = C_{PAHs} / C_{QV(MPCs)}$

Where $C_{QV(NCs)}$ was the quality values of the NCs of PAHs in the medium and $C_{QV(MPCs)}$ was the quality values of the MPCs of PAHs in the same medium. The $RQ_{\sum PAHs}$, $RQ_{\sum PAHs(NCs)}$ and $RQ_{\sum PAHs(MPCs)}$ are defined as follows:

$RQ_{\sum PAHs}=\sum RQi\ (RQi\geq 1)$

$RQ_{\sum PAHs(NCs)}=\sum RQi_{(NCs)}\ (RQi_{(NCs)}\geq 1)$

$RQ_{\sum PAHs(MPCs)}=\sum RQi_{(MPCs)}\ (RQi_{(MPCs)}\geq 1)$

To calculate $RQ_{\sum PAHs(NCs)}$ and $RQ_{\sum PAHs(MPCs)}$ of $\sum$PAHs, $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ of individual PAHs which were not less than 1 were only considered. This method thus provides an approach to fully consider the ecosystem risk of individual PAHs.

The mean concentrations of $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ in Bharalu River water during post-monsoon and pre-monsoon season were listed in Table 4.34. Basically, $RQ_{(NCs)} < 1.0$ indicated individual PAH might be of little concern, whereas $RQ_{(MPCs)} >$ 1expressed that individual PAHs with much severe load of contamination and necessary remedial action and control measures must be launched. In case of $RQ_{(NCs)} >1.0$ and $RQ_{(MPCs)} <1.0$ was an indication of intermediate level of contamination of individual PAH and some control measures need be undertaken in such situation.

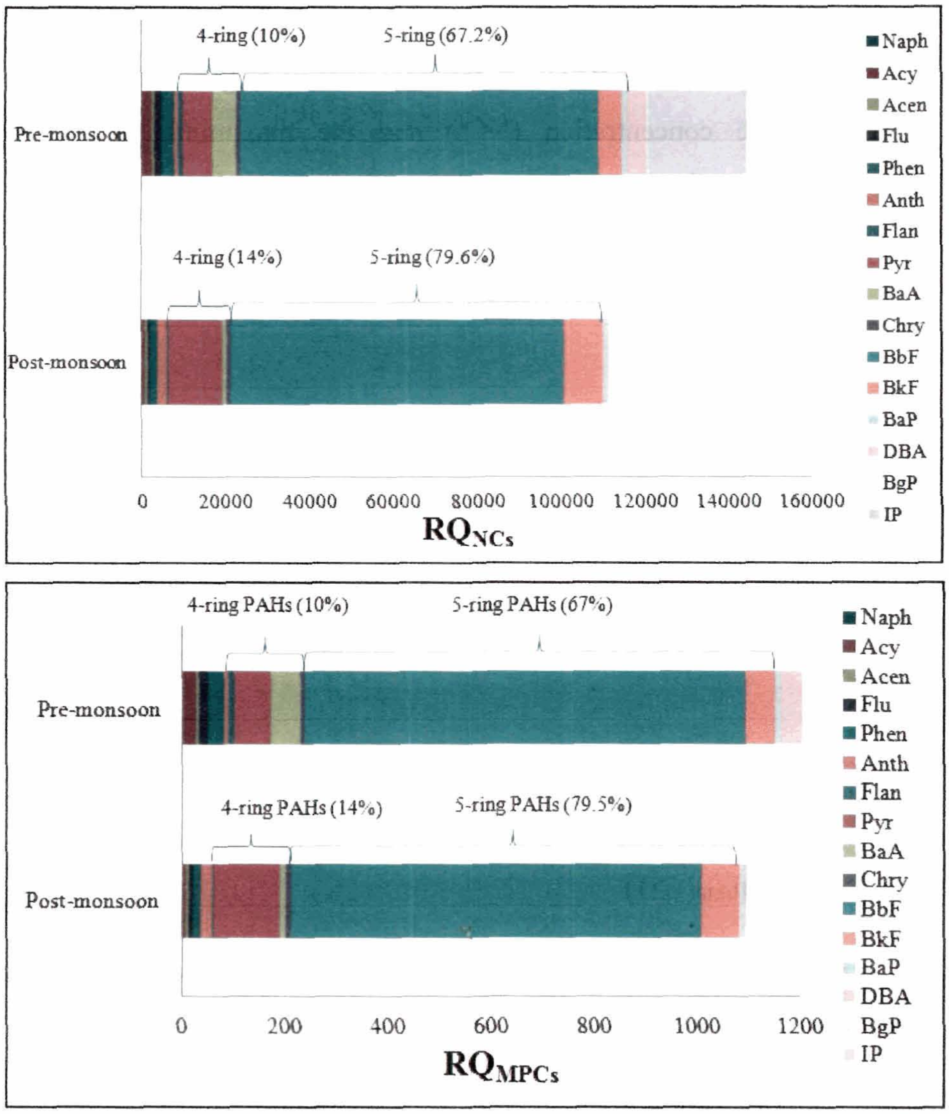


Figure 4.24: Mean RQ_{NCs} and Mean RQ_{MPCs} values of individual PAHs in water of Bharalu River during post-monsoon and pre-monsoon season.

Individually, $RQ_{(MPCs)}$ value of all the individual PAHs were >1.0 during both post-monsoon and pre-monsoon season except for Naph during pre-monsoon indicating severe toxicity to aquatic organisms by the 16PAHs. $RQ_{(MPCs)}$ value of 16 individual PAH were also found to be > 1.0 showing high ecosystem risk. High coefficient of variation (CV) for $RQ_{(MPCs)}$ and $RQ_{(MPCs)}$ values of some of the individual PAHs indicated variation in ecosystem risk for those PAHs in different sampling sites.

Figure 4.24 illustrated that 4 and 5-ring PAHs mainly BbF, Pyr and BkF contributed to the main ecosystem risk burden. The ecosystem risk was observed to be higher during pre-monsoon than that of post-monsoon. Higher ecosystem risk was observed by IP during pre-monsoon than that of post-monsoon season. Among the LMWPAHs higher contribution of Acy and Phen was observed which could probably be due to their high water solubility.

$RQ_{(MPCs)}$ of $\sum$PAHs in water of Bharalu River was >1 during both post-monsoon and pre-monsoon seasons. Value $RQ_{(NCs)}$ of $\sum$PAHs was also >800 during both post-monsoon and pre-monsoon. This indicated high ecosystem risk of Bharalu River water during both the season. Moreover, very high percentage of coefficient of variation (CV) for $\sum$PAHs during both the sampling season also revealed great variation of ecosystem risk during both the seasons. From the Figure 4.25 it was also observed that $RQ_{\sum PAHs(NCs)}$ and $RQ_{\sum PAHs(MPCs)}$ values were very high at site R3 during post-monsoon season whereas during pre-monsoon high value was detected at site R5. Site R3 being a commercial area and traffic site could probably attribute to such high RQ value. River channel at site R5 receives input from catchment of the industrial belt of the city where Guwahati refinery and many other industries located there. On the whole, the results marked that PAHs in water of Bharalu River resulted in severe ecosystem risk. Therefore, some control measures and remedial actions may be undertaken to protect the ecosystem of the Bharalu River and surroundings.

Table 4.34 $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ values of PAHs (ng/gm) with their risk classification during post-monsoon and pre-monsoon in Bharalu River water

	Post-monsoon (NCs)			Post-monsoon (MPCs)			Risk Classification	Pre-monsoon (NCs)			Post-monsoon (MPCs)			Risk Classification
	Range	Mean	CV(%)	Range	Mean	CV(%)		Range	Mean	CV(%)	Range	Mean	CV(%)	
Naph	30.2-546.2	244.5	74.9	0.3-5.5	2.8	61.3	High-risk	BDL-181.8	52.3	140.6	BDL-1.8	0.5	140.6	Moderate risk
Acy	BDL-1284.3	471.1	119.4	BDL-12.8	4.7	119.4	High-risk	BDL-10277.1	2695.4	159.2	BDL-102.8	27.0	159.2	High-risk
Acen	BDL-583.4	564.1	4.8	BDL-5.8	5.6	4.8	High-risk	114.9-2606.3	656.3	132.9	1.1-26.1	6.6	132.9	High-risk
Flu	BDL-3707.1	892.0	177.4	BDL-37.1	8.9	177.4	High-risk	BDL-5578.6	1749.8	113.1	BDL-55.8	17.5	113.1	High-risk
Phen	BDL-3514.7	1665.2	97.1	BDL-35.1	16.7	97.1	High-risk	779.3-4577.3	3117.6	37.7	7.8-45.8	31.2	37.7	High-risk
Anth	BDL-6951.4	2062.3	138.5	BDL-70	20.6	138.5	High-risk	BDL-2888.6	980.0	123.4	BDL-28.9	9.8	123.4	High-risk
Flan	BDL-676.7	323.2	71.0	BDL-6.8	3.2	71.0	High-risk	180.7-1853.3	885.6	64.0	1.8-18.5	8.9	64.0	High-risk
Pyr	BDL-24201.4	12943.6	123.0	BDL-242	129.4	123.0	High-risk	BDL-14351.4	7392.1	133.1	BDL-143.5	73.9	133.1	High-risk
BaA	BDL-2920	1047.0	155.1	BDL-29.2	10.5	155.1	High-risk	BDL-12070	5483.3	95.2	BDL-120.7	54.8	95.2	High-risk
Chry	BDL-1613.8	1075.0	46.3	BDL-16.1	10.8	46.3	High-risk	282.1-2452.4	864.7	83.6	2.8-24.5	8.6	83.6	High-risk
BbF	BDL-444600	79520.0	225.0	BDL-4446	795.2	225.0	High-risk	10850-398220	85394.3	166.3	108.5-3982.2	853.9	166.3	High-risk
BkF	BDL-36435	9174.9	198.1	BDL-364.4	122.3	171.4	High-risk	80-27792.5	5870.0	169.1	BDL-277.9	58.7	169.1	High-risk
BaP	BDL-146	83.6	66.9	BDL-1.5	1.0	47.4	High-risk	272-5216	1216.6	146.2	2.7-52.2	12.2	146.2	High-risk
DBA	BDL-36	36.0		BDL			High-risk	BDL-15348	4747.5	148.9	BDL-153.5	47.5	148.9	High-risk
BgP	BDL-446.7	260.0	101.5	BDL-4.5	2.6	101.5	High-risk	BDL-103.3	103.3		BDL-1	1.0		High-risk
IP	BDL-1112.5	1106.3	0.8	BDL-11.1	11.1	1.0	High-risk	BDL-59705	23881.7	132.0	BDL-597.1	238.8	132.0	High-risk
∑PAHs	4441.5-485884	82548.5	215.8	44.4-4859	824.6	216.0	High-risk	20914-434523	121942.2	120.1	209.1-4344.9	1219.0	120.1	High-risk

