Study on correlations among PAHs and SPM during crop residue burning events at a semi-urban site of Patiala

A Dissertation

submitted in partial fulfilment of the requirement

for the award of degree of

Masters in Technology

in

Environmental Science and Technology

Submitted

By

Ritika Arora

(Reg. No. 601201018)

Under Supervision of

Dr. Susheel Mittal
Senior professor
(Department of Chemistry and Biochemistry)

Dr.Sukhrishpal Kaur
Research Scientist
SAI Labs, Patiala

School of Energy and Environment
Thapar University, Patiala
July 2014

CERTIFICATE

This is to certify that thesis entitled, "**Study on correlations among PAHs and SPM during crop residue burning events at a semi-urban site of Patiala**" submitted by **Ms. Ritika** in partial fulfillment of the requirements for the award of **Masters in Technology** Degree in **Environmental Science & Technology** at **Thapar University, Patiala** is an authentic work carried out by her under our joint supervision and guidance.

To the best of our knowledge, the matter embodied in this thesis has not been submitted to any other university/ institute for award of any Degree or Diploma.

Susheel Mittal

Dr. Susheel Mittal (Supervisor)
Senior Professor
School of Chemistry and Biochemistry
Thapar University
Patiala

Dr. Sukhrishpal Kaur
Research Scientist
SAI Labs, Patiala

Dr. A.S. Reddy
Head
School of Energy and Environment
Thapar University, Patiala

Dr. S. K. Mohapatra
Dean
Academic Affairs
Thapar University, Patiala

DECLARATION

I, the undersigned, hereby declare that the research work presented in the M.Tech dissertation entitled "**Study on correlations among PAHs and SPM during crop residue burning events at a semi-urban site of Patiala**" has been carried out by me under the supervision and guidance of *Dr. Susheel Mittal, Senior Professor, School of Chemistry and Biochemistry, Thapar University, Patiala and Dr. Sukhrishpal Kaur, Research Scientist, SAI Labs, Patiala.*

Further, I declare that no part of this Dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

Ritika Arora
(Reg. No. 601201018)
M.Tech – Environmental Science and Technology
Thapar University
Patiala

ACKNOWLEDGEMENTS

First of all I would like to thank the Almighty, who has always guided me to work on the right path of the life.

It is matter of immense pleasure to acknowledge my debt to my Supervisors **Dr. Susheel Mittal,** Senior Professor, School of Chemistry and Biochemistry, Thapar University, Patiala and **Dr.Sukhrishpal Kaur**, Research scientist, SAI Labs, Patiala. It is because of his priceless intellectual guidance, innovative and constructive ideas for having given me complete independence, encouragement to put my desire and thoughts, which paved the way for the successful completion of this work. It is indeed my privilege to work under him.

I also feel very much obliged to **Dr. A.S. Reddy,** Professor and Head, School of Energy And Environment, Thapar University, Patiala for giving me the opportunity to work on this project.

I am equally grateful to **Mr. Sandeep Chandra** (Head) **and Dr**. **Sukhrishpal Kaur (**Research Scientist), Sophisticated Analytical Instrument Laboratories (SAI Labs) Thapar University Campus, Patiala (Punjab) for motivation and inspiration that triggered me for the thesis work.

I am also very thankful to **Mr. Inderpreet Singh Grover** for his invaluable guidance and support.

I am also thankful to the **entire faculty and staff members** for their direct-indirect help, cooperation, love and affection, which made my stay at Thapar University memorable.

Last but not least, I would like to thank my parents for their wonderful love and encouragement, without their blessings none of this would have been possible. I would also like to thank my close friends for their constant support.

(Ritika Arora)

ABSTRACT

Burning agriculture waste has long been practiced to prepare land for planting, saving time in clearing the land for the next crop, return nutrients to the soil, increase harvests and control pests, etc. These burning events of wheat and rice crop residues after harvesting of respective crops are important contributors to the higher concentration levels of suspended particulate matter (SPM) in the ambient air of Punjab. Besides being career of other pollutants, these are vehicles of unburnt hydrocarbons including polycyclic aromatic hydrocarbons (PAHs). A study was done to analyze aerosol samples collected previously using high volume sampler with GMF/A sheets for 24h period at Thapar University Campus (TUC) site of Patiala, Punjab.