Note: CV = coefficient of variation, BDL=Below Detection Limit

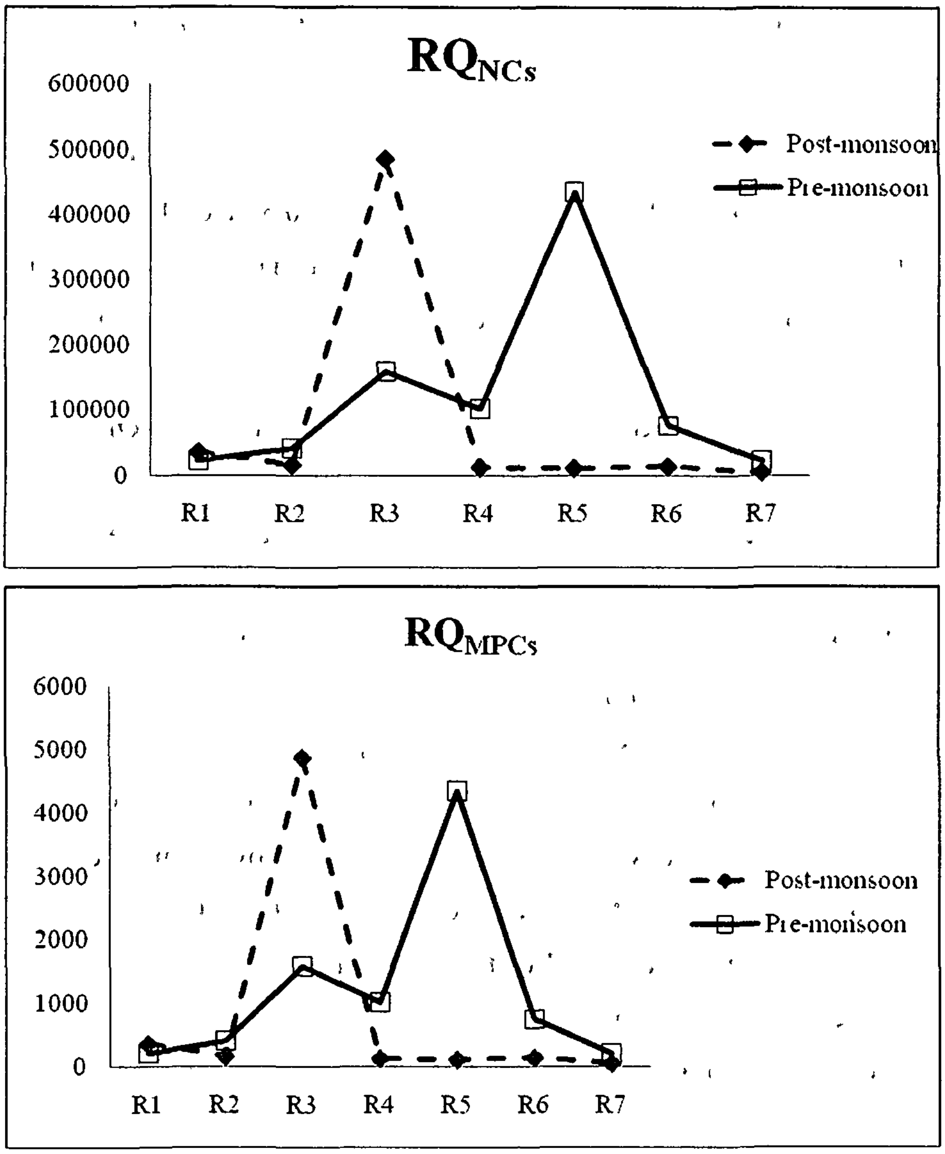


Figure 4.25: RQ$_{NCs}$ and RQ$_{MPCs}$ of $\sum$PAHs in water of Bharalu River during post-monsoon and pre-monsoon season.

4.4.6 PAHs Ratios and Source Identification

PAHs ratios are shown in Table 4.35. Mean IP/(IP+BgP) during post-monsoon and pre-monsoon period were found to be 0.664±0.27 and 0.692±0.1 respectively, which indicated that diesel exhaust emission could be an important source of PAHs in Bharalu water. The ratio Flu/(Flu+Pyr) >0.5 has been inferred to indicate diesel engine emission of PAHs [204-207]. In water samples the average ratios were found to be 0.664±0.4 and 0.813±0.4 during post-monsoon and pre-monsoon respectively. This further confirmed that there could have been input of diesel exhaust emitted matter into Bharalu River water.

In the present study, during pre-monsoon and post-monsoon Anth/(Anth+Phen) and Flan/(Flan+Pyr) ratio ranged from 0.088±0.2 to 0.372±0.3 and 0.796±0.3 to 0.877±0.2 respectively indicating mixed petrogenic and pyrogenic origins of PAHs. Similarly, Naph/Phen ratio was found to be << 1 during pre-monsoon time, which also indicated petrogenic origin of PAHs during that period [211].

Phen/(Phen+Anth) of 0.76 is considered as specific marker for coal combustion [322]. Phen/(Phen+Anth) ratios of 0.628±0.311 and 0.912±0.17 found during post-monsoon and pre-monsoon respectively indicated coal combustion as one of the sources of PAHs in water.

C*PAHs/TPAHs of Bharalu water was found to be 0.465±0.3 and 0.487±0.2 during post-monsoon and pre-monsoon periods respectively. This would mean that there is considerable input of PAHs from combustion sources with some moderate input from petrogenic sources also. PAHs of combustion origin would have met the Bharalu River through atmospheric deposition directly to the water body or carried by storm water from the land and streets that were deposited there. The petrogenic PAHs could be a result of direct release of effluents or those carried by stormwater from fuel stations, vehicle workshops and storage tanks besides the inputs from the refinery. Biomass burning is traditionally practiced for agricultural clearing and for household energy in Northeast India.

Table 4.35 Mean diagnostic ratios of PAHs in water Bharalu River

	Post-monsoon water	Pre-monsoon water.
IP/(IP+BgP)	0.664±0.2	0.692±0.1
Flu/(Flu+Pyr)	0.664±0.4	0.813±0.4
Phen/(Phen+Anth)	0.628±0.3	0.912±0.2
Naph/Phen	42.153±53.4	0.058±0.1
Anth/(Anth+Phen)	0.372±0.3	0.088±0.2
Flan/(Flan+Pyr)	0.796±0.3	0.877±0.2
C*PAHs/TPAHs	0.465±0.3	0.487±0.2

Note: C*PAHs=Flu+Pyr+BaA+Chry+BbF+BkF+BaP+IP+BgP

4.4.7 Source Apportionment

The six factors of PCA accounting for 84.6 % of the total variance along with their Eigen values are depicted in Table 4.36. Factor 1, explained 28.7 % of total variance, had high loading of Acy, Acen, Flu, Phen, BbF and BaP. BbF in is an indication of diesel-engine vehicle [208, 323]. Moreover, higher loading of Acy, Acen, Flu, Phen and BaP are marker of vehicular emission [208, 325, 329]. So, first factor can be attributed to Diesel powered vehicles or mobile sources (traffic) source. Factor 2 explained 16.1% to the total variance had high load of Flan, Pyr and Chry. Masclet et al. [334] found diesel exhaust enriched with Flan, Pyr and Chry. Therefore, this factor is assigned for diesel emission. Factor 3 had high loading of BaA, DBA and IP with moderate loading of Phen and Flan contributing 14.812% variance. BaA, Phen, Flan and IP are considered as marker for coal combustion [208, 279]. While DBA and IP are also indicator of vehicular emission mainly gasoline engine exhaust [208, 329]. Thus factor 3 is a mixer of coal and vehicular combustion. Factor 4 having 10.03% variance, showed high contribution of Flu, BbF and BkF and moderate loading of Naph, Pyr and Chry. This factor is also considered for vehicular exhaust. Factor 5 showed 8.1% of total variance with high weightage of Phen, Flan, and IP. Phen and Flan is marker of wood combustion [208, 279]. IP is an indicator of vehicular emission. Thus this factor is a mixer of wood and vehicular combustion. Factor 6 with 6.2% variance depicted high loading of Naph, Phen, Chry and IP. This factor is also considered for vehicular traffic.

PCA Factor scores 1-6 corresponding diesel powered vehicle, diesel exhaust, gasoline + coal combustion, vehicular or mobile source, wood and vehicular emission and vehicular traffic respectively, were taken as independent variable and z-score values of sum PAH ($\sum PAH_i$) as dependent variable. In order of their individual simple correlation from highest to lowest, each independent variable was added into stepwise regression. The resulting equation 8 was obtained as –

$$Z = 0.577FS1 + 0.111FS2 + 0.289FS3 + 0.636FS4 + 0.174FS5 + 0.286FS6 \quad (r^2 = 0.946) \text{ -- eq8}$$

Thus the mean contributions were found to be 27.834%, 5.355%, 13.941%, 30.68%, 8.394% and 13.796% for factors 1 to 6 respectively. So, vehicular emission dominated the source of PAHs in Bharalu water.

Table 4.36 Principal Component Analysis of PAHs in Bharalu River Water (extraction method: Principal Component Analysis (Rotation method: Varimax with Kaiser normalization), loading>0.3 are shown in bold)

Rotated Component Matrix

	Component					
	1	2	3	4	5	6
Naph	-0.368	-0.510	-0.344	0.206	0.040	**0.316**
Acy	**0.947**	-0.036	-0.003	0.062	-0.038	-0.011
Acen	**0.935**	-0.027	-0.077	-0.041	0.019	0.164
Flu	**0.827**	-0.208	0.004	**0.449**	0.164	0.042
Phen	**0.438**	0.085	0.251	-0.478	**-0.467**	**0.383**
Anth	-0.107	0.106	0.091	-0.087	-0.888	0.157
Flan	-0.129	**0.800**	0.179	-0.067	**0.332**	0.149
Pyr	-0.135	**0.737**	-0.157	0.132	-0.159	-0.059
BaA	-0.117	0.114	**0.965**	-0.021	-0.033	0.111
Chry	-0.075	**0.807**	-0.063	0.133	-0.311	**0.367**
BbF	**0.615**	-0.255	-0.007	**0.715**	0.105	0.045
BkF	0.042	0.274	-0.001	**0.920**	0.018	0.091
BaP	**0.979**	-0.032	0.000	-0.025	0.086	0.026
DBA	0.189	-0.030	**0.760**	0.030	-0.198	-0.252
BgP	-0.187	-0.153	-0.040	-0.071	0.125	-0.805
IP	-0.204	-0.160	**0.694**	-0.065	**0.321**	**0.298**
Eigenvalues	4.588	2.577	2.37	1.605	1.304	1.091
% of Variance	28.674	16.105	14.812	10.03	8.148	6.819
Cumulative %	28.674	44.78	59.591	59.621	77.77	84.589

4.4.8 Association with Carbon

Range of TC, OC and IC in Bharalu water during post-monsoon were 157.5-1040 mg/l, 287-859 mg/l and 110-220 mg/l respectively (Table 4.37). The concentration range of TC, OC and IC in Bharalu water during pre-monsoon were 177-9690 mg/l, 8.01-9500 mg/l and 108-218 mg/l respectively. The mean concentrations of TC, OC and IC during post-monsoon were found to be 557.2±320 mg/l, 530±258 mg/l and 182±40 mg/l respectively. However, the mean concentrations of TC, OC and IC during post-monsoon were found to be 3344.7±4344 mg/l, 3175±4326mg/l and 171.6±38 mg/l respectively. Mean concentration of TC and OC were very high during pre-monsoon season while in case of IC mean value was slightly lower than that of post-monsoon season.

Correlation analysis was performed to explore the relationship of PAHs in Bharalu water with TC, OC and IC (Table 4.38). Good correlation was observed for BaA and IP with both TC and OC, while Flan only with TC. However, IC showed significant negative correlation only with BaP. Thus OC could play important role in dispersion of BaA and IP of Bharalu River water. This would also mean that organic content of water favoured solubility of these individual PAH.

Table 4.37 Range and mean concentration (mg/l) of total carbon (TC), organic carbon (OC) and inorganic carbon (IC) in Bharalu River water during post-monsoon and pre-monsoon season

	TC		OC		IC	
	Mean	Range	Mean	Range	Mean	Range
Post-monsoon	557.2±320	157.5-1040	530±258	287-859	182±40	110-220
Pre-monsoon	3344.7±4344	177-9690	3175±4326	801-9500	171.6±38	108-218

Table 4.38 Correlations of PAHs with total carbon (TC), organic carbon (OC) and inorganic carbon (IC) in Bharalu River water

	TC	OC	IC
Naph	-0.137	-0.133	-0.026
Acy	-0.061	-0.06	-0.488
Acen	-0.105	-0.115	-0.601
Flu	-0.238	-0.248	-0.585
Phen	0.052	0.028	-0.515
Anth	0.099	0.082	0.256
Flan	**0.602***	0.594	0.001
Pyr	0.277	0.269	0.106
BaA	**0.738****	**0.733****	0.144
Chry	0.462	0.438	-0.093
BbF	-0.159	-0.169	-0.462
BkF	0.303	0.295	-0.029
BaP	-0.108	-0.113	-0.569*
DBA	0.101	0.096	-0.192
BgP	-0.154	-0.112	-0.111
IP	**0.673****	**0.675****	0.105
∑PAHs	0.314	0.293	-0.505

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

4.5 PAHs in River Sediment of Guwahati City

4.5.1 Summary Statistics of River Sediment PAHs

Mean and range of 16 PAHs in sediment of Bharalu River during post-monsoon and pre-monsoon season are shown in Table 4.39. On dry weight basis, ∑PAHs concentration in post-monsoon sediment samples ranged from 337.6-23140.5ng/gm with mean value of 4968.2±8135ng/gm, whereas they varied from 608.8-8618.6ng/gm in pre-monsoon with mean value of 3812.4±2820 ng/gm. BaP concentration varied from 0.7-33.2ng/gm with mean concentration 17.8±13ng/gm during post-monsoon, whereas it ranged between BDL and 58.0ng/gm with mean value of 21.9±27ng/gm during pre-monsoon season.

Table 4.39 Mean± standard deviation (SD) and range value of PAHs (ng/gm) in Bharalu River sediment during post-monsoon and pre-monsoon season

	Post-monsoon		Pre-monsoon	
	Mean	**Range**	**Mean**	**Range**
Naph	1.2±1	(0.3-4.0)	6.1±8	(0.03-21.0)
Acy	120.8±105	(20.5-287.2)	290.6±251	(BDL-518.1)
Acen	54.0±74	(BDL-203.4)	73.4±54	(BDL-145.1)
Flu	39.5±29	(BDL-84.102)	12.3±14	(0.9-40.7)
Phen	3116.8±7020	(BDL-17419.6)	639.7±483	(101.9-1290.5)
Anth	46.3±77	(BDL-199.6)	58.7±42	(BDL-94.9)
Flan	548.4±881	(BDL-2323.0)	777.6±759	(75.5-1757.3)
Pyr	272.7±484	(BDL-1229.1)	103.3±68	(31.0-216.5)
BaA	12.0±10	(BDL-27.8)	4.3±3	(0.7-10.8)
Chry	572.3±646	(22.8-1871.6)	984.3±1294	(51.7-3419.8)
BbF	102.6±120	(BDL-280.3)	153.7±348	(BDL-864.3)
BkF	18.8±11	(BDL-31.8)	67.3±120	(BDL-280.9)
BaP	17.8±13	(0.7-33.2)	21.9±27.0	(BDL-58.0)
DBA	160.7±251	(BDL-533.9)	108.3±158	(BDL-371.8)
BgP	24.5±20	(BDL-53.0)	50.7±90	(BDL-232.4)
IP	807.4±925	(BDL-2156.2)	822.4±1559	(BDL-3990.1)
∑PAHs	4968.2±8135	(337.6-23140.5)	3812.4±2820	(608.8-8618.6)

4.5.2 Spatial and Seasonal Variation of PAHs

Mean concentration of ∑PAHs during post-monsoon was found to be higher than that of pre-monsoon. However, mean values of most of the individual PAH increases during pre-monsoon than post-monsoon except Flu, Phen, Pyr, BaA and DBA (Table 4.39).

Most of the sites experienced a rise in ∑PAHs concentration during post-monsoon season except R2 and R7 site where maximum ∑PAHs concentration was observed during pre-monsoon season (Figure 4.26). Site R2 was observed as most polluted site.

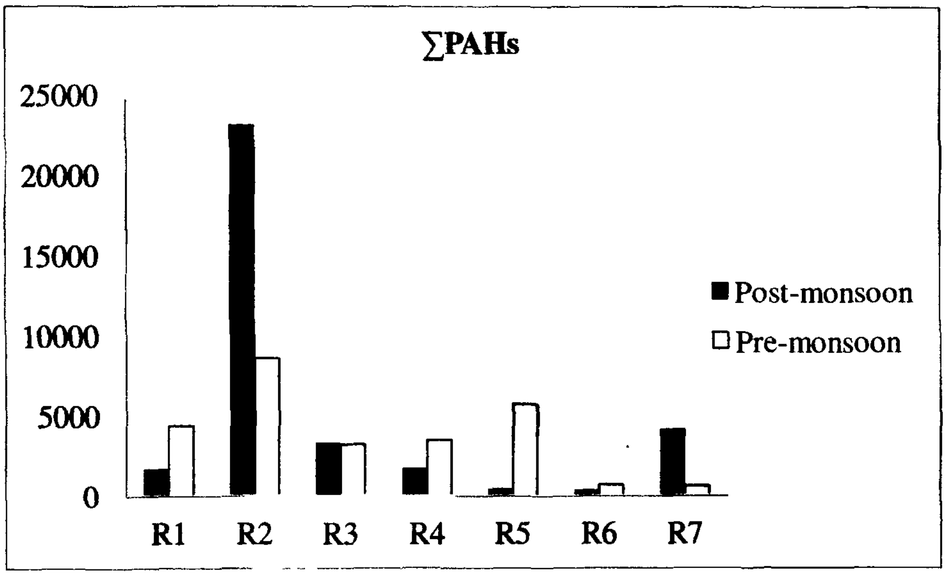


Figure 4.26: ∑PAHs concentrations (ng/gm) during post-monsoon and pre-monsoon season at sampling sites (R1-R7).

The possible reason of such PAHs pattern in sediment might be the input of high PAHs in the river system along with heavy discharges from all municipal, commercial and industrial outlets during monsoon season and their subsequent partition into sediment during post-monsoon season. High total PAHs concentration during pre-monsoon season in R2 site could be due to their closeness to the confluence of Bharalu into Brahmaputra River. Re-suspension of surface sediment and absorption of PAHs from water to sediment particles in mixing zone [343] might lead to accumulation of PAHs in sediment. Moreover, R2 was a high traffic density sites. Continuous PAHs deposition from traffic, re-suspension of road dust and wind from Brahmaputra side might be another cause of such observations. However, lower level of ∑PAHs at R1 could be due to dilution of contaminants at the confluence.

4.5.3 PAHs profiles

PAHs profile (Figure 4.27) during post-monsoon season was dominated mainly by 3 and 4-ring PAHs with more than 60% contribution. However, R3 was dominated by 6-ring PAHs with ~70% loading during post-monsoon season. Similar PAHs profile with dominance of 3and 4 ring PAHs was also observed in pre-monsoon samples in all the sites except R2 with ~50% contribution from 6-ring PAHs. Thus, PAHs profile was dominated by 3-, 4- and 6-ring PAHs in sediment during both the season with high dominance of 3-ring PAHs during post-monsoon and by 4-ring during pre-monsoon season.

Individually, mean highest percentage contribution was found for Phen during post-monsoon season followed by IP>Chry>Flan>Pyr. However, during pre-monsoon period the order was Chry>IP>Flan>Phen.