After extraction of all the samples with dichloromethane, each sample was injected in Gas chromatograph fitted with stainless steel capillary column (dimethyl polysiloxane). The four PAHs namely pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene were identified as these are the four compounds observed frequently throughout the study. The concentration levels of individual PAH compound varied from 0.36 to 625 $\mu gm^{-3}$with mean value of total PAH concentration (TPAH) of 275 ± 161 μgm^{-3}.

In the present study, concentration levels of each one of these have been correlated with respective concentration levels of TSPM in the ambient air of TUC. A seasonal trend was observed for both SPM and the PAH concentration. Concentration of PAH varied inversely with temperature. Hence, the situation of ambient air quality during the months of October and November is much worse than that in the months of April and May. The reason for sharp increase in PAH content in Oct-Nov is that the stubble burning after rice crop harvesting happens at much lower temperature and in more humid environment as compared to that in April and May when the dry stubble burns quickly in the peak summer season. Low ambient temperature results in relatively incomplete burning hence leads to more soot formation.

LIST OF TABLES

TABLE NO.	DESCRIPTION	PAGE NO.
Table 3.1	Conditions for Gas Chromatograph with FID (GC-FID)	26
Table 3.2	Retention times (R_t) of 16 PAHs for standard solution (Supelco)	27
Table 4.1	Statistical summary of PAH concentration (μgm^{-3})	29
Table 4.2	Correlations of SPM and PAHs in terms of correlation coefficients(r)	36

LIST OF FIGURES

S. NO.	DESCRIPTION	PAGE NO.
Figure 1.1	Crop Residue Burning during harvesting months	2
Figure 1.2	Particle Aerodynamic Diameter	3
Figure 1.3	Structures of polycyclic aromatic hydrocarbons	5
Figure 3.1	Diagrammatic view of High Volume Sampler	23
Figure 3.2	Diagrammatic view of Gas Chromatograph	25
Figure 4.1-4.4	PAHs content in ambient air of Thapar University site during Dec 2008- Nov 2009	29-33
Figure 4.5-4.8	Concentration levels of pyrene (PAH1) and suspended particulate matter (SPM) in ambient air of Thapar University Campus site (TUS) over a period of Dec 2008 till Nov 2009	34-35

TABLE OF CONTENTS

Certificate i

Declaration ii

Acknowledgements iii

Abstract iv

List Of Tables v

List Of Figures vi

Chapter-1 Introduction 1

Chapter-2 Literature Survey 9

2.1 Purpose of review 19

2.2 Summary of findings 20

Chapter-3 Material and Methods 21

3.1 Study plan 21

3.2 Study region and characteristics of sampling site 21

3.3 Collection of SPM samples 22

3.4 Characterization of aerosol samples 24

3.5 Gas chromatographic analysis 24

3.6 Quantification of polycyclic aromatic hydrocarbons (PAHs) 25

3.7 Optimization of GC-FID parameter 26

3.8 Identification and quantification of PAHs 27

Chapter-4 Results and Discussion 28

Chapter-5 Conclusions and Recommendations 38

CHAPTER 1

INTRODUCTION

The sustaining condition of our earth is due to its distinctive atmosphere and air is one of the imperative things necessary for life on the planet. The atmosphere of earth is a layer of gases adjoining the planet earth that is retained by earth's gravity. The lowest region of the atmosphere is the troposphere containing 80% of the total mass of air and almost all of the water vapors. By volume, dry air contains 78.09% nitrogen, 20.95% oxygen, 0.93% argon, 0.039% carbon dioxide, and small amounts of other gases. Air also contains a variable quantity of water vapor, on average around 1%. The air may be best described as dilute polluted air at the most isolated locations at the poles, mountains, sea and in deserts.

The introduction of chemicals, particulates, biological materials or other harmful materials into the earth's_atmosphere, possibly causing disease, death to humans, damage to other living organisms such as food crops, or the natural or built environment known as air pollution . Air pollutants are the contaminants which degrade the quality of air. Advances in science and medicine have led to a greater understanding of different health effects, including heart disease (Pope *et al*., 2004, Henneberger *et al*., 2005) and cancer, which results from products of incomplete combustion. Although industrialization and use of motor vehicles are enormously the most considerable contributors to air pollution, biomass or crop residue burning also play an important role.

Agriculture crop residue burning (ACRB) is a well-known practice especially in the developing countries like India. In Punjab, 23 million tons of rice straw and 17 million tons of wheat straw are produced annually. Burning of crop residue has been an agricultural practice