Percentage contribution of 2-ring PAHs was less than 0.5% in sediment samples. Thus sediment of Bharalu was more contaminated with HMWPAHs. Moreover, surface water carrying HMWPAHs easily undergoes partition to solid particles of sediment as LMWPAHs are more soluble in water.

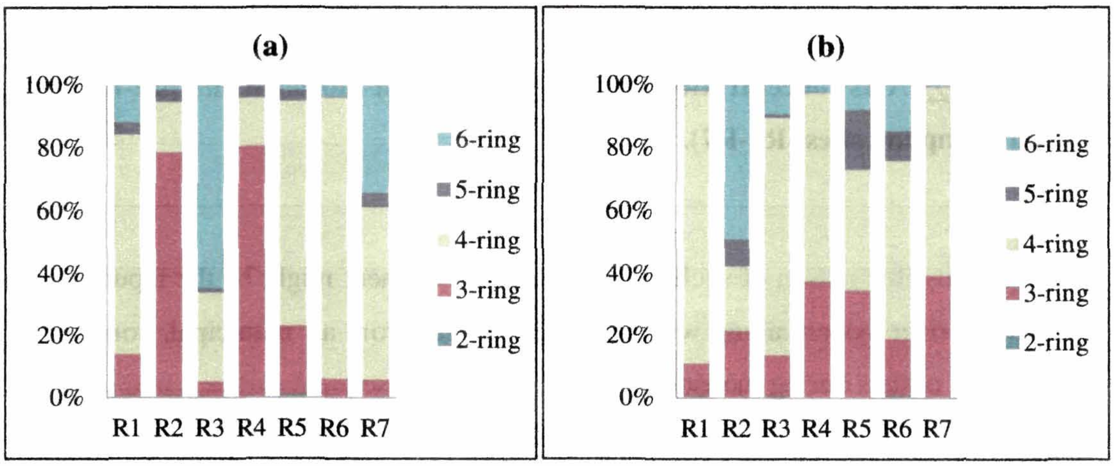


Figure 4.27: Percentage composition of two, three-, four-, five- and six-ring PAHs in Bharalu River sediment during- (a) post- monsoon and (b) pre-monsoon seasons.

4.5.4 Toxicity

PAHs profile in terms of CPAHs to rest of the 16 PAHs showed 57% and 46% contribution during post-monsoon and pre-monsoon season respectively in Bharalu River sediment (Figure 4.28). This indicated similar trend of CPAHs and possible threat of exposure from sediment in both the sampling seasons. The continuous process of dissolution, evaporation, adsorption and desorption in water, air and sediment interface in turn elevates the potential risk of these compounds.

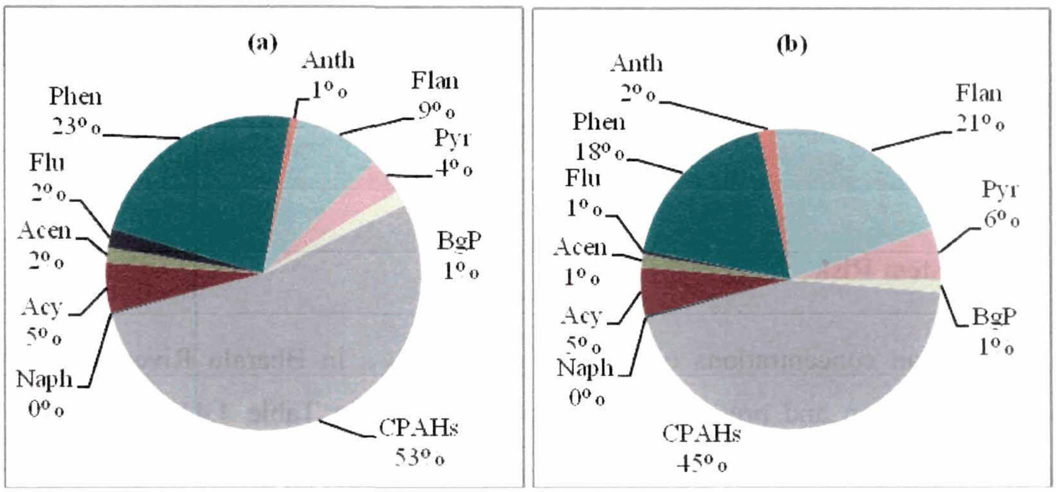


Figure 4.28: Abundance of carcinogenic PAHs (CPAHs) to other PAHs in Bharalu River sediment during – (a) post-monsoon and (b) pre-monsoon seasons.

Mean BaPq concentration of ∑PAHs was found to be 184.9±233ng/gm and 197.5±318ng/gm during post-monsoon and pre-monsoon season respectively (Table 4.40). The maximum concentration was observed at R2 site and minimum at R7 both during pre-monsoon season.

This indicated high risk of toxicity in sediment of Bharalu River during pre-monsoon season. In India, regulation has not been developed for concentration of PAHs in aquatic environment. Because of the possible toxic nature of the PAHs in the river water and sediment, a regulatory mechanism is highly required for its control and regular monitoring.

Table 4.40 BaPeq concentration (ng/gm) of ∑PAHs in sediment of Bharalu River

	Post-monsoon	Pre-monsoon
R1	72.2196	43.455
R2	644.9706	870.6217
R3	256.0336	62.4883
R4	19.3341	24.1688
R5	17.0508	335.3834
R6	3.9233	43.7575
R7	281.0445	2.3579
Mean	184.94±233	197.46±318

4.5.5 Ecosystem Risk

The mean concentrations of $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ in Bharalu River sediment during post-monsoon and pre-monsoon season are listed in Table 4.41. Individually, $RQ_{(MPCs)}$ value of Acy, Phen and Pyr were >1.0 during both post-monsoon and pre-monsoon season indicating some severe toxicity to aquatic organisms by these three compounds. $RQ_{(NCs)}$ value of all individual PAH were > 1.0 except for BgP during post-monsoon season. This indicated that Naph, Acen, Flu, Anth, Flan, BaA, Chry, BbF, BkF, BaP, DBA and IP expressed middle level of ecosystem risk in Bharalu River sediment while BgP showing no ecosystem risk. Coefficient of variation (CV) of all individual PAHs were higher than 60% and in case of some PAHs exceeded 200%, indicating strong variation in ecosystem risk of individual PAH in different sampling sites.

Moreover, Figure 4.29 illustrated that 3 and 4-ring PAHs mainly Acy, Phen and Pyr contributed to the main ecosystem risk burden. And higher ecosystem risk was observed by Phen and Pyr during post-monsoon season than that of pre-monsoon season. The contribution of 2-ring PAHs was negligible which could probably due to their high water solubility.

$RQ_{(MPCs)}$ of ∑PAHs in sediment of Bharalu River was >1 during both post-monsoon and pre-monsoon season. $RQ_{(NCs)}$ of ∑PAHs during post-monsoon was >800 while during pre-monsoon was <800. This indicated high ecosystem risk during post-monsoon season and moderate risk inclined towards higher side during pre-monsoon season in Bharalu River sediment. Moreover, very high percentage of coefficient of variation (CV) for ∑PAHs during post-monsoon also revealed great variation of ecosystem risk in this season. The mean ecosystem risk during post-monsoon ($RQ_{\sum PAHs(MPCs)}$=19.0) was 3.3 times higher than that of pre-monsoon season ($RQ_{\sum PAHs(MPCs)}$=5.8) (Table 4.41). From the Figure 4.30 it was also observed that $RQ_{\sum PAHs(NCs)}$ value was very high at site R2 during post-monsoon season whereas during pre-monsoon high value was detected at site R5. Site R2 being near to confluence of point could probably attribute such high RQ value. River channel at site R5 receives input from catchment of the industrial belt of the city where Guwahati refinery and many industries are located. On the whole, the results marked that PAHs in aquatic sediment of Bharalu River resulted in severe ecosystem risk mainly during post-monsoon season.

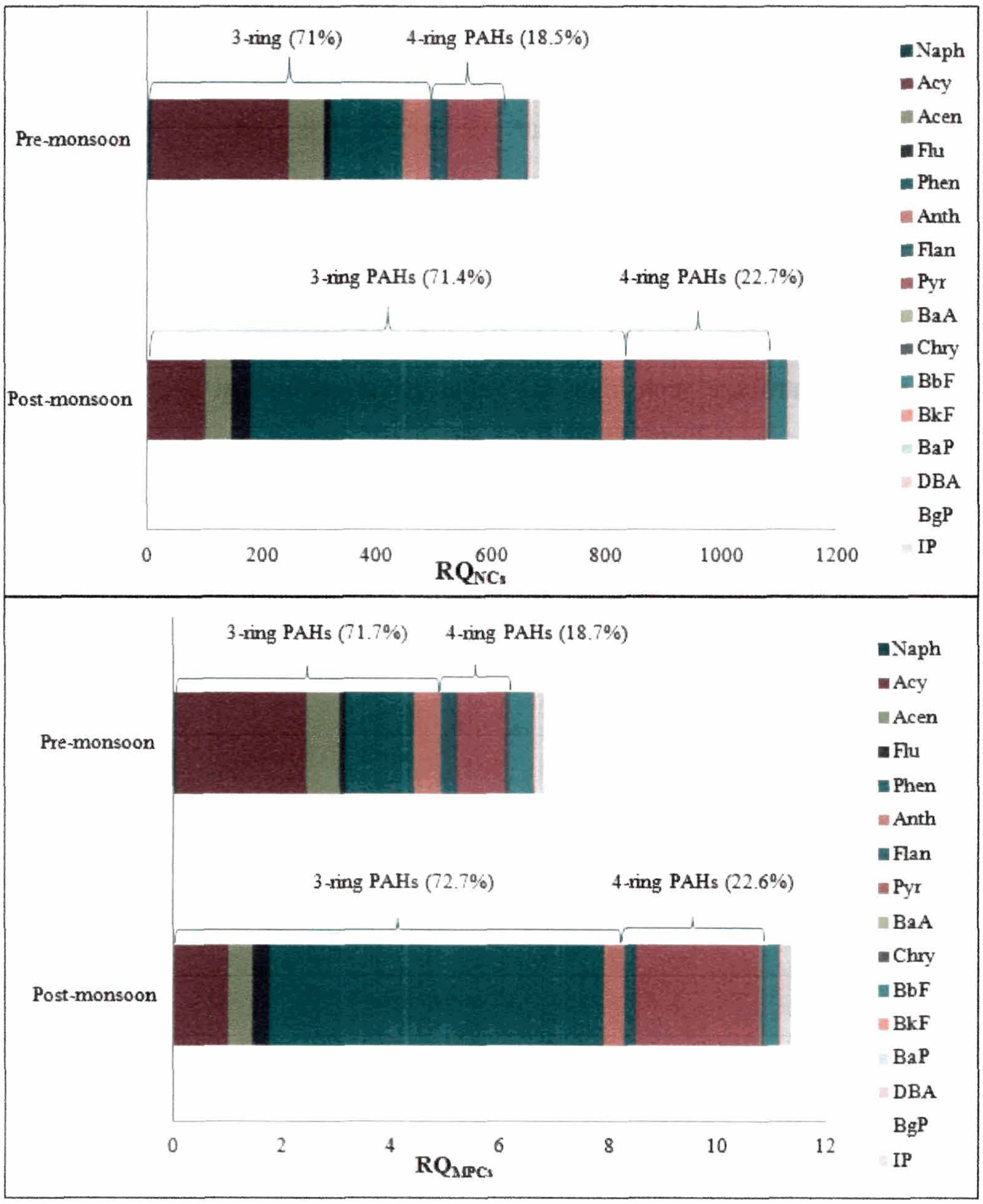


Figure 4.29: Mean RQ_{NCs} and Mean RQ_{MPCs} values of individual PAHs in sediment of Bharalu River during post-monsoon and pre-monsoon season.

Table 4.41 $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ values of PAHs (ng/gm) with their risk classification during post-monsoon and pre-monsoon in Bharalu River

	Recommended		Post-monsoon (NCs)			Pre-monsoon (MPCs)				Pre-monsoon (NCs)			Pre-monsoon (MPCs)			
	NCs	MPCs	Range	Mean	CV(%)	Range	Mean	CV(%)	Risk Classification	Range	Mean	CV(%)	Range	Mean	CV(%)	Risk Classification
Naph	1 4	140	0 2-2 9	1 0	110 6	0 002-0 03	0 01	110 6	Moderate risk	0 02-15	4 4	136 3	0 0002-0 2	0 04	136 3	Moderate risk
Acy	1 2	120	17 1-239 3	100 7	87 1	0 2-2 4	1 0	87 1	High Risk	BDL-432	242 2	86 5	BDL-4 3	2 4	86 5	High Risk
Acen	1 2	120	BDL-169 5	45 0	137 7	BDL-1 7	0 4	137 7	Moderate risk	BDL-121	61 2	74 1	BDL-1 2	0 6	74 1	Moderate risk
Flu	1 2	120	BDL-70 1	32 9	73 3	BDL-0 7	0 3	73 3	Moderate risk	0 8-33 9	10 3	111 1	0 01-0 34	0 1	111 1	Moderate risk
Phen	5 1	510	BDL-3416	611 1	225 2	BDL-34 2	6 1	225 2	High Risk	20-253	125 4	75 5	0 2-2 5	1 3	75 5	High Risk
Anth	1 2	120	BDL-166 3	38 6	165 7	BDL-1 7	0 4	165 7	Moderate risk	BDL-79	48 9	71 4	BDL-0 8	0 5	71 4	Moderate risk
Flan	26	2600	BDL-89 4	21 1	160 6	BDL-0 9	0 2	160 6	Moderate risk	2 9-67 6	29 9	97 6	0 03-0 7	0 3	97 6	Moderate risk
Pyr	1 2	120	BDL-1024	227 2	177 5	BDL-10 2	2 3	177 5	High Risk	26-180 4	86 1	66 2	0 3-1 8	0 9	66 2	High Risk
BaA	3 6	360	BDL-7 7	3 3	84 8	BDL-0 1	0 03	84 8	Moderate risk	0 2-3	1 2	79 8	0 002-0 03	0 01	79 8	Moderate risk
Chry	107	10700	0 2-17 5	5 3	112 9	0 002-0 2	0 1	112 9	Moderate risk	0 5-32	9 2	131 5	0 004-0 3	0 1	131 5	Moderate risk
BbF	3 6	360	BDL-77 9	28 5	116 6	BDL-0 8	0 3	116 6	Moderate risk	BDL-240	42 7	226 6	BDL-2 4	0 4	226 6	Moderate risk
BkF	24	2400	BDL-1 3	1 0	93 5	BDL-0 01	0 01	60 2	Risk-free	BDL-11 7	2 8	177 8	BDL-0 1	0 03	177 8	Moderate risk
BaP	27	2700	0 03-1 2	1 0	72 3	0 0003-0 01	0 01	72 3	Moderate risk	BDL-2 1	1 0	123 2	BDL-0 02	0 01	123 2	Moderate risk
DBA	27	2700	BDL-19 8	6 0	156 2	BDL-0 2	0 1	156 2	Moderate risk	BDL-13 8	4 0	145 5	BDL-0 1	0 04	145 5	Moderate risk
BgP	75	7500	BDL-0 7	0 3	82 4	BDL-0 01	0 003	82 4	Risk-free	BDL-3 1	1 0	177 4	BDL-0 03	0 01	177 4	Moderate risk
IP	59	5900	BDL-36 5	13 7	114 6	BDL-0 4	0 1	114 6	Moderate risk	BDL-67 6	13 9	189 6	BDL-0 7	0 1	189 6	Moderate risk
∑PAHs			19 9-5283	970 9	196 7	2 7-50 2	19 0	141 9	High Risk	108 8-1170 3	536 4	82 6	1 5-9 0	5 8	57 3	Moderate risk$_2$

Note CV = coefficient of variation, BDL=Below Detection Limit

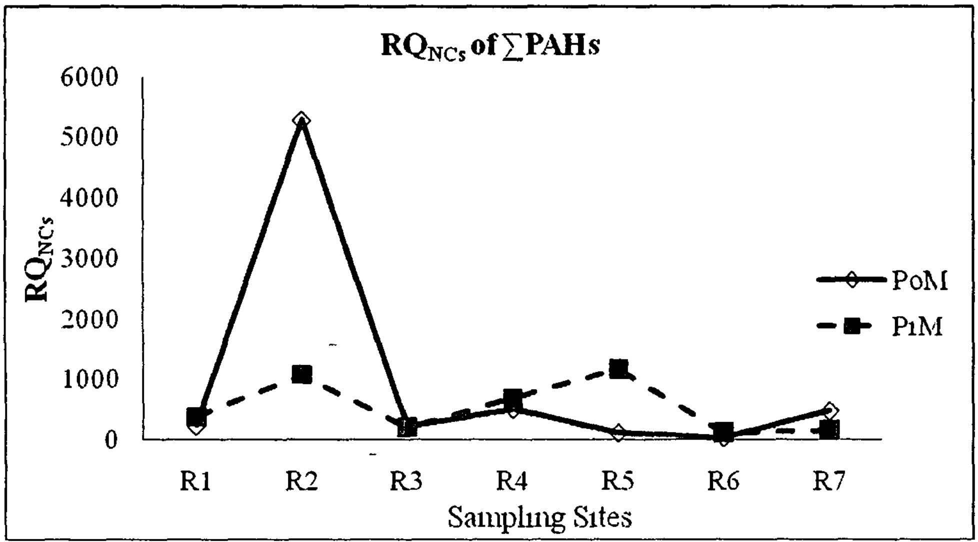


Figure 4.30: RQ_{NCs} of ∑PAHs in sediment of Bharalu River during post-monsoon and pre-monsoon season.

4.5.6 PAHs Ratios and Source Identification

Mean IP/(IP+BgP) ratio during post-monsoon and pre-monsoon season of 0.67±0.4 and 0.81±0.3 (Table 4.42) respectively indicated that wood burning was a major source of PAHs during post-monsoon in Bharalu River sediment. In sediment samples the mean ratio of Flu/(Flu+Pyr) was found to be 0.45±0.3 and 0.14±0.2 during post-monsoon and pre-monsoon respectively inferred gasoline emission as the source of PAHs during both the season. In this study Anth/(Anth+Phen) ratio was 0.17±0.2 and 0.06±0.04 during post-monsoon and pre-monsoon respectively showed mixed petrogenic and pyrogenic origin of PAHs. However, Flan/(Flan+Pyr) ratio was 0.72±0.3 and 0.76±0.2 during post-monsoon and pre-monsoon season respectively indicated pyrogenic origin of PAHs. Naph/Phen ratio 0.02 and 0.07 during both pre-monsoon and post-monsoon respectively also confirmed petrogenic origin of PAHs in sediment. Moreover, the ratio of CPAHs/TPAHs 0.62±0.4 and 0.52±0.3 during post-monsoon and pre-monsoon period respectively indicating combustion derived PAHs in sediment of Bharalu.

Petrogenic sources that revealed from diagnostic ratio in the river possibly originated from leakage of crude oil and refined products like gasoline from road run-off and industries. Pyrogenic sources were mostly found to be from combustion of diesel or gasoline fuel and fuel oil from vehicular traffic and industries. Once they entered into the environment they are easily dissipated through atmospheric transport and finally get deposited on the river system [343, 344]. Moreover, street dust might be another possible source of petrogenic PAHs. Cremation ground in the upper stream of the river could be possible source of wood burning PAHs in the river. In addition, biomass burning is also a traditional practice in Northeast India.

Table 4.42 Mean diagnostic ratios of PAHs in sediment of Bharalu River during post-monsoon and pre-monsoon season

	Post-monsoon sediment	Pre-monsoon sediment	Prescribed ratio	Sources
IP/(IP+BgP)	0.67±0.4	0.81±0.3	0.62	Wood burning
Flu/(Flu+Pyr)	0.45±0.3	0.14±0.2	<0.5	Gasoline
Phen/(Phen+Anth)	0.83±0.2	0.95±0.04	>0.7	Fossil fuels
Naph/Phen	0.07±0.1	0.02±0.03	<<1	Petrogenic
Anth/(Anth+Phen)	0.17±0.2	0.06±0.04	>0.1	Pyrolytic
			<0.1	Petrogenic
Flan/(Flan+Pyr)	0.72±0.3	0.76±0.2	>0.5	Pyrolytic
C*PAHs/TPAHs	0.62±0.4	0.52±0.3	~1	Combustion

C*PAHs=Flu+Pyr+BaA+Chry+BbF+BkF+BaP+IP+BgP

4.5.7 Source Apportionment

PCA for sediment data revealed 4 factors and explained 85.98% of variance. The variance of individual factors and their eigen values are shown in Table 4.43. Factor 1, explained 44.98% of total variance, had high loading of Acen, Flu, Phen, Anth, Flan, Pyr and DBA. Khalili et al. [208] identified Anth, Phen, Flan and Pyr markers for wood combustion. So, the 1st factor was attributed as wood combustion source. Factor 2 explained 20.41% of total variance and had high loading for Acy, Acen, BkF, BaP, BgP and IP. This factor is considered for vehicular source. Factor 3 showed 12.08% contribution with high loading of Naph and Chry. This factor was attributed to coal combustion [279]. Factor 4 explained 8.51% variance with high loading of Acy, BbF and BaP. This factor was regarded as source of diesel engine vehicles. Thus PCA recognized four distinct sources of PAHs wood combustion, vehicular combustion, coal combustion and diesel engine combustion with 44.98%, 20.41%, 12.08% and 8.51% contribution respectively.

Table 4.43 Factor analysis scores for PAHs in sediment of Bharalu River from seven sampling locations in Guwahati city (extraction method: Principal Component Analysis. Rotation method: Varimax with Kaiser normalization, loading>0.4 are shown in bold)

	Rotated Component Matrix			
	Component			
	1	2	3	4
Naph	-0.05	-0.15	**0.94**	-0.08
Acy	0.37	**0.66**	-0.32	**0.46**
Acen	**0.85**	**0.44**	0.19	0.07
Flu	**0.75**	-0.03	-0.08	0.37
Phen	**0.98**	-0.08	-0.09	-0.01
Anth	**0.88**	0.23	-0.29	0.21
Flan	**0.76**	0.25	-0.20	0.36
Pyr	**0.95**	-0.11	0.02	-0.13
BaA	0.10	0.23	-0.35	-0.37
Chry	-0.11	0.01	**0.91**	-0.06
BbF	0.28	0.04	-0.12	**0.90**
BkF	0.13	**0.96**	-0.04	-0.06
BaP	0.10	**0.76**	-0.14	**0.52**
DBA	**0.84**	0.49	-0.11	0.07
BgP	0.11	**0.96**	-0.07	-0.07
IP	0.01	**0.93**	-0.05	-0.06
Eigen values	7.20	3.27	1.93	1.36
% of Variance	44.98	20.41	12.08	8.51
Cumulative %	44.98	65.38	77.46	85.98
Identified Sources	**Wood Combustion**	**Vehicular Source**	**Coal combustion**	**Diesel Engine**

4.5.8 Association with Carbon

Organic carbon (OC) and black carbon (BC) concentrations in sediment of Bharalu River varied from 2.014-7.282% and BDL-2290µg/gm respectively (Table 4.44). Both OC and BC concentration in sediment Bharalu River sediment was found to be higher during pre-monsoon (5.23±2 µg/gm and 1190.3±899µg/gm respectively) than that of post-monsoon (3.87±2µg/gm and 214.05±196µg/gm respectively) season. Sediment OC did not show any significant correlation with PAHs (Table 4.45). However, BC and BC/OC showed significant correlation with Naph and Chry. This inferred that these compounds are combustion derived in sediment of Bharalu River. Thus, BC was found to influence in sediment PAHs dissipation in Bharalu River.

Table 4.44 Concentrations ((µg/g) of organic carbon (OC), black carbon (BC) and BC/OC in sediment of Bharalu River sediment

	OC	BC	BC/OC
Post-monsoon	3.87±2	214.05±196	0.007±0.01
	2.01-7.28	BDL-530	BDL-0.03
Pre-monsoon	5.23±2	1190.3±899	0 04±0.04
	2.30-7.198	434.1-2290	0.006-0.10

Table 4.45 Correlations of PAHs with organic carbon (OC), black carbon (BC) and BC/OC in sediment of Bharalu River sediment

	OC	BC	BC/OC
Naph	-0.29	**0.77****	**0.68****
Acy	0.30	-0.36	-0.35
Acen	0.14	-0.11	-0.19
Flu	-0.26	-0.39	-0.27
Phen	-0.08	-0.19	-0.15
Anth	0.20	-0.28	-0.30
Flan	0.27	-0.16	-0.23
Pyr	-0.11	-0.09	-0.09
BaA	-0.29	-0.32	-0.21
Chry	-0.32	**0.68****	**0.61***
BbF	0.14	-0.17	-0.16
BkF	0.39	-0.11	-0.16
BaP	0.11	-0.33	-0.28
DBA	0.15	-0.24	-0.22
BgP	0.32	-0.13	-0.15
IP	0.22	-0.19	-0.17
∑PAHs	-0.01	-0.13	-0.11

**Correlation is significant at 0.01 level (2-tailed)

*Correlation is significant at 0.05 level (2-tailed)

4.6 Source signature of PAHs Bulk Deposition on Soil, Road Dust, River Water and River Sediment

To understand influence of bulk deposition on concentrations of PAHs in other environmental matrices – soil, road dust, surface water and sediment – mean signatures of PAHs, as PAHi/$\sum_{16}$PAHs and vital diagnostic ratios, of environmental matrices of the study area have been computed (Table 4.46). Pearson's correlations among mean PAH signatures of various matrices were also built (Table 4.47) to explore the extent of source/sink relationships if existed.

PAH signatures of bulk deposition correlated significantly with signatures of soil (r=0.79), road dust (r=0.65), surface water (r=0.51) and sediment (r=0.50). This could *imply that atmospheric bulk deposition is the major contributor of PAHs in soil,* road dust, water and sediment. Correlations of PAH signatures of bulk deposition appeared to stronger with PAH signatures of soil and road dust compared to river water and sediment. This could mean that land and roads receive much of the PAHs through atmospheric deposition. On the other hand, river water and sediments could have additional inputs from other sources besides atmospheric deposition.

It was interesting to find strong correlations of PAH signatures of sediment with signatures of road dust (r=0.87 and soil (r=0.65). Moreover, correlations were also observed between PAH signatures of river water with soil (r=0.45) and road dust (r=0.45). The region being high rainfall area there could be sufficient transport of PAHs from road and soil by storm water to the river water and then to river bed sediments, as significant correlation was found between river water and sediment (r=0.55). Correlation of soil and road dust with sediment was stronger than that of river water might be due to low solubility of PAHs in water, much of the PAHs carried by storm water could have partitioned to the solid phase in the sediments. High significant correlation was also found between PAH signatures of soil and road dust (r=0.89), indicating common source which could be atmospheric deposition.

Table 4.46 Average of signatures of PAHs as PAH (PAHi/∑16PAHs) and source diagnostic ratios in various environmental matrices of Guwahati

Signature	Bulk Deposition n=63	Soil n=15	Road Dust n=15	River Water n=14	Sediment n=14
Nap/∑PAHs	0.294	0.600	0.747	0.057	0.001
Acy/∑PAHs	0.005	0.010	0.008	0.026	0.033
Ace/∑PAHs	0.016	0.004	0.002	0.010	0.011
Flu/∑PAHs	0.003	0.001	0.001	0.025	0.005
Phe/∑PAHs	0.031	0.019	0.027	0.191	0.377
Ant/∑PAHs	0.012	0.002	0.001	0.025	0.009
Fth/∑PAHs	0.036	0.019	0.021	0.058	0.142
Pyr/∑PAHs	0.005	0.006	0.006	0.068	0.038
BaA/∑PAHs	0.297	0.200	0.088	0.009	0.002
Chry/∑PAHs	0.260	0.125	0.084	0.093	0.177
BbF/∑PAHs	0.002	0.002	0.001	0.256	0.022
BkF/∑PAHs	0.002	0.001	0.001	0.074	0.007
BaP/∑PAHs	0.003	0.006	0.001	0.011	0.004
DBA/∑PAHs	0.002	0.001	0.000	0.024	0.019
BghiP/∑PAHs	0.002	0.001	0.001	0.001	0.007
IcdP/∑PAHs	0.018	0.006	0.010	0.072	0.146
IcdP/(IcdP+BghiP)	0.90	0.86	0.92	0.99	0.95
Pyr/BaP	1.59	0.98	4.08	6.28	9.13
Fth/Pyr	7.28	3.45	3.53	0.86	3.70
Phe/Ant	2.58	24.94	19.65	7.52	40.39
Nap/Phe	9.46	32.10	27.39	0.30	0.00
Ant/(Ath+Phe)	0.28	0.11	0.05	0.12	0.02
Fth/(Fth+Pyr)	0.88	0.78	0.78	0.46	0.79
Flu/(Flu+Pyr)	0.40	0.13	0.09	0.27	0.11
Phe/Flu	9.38	23.49	48.02	7.60	80.45
BaP/(BaP+Chry)	0.01	0.04	0.02	0.10	0.02
BbF/BkF	0.79	2.70	1.71	3.44	3.34
BaP/BghiP	1.68	5.74	1.55	13.00	0.57
Phen/(Phen+Anth)	0.72	0.89	0.95	0.88	0.98

Table 4.47 Correlations of average source signatures [a] of PAH of bulk deposition, soil, road dust and sediment

	Bulk_Deposition	Soil	Road_Dust	River_Water	Sediment
Bulk_Deposition	1.00				
Soil	**0.79****	1.00			
Road_Dust	**0.65****	**0.89****	1.00		
River_Water	**0.51****	**0.45***	**0.45***	1.00	
Sediment	**0.50****	**0.65****	**0.87****	**0.55****	1.00

**Correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2-tailed)

[a] Source Signatures of Table 4.48

4.7 Comparison with Previous Works

4.7.1 Bulk Deposition

The comparison of PAHs concentrations observed in the present study with previous works (Table 4.48) indicates higher levels of PAHs in the present study. The level of PAHs flux estimated in this study were also show much higher values than that of other highly industrial cities like Manchester and Cardiff (UK) (1-24.2 μg/m^2/day and 8-19.6 μg/m^2/day respectively as reported by Halsall et al. [345]. Similar observations were also reported for the fluxes of Paris (0.17-2.03μg/m^2/day); Ollivon et al. [118]; Northern Greece (0.21-1.1μg/m^2/day); Manoli et al. [78]; Southern Germany (0.2-1.06μg/m^2/day); Gocht et al. [72]; Hungary (1.04-13.73μg/m^2/day; Kiss et al. [225]; in New Jersey, Mid-Atlantic east coast Region (0.0004-3 to 0.14μg/m^2/day); Gigliotti et al. [125]; Sweden (0.78μg/m^2/day); Brorström-Ludén et al. [346], Beijing, North China (1.7±1.09 to 14.25±12.33μg/m^2/day); Wang et al. [123] and Shanghai, China (1.6μg/m^2/day); Yan et al. [226].

Table 4.48 PAHs concentrations (ng/ml) in bulk precipitation reported elsewhere

Site	Period	Studied PAHs	∑PAHs	BaP	Reference
Hungary[1]	1995-1996	12 PAHs	0.156-1.993	0.002-0.147	[225]
Northern Greece[2]	1996-1997	14 PAHs	0.143-1.397	0.7×10^{-3}-6×10^{-3}	[78]
Poland[3]	1998-1999	16 PAHs	0.079-0 891	0.41×10^{-3}-0.025	[119]
Paris[4]	1999-2000	14 PAHs	0.051-0.323		[77]
West Paris[5]	2001-2002	14 PAHs	0.001-0.222	n.d.-0.012	[115]
Seine estuary, France[6]	2001-2002	14 PAHs	0.006-1 659	n.d.-0.134	[120]
Mumbai, India[7]	2001	8 PAHs	0.084-0.778	0.002-0.025	[252]
France[8]	2002 - 2003	17 PAHs	0.103-3.865	0.004-0.955	[121]
Turkey[9]	2008 - 2009	12 PAHs	[a]0.290 /[b]0.665	[a]1.04×10^{-3}-6.76×10^{-3} [b]4.11×10^{-3}-0.172	[62]
Guwahati	2011- 2012	16 PAHs	2.2-1035	BDL -5 6	Present study

[a]in dissolved phase; [b]in particle phase; n.d. – not detected

[1]Precipitation in rural site; [2]Bulk precipitation in; [3]Precipitation in urban region; [4]Bulk deposition ; [5] Bulk deposition; [6]Bulk deposition; [7]Rainwater; [8]Rainwater; [9]Rainwater

Bezo(a)pyrene (BaP) flux in Guwahati city was also found to be many times higher than that of the studies carried out in Sweden (0.030μg/m^2/day); Brorström-Ludén et al. [346], Hungary (0.02-0.43μg/m^2/day; Kiss et al. [225] and Germany (0.01-0.03μg /m^2/day; Gocht et al. [72].

4.7.2 Soil

The comparative account of the soil PAHs concentrations observed in the present study with earlier works (Table 4.49) represents higher levels of PAHs in the present study. Soil ∑PAHs concentrations including BaP estimated in Guwahati were found to be comparable with concentrations reported from soils of Shanghai [147], Delhi [97, 279], South Korea [171; 347], and Beijing [152]. It was also to be noted that BaP levels in the UK surface soil [168] and urban soil of Shanghai, China [147] were much higher than that of Guwahati soil. Compared to Dutch (20-50 ng/gm) and Polish (200-10,000 ng/gm) standards of $\sum_{16}$PAHs [236], it was observed that industrial soil PAHs in Guwahati was higher than both the standards.

Table 4.49 Concentrations (ng/gm) of soil PAHs reported elsewhere

Site	Period	Number of PAHs	$\sum$PAHs Conc. (ng/gm)	BaP conc.(ng/gm)	Reference
Surface soil, UK	1951-1974 and 1993	12 PAHs	20-7,400	BDL-1200	[168]
Surface soil, Mc.Murdo station, Antarctica	1997	15 PAHs	27,000 (individual maximum)	-	[348]
Agricultural soil, South Korea	-	16 PAHs	23.3-2834	<0.42–294	[171]
Urban soil, Sevilla (Southern spain)	-	15 PAHs	89.5-4,004.2	7.7-377.6	[140]
Arable soil, Poland	2005	16 PAHs	80-7,264	-	[169]
Traffic soil, Delhi, India	2006	16 PAHs	1062-9,652	34.56-461.27	[97]
Soil of Isola Della Femmine Natural Reserve, Italy	2006	15 PAHs	35-545	-	[349]
Urban soil, Shanghai, China	2007	16 PAHs	3279-38,868	BDL-6719.6	[147]
Urban and surrounding rural soil, Beijing China	2008	16 PAHs	146-502 (median value)	-	[152]
Indira Gandhi International Airport, New Delhi	2008	12 PAHs	2394–7,529	112-260(mean value)	[279]
Swizerland soil	-	16 PAHs	32-8,465	-	[151]
Roadside soil, Punjab, India	2009	16 PAHs	4040-16380	-	[170]
Soil of Hunpu, northeast China	-	16 PAHs	7.88-2231.42	-	[350]
South Korea, Soil	2010	16 PAHs	65-12,000	-	[347]
Present study	2011-2012	16 PAHs	799.73-51,299.67	BDL-322.410	Present study

4.7.3 Street Dust

The comparison of street dust PAHs concentrations estimated in the present study with previous works (Table 4.50) depicts higher levels of PAHs in the present study. The total PAHs content in Guwahati street dust was assessed (Table 4.50) to street dust of Niterói, Rio de Janeiro, Brazil (434-1,247ng/gm); Pereira Netto et al. [233], road dust of Shanghai, China (6,875-27,766ng/gm); Liu et al. [234], road side soil of Punjab, India (770-4,646ng/gm); Kumar et al. [170], traffic soil of Delhi, India (1062-9652ng/gm); Agarwal, [97], urban street dust of Dalian, China (1,890-17,070ng/gm); Wang et al. [351], highway dust in Tehran, Iran (11,107-24,342ng/gm); Samimi et al. [160], street dust of urban region of Hunan, china (3,515-24,488ng/g); Long et al. [352] and found to be in much higher side. However, road dust of an industrial city, Korea (11840-245120ng/gm); Lee et al. [353] was found to be higher than that of Guwahati city.

Table 4.50 Concentrations of PAHs in street dust reported elsewhere

Site	Period	Total studied PAHs	∑PAHs conc.(ng/gm)	Reference
Street dust of Niterói, Rio de Janeiro, Brazil	2002	21 PAHs	434-1,247	[233]
Road dust of Shanghai, China	2004	16 PAHs	6,875-32,573	[234]
Traffic soil of Delhi, India	2006	16 PAHs	1,062-9,652	[97]
Urban street dust of Dalian, China	2007	16 PAHs	1,890-17,070	[351]
Highway dust in Tehran, Iran		10 PAHs	11,107-24,342	[160]
Street dust of Hunan, china	2009	16 PAHs	3,515-24,488	[352]
Road side soil of Punjab, India	2009	16 PAHs	770-4,6460	[170]
Road dust of an industrial city, Korea	2008	16PAHs	11,840-2,45,120	[353]
Street dust of Guwahati city, India	2011-12	16PAHs	5153-43789	Present Study

4.7.4 River Water

Report on river water PAHs is found to be limited relative to other matrices of the environment. Total PAHs concentration in Bharalu River water, Guwahati was analysed with some previous works over the world (Table 4.51). The comparison indicates higher level of ∑PAHs concentration in the present study than that of Qiantang river of China (0.0703-1.844 ng/ml; Chen et al. [343], however comparable to that of Tiber river of Italy (0.024-0.072 ng/ml; Patrolecco et al. [354]. It was also observed that total PAHs concentration in Bharalu River water was higher than that of Kori river of Iran (45.4-375.1 ng/ml); Kafizadeh et al. [355]. However, the concentration of Bharalu River water was found to be higher than Yellow river of China (48.2-206 ng/ml); Yu et al. [356].

Table 4.51 Concentrations of PAHs (ng/ml) reported from river waters elsewhere

Site	Period	Total studied PAHs	∑PAHs Conc.	Reference
Qiantang River, China	2005	15 PAHs	0.0703-1 844	[343]
Yellow river, China^a	2005	16 PAHs	48.2-206	[356]
Tiber River, Italy	2007	6 PAHs	0.024-0.072	[354]
Kori River, Iran	2010	16 PAHs	0.045-0.38	[355]
Bharalu River, India (Present study)	2012	16 PAHs	3.351-72.893	Present study

^{a}sediment-pore water

4.7.5 River Sediment

The comparison of PAHs concentrations in Bharalu River sediment with previous works (Table 4.52) depicts higher levels of PAHs in the present study. The level of PAHs flux estimated in this study were show much higher values than that of canal and river of Thiland (2290±2556ng/gm and 263±174ng/gm; Boonyatumanond et al. [357], Beiluohe River in Northern China (17.7-407.7ng/gm); Zhang et al. [358], Qiantang River in China

(91.3-614.4ng/gm; Chen et al. [343], Yellow River in China (464-2621ng/gm); Yu et al. [356], Gomti River in India (68-3153ng/gm); Tripathi et al. [287]; Tiber River, Italy (157.8-271.6ng/gm); Patrolecco et al. [354], Tuhai-Mjia River, China (311.69-3736.32ng/gm); Liu et al. [359], Kori River, Iran (167.4-530.3ng/gm); Kafizadeh et al. [355]. However, ∑PAHs level in Bharalu River sediment is found to be lower than that of Bank sediment of Yamuna River, Delhi, India (4500-23530ng/gm); Agarwal et al. [286] and Kaoping River in Taiwan (22.6-45,100mg/gm); Fang et al. [360].

Table 4.52 Concentrations ranges of PAHs in sediment reported elsewhere

Site	Period	Total studied PAHs	Concentration (ng/gm)	Reference
Bank sediment of Yamuna River, Delhi, India	2003	16 PAHs	4500-23530	[286]
Canal and River system, Thiland'	2003	3-7 ring PAHs	2290±2556 (canal) 263±174 (river)	[357]
Kaopine River, and submarine canyon system, Taiwan	2003	28 PAHs	22.6-45,100	[360]
Beiluohe River, Northern China	2005	16 PAHs	17.7-407.7	[358]
Qiantang River, China	2005	15 PAHs	91.3-614.4	[343]
Yellow River, China	2005	16 PAHs	464-2621	[356]
Bank sediment of River Gomti, Lucknow city, Uttar Pradesh, India	2005-2007	16 PAHs	68-3153	[287]
Tiber River, Italy		6 PAHs	157.8-271.6	[354]
Tuhai-Mjia River system, China	2010	16 PAHs	311.69-3736.32	[359]
Kori River, Iran	2010-11	16 PAHs	167.4-530.3	[355]
Bharalu River, Guwahati, India	2012	16 PAHs	337.58-8618.65	Present study

4.7.6 Need for Concerted Study

The PAHs in different environmental matrices were studied by various researchers in th past. However, investigation for interrelationship of PAHs among all the environmental compartments is rather limited. Atmosphere being a principal pathway for dispersion of PAHs in the environment, its contribution to other environmental matrices need to be estimated. According to Manoli et al. [78] bulk deposition was observed to be major contributing source of PAHs into surface waters in Northern Greece which was estimated by using PAHs signature ratios. The role of atmospheric compartment in PAHs distribution was established by Montelay-Massei et al. [63] with mass balance for PAHs on the scale of the Seine estuary, France in various environmental compartment including ambient air, atmospheric deposition, soils, sediments, runoff and surface waters. Spatial distribution of PAHs in surface water, suspended particulate matter (SPM) and sediment of Daliao River watershed composed of the Hun River, Taizi River, and Daliao River was investigated by Guo et al. [237]. Composition of PAHs was found to be dominated by 4-6 ring PAHs in the entire three medium. High occurrence of LMWPAH in water and SPM was recommended for recent local source and atmospheric deposition. High pollution load in water and sediment near industrial area was suggested by industrial wastewater. It was also observed that PAHs levels are relatively higher in water and SPM, and lower in case of sediments. Samimi et al. [160] investigated PAHs contamination level in the form of settled dust in different types of samples including street dust, soil and water of a western highway in Tehran, Iran. Very high PAHs contamination was observed in the samples close to the highway. Naph and phen were found as most common PAH in all the samples. The presence of these compounds was considered as indication of emission from incomplete combustion of vehicular fuels and their subsequent adsorption to atmospheric suspended particles which were finally settled in surface of street dust, soil and water near to highway. To assess potential risk of PAHs from street dust to urban streams reflecting source-sink mechanism through stromwater, Hongtao et al. [238] assessed PAHs in street dust particles and river sediments (Yangtze River Delta) in Xincheng, China. The sediments of the urban stream reaches in town were found to act as sinks for street dust PAHs. To better understand the environmental transport of PAHs with organic matter and carbonaceous materials, Han et al. [361], investigated their association in char and soot with that of topsoil and sediment. Stronger association was observed for PAHs in both soil and sediment with that of soot than with

Char. In our study, an attempt has been made to estimate the contribution of bulk deposition PAHs into various other environmental compartments including soil, street dust, river water and sediment. The results can also act as a baseline data for various South-Asian countries.

Chapter 5

Conclusions

Chapter5: Conclusions

5.1 Conclusions

From the present investigation, following conclusions are drawn:

- Strong Seasonality was observed in bulk deposition of PAHs with maximum concentration during dry season and minimum during wet season. ∑PAHs concentration in bulk deposition were ranged between 2.2ng/ml and 1035ng/ml with mean value of 71±140ng/ml. Whereas benzo(a)pyrene concentration were ranged from BDL-5.6ng/ml with mean of 0.2±0.9ng/ml. The maximum concentrations of ∑PAHs and BaP were observed to be on higher side than many industrial cities over the world. Total PAHs concentration was found to be contributed mainly by LMWPAHs (low molecular weight) with high dominance of 2 and 4-ring PAHs which could be due to their high water solubility.

- PAH scavenging was found to be influenced by various meteorological parameters. Temperature and relative humidity were found to influence deposition of LMWPAHs.

- Two sources of bulk deposition were identified and quantified by PCA-MLR. Source 1 represented mixed inputs from diesel, coal and wood combustion and source 2 from gasoline vehicles. Source contributions estimated by the model were found to ~ 90% and ~10% for source 1 and 2 respectively.

- Maximum mean ∑PAHs in soil and street dust was observed during post-monsoon season. Mean concentrations of ∑PAHs (USEPA 16) in soil samples were found to be 5570.7±7830ng/gm (799.7-19492ng/gm), 19292.1±19932ng/gm ((1271.4-51299.7ng/gm) and 9052.3±11508 ng/gm (1639.7-29492ng/gm) during monsoon, post-monsoosn and pre-monsoon season respectively. PAHs profile was found to be dominated by 2- and 4-ring PAHs which could be attributed to multi-hop nature of LMWPAHs with continuous cycle of atmospheric deposition and re-suspension.

Mean ∑PAHs concentration in street dust samples were observed to be 8500.8±4608ng/gm (2248.8-13550ng/gm), 23294.7±15164ng/gm (1394.7-43789ng/gm) and 14770.5±9899ng/gm (5153.5-28796 3ng/gm) during monsoon, post-monsoon and pre-monsoon respectively. However, mean BaPq concentration was found to be maximum during pre-monsoon season 541.7±550ng/gm. PAHs profile in street dust was also found to be dominated by 2 and 4-ring PAHs.

- High dependencies of soil and street dust PAHs on BC/OC ratios were found during pre-monsoon season indicating that BC could be interfering with the association of PAHs and OC during pre-monsoon. However, such relationships showed seasonal bias and high positive dependencies were found during pre-monsoon season only.
- Diagnostic ratio -recommended emission from coal, wood and vehicular combustion were the major signature sources of PAHs in soil and street dust samples of the city.
- ∑PAHs concentration in Bharalu River water was maximum during pre-monsoon season than that of post-monsoon season. Concentration of ∑PAHs in Bharalu River water was found to be in the range of 3.4-72.9ng/ml with mean value of 29.8±22ng/ml. Moreover, ∑PAHs concentration was found to be on higher side during pre-monsoon season than that of post-monsoon season. PAHs Profile was found to be dominated mainly by 3-, 4- and 5-ring compounds Predominance of HMWPAHs (high molecular weight) (throughout the study period) despite of their low solubility in water could be attributed to their continuous input as urban waste or discharge of wastewater into Bharalu River.
- ∑PAHs concentration in Bharalu River sediment was maximum during post-monsoon season than that of pre-monsoon season. ∑PAHs concentration in Bharalu River sediment was varied from 337.6-23140ng/gm with mean value 4968.2±8135ng/gm during post-monsoon season, while they ranged from 608.8-8618.6ng/gm with mean concentration of 3812.4±2820 ng/gm during pre-monsoon season. The PAHs profile was found to be dominated by 3, 4 and 6-ring PAHs in sediment.

- The diagnostic ratios revealed mixed petrogenic and pyrogenic sources of PAHs in both water and sediment samples contributed mainly from diesel, gasoline and wood combustion in case of pyrogenic source.

- Exposure risk for PAHs in all matrices was found to be maximum during dry season. Mean BaPeq concentration of ∑PAHs in bulk deposition was found to be maximum at industrial site (4.6±10ng/ml) which was 11.5 times higher than forest site (0.4±0.5ng/ml). It is also to be mentioned that the ecosystem risk was very high in aquatic environment of Bharalu River water which was estimated using risk quotient (RQ). Therefore, some control measures and remedial actions must be undertaken urgently to protect the ecosystem of the Bharalu River and its surroundings.

- PAH signatures of bulk deposition correlated significantly with signatures of soil (r=0.74), road dust (r=0.79), surface water (r=0.54) and sediment (r=0.59) which could support the hypothesis that atmospheric deposition is the major contributor of PAHs in soil, road dust, surface water and sediment.
  It was interesting to find strong correlations of PAH signatures of sediment with signatures of road dust (r=0.87 and soil (r=0.65). Moreover, correlations were also observed between PAH signatures of river water with soil (r=0.45) and road dust (r=0.45). The region being high rainfall area there could be sufficient transport of PAHs from road and soil by storm water to the river water and then to river bed sediments, as significant correlation was found between river water and sediment (r=0.55). Correlation of soil and road dust with sediment was stronger than that of river water might be due to low solubility of PAHs in water, much of the PAHs carried by storm water could have partitioned to the solid phase in the sediments. High significant correlation was also found between PAH signatures of soil and road dust (r=0.89), indicating common source which could be atmospheric deposition.

5.2 Scope for Future Work

- To study on gas/particle partitioning of PAH and influence of meteorological parameter on the phase partitioning of PAHs.
- To use other model for source apportionment.
- To study reactivity of PAHs and formation of secondary PAH.

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Annexure

Annexure A

Name	Abbreviation	LOD (µg/l)*	Solubility in water (mg/L)
Napthalene	Naph	32.9	3.93
Acenaphthylene	Acy	8.5	3.93
Acenaphthene	Acen	6.2	1.93
Fluorene	Flu	7.9	1.68-1.98
Phenanthrene	Phen	5.4	1.2
Anthracene	Anth	3.6	0.076
Fluoranthene	Flan	22.2	0.2-2.6
Pyrene	Pyr	1.4	0.077
Benzo(a)anthracene	BaA	4.2	0.01
Chrysene	Chry	29.0	0.0028
Benzo(b)fluoranthene	BbF	4.8	0.0012
Benzo(k)fluoranthene	BkF	5.1	0.00076
Benzo(a)pyrene	BaP	6.9	0.0023
Dibenzo(a,h)anthracene	DBA	7.9	0.0005
Benzo(g,h,i)perylene	BgP	2.8	0.00026
Indeno(1,2,3-cd)pyrene	IP	4.3	0.062

*values are of present study

Annexure B

Name	Abbreviation	LOD (ppm)*
Cadmium	Cd	0.004
Chromium	Cr	0.001
Copper	Cu	0.005
Iron	Fe	0.001
Manganese	Mn	0.0003
Nickel	Ni	0.004
Lead	Pb	0.02
Zinc	Zn	0.001

*values are of present study

List of publications

List of Publications

Paper (Published)

- **Hussain, K.,** Rajbangshi, R. and Hoque, R.R. (2014). "Understanding levels and sources of PAHs in water of Bharalu Tributary of the Brahmaputra River". *Asian Journal of Water, Environment and Pollution* **11** (2), 89-98.

- **Hussain, K.** and Hoque, R.R. (2015). "Seasonal attributes of Urban Soil PAHs of the Brahmaputra Valley". *Chemosphere* **119,** 794-802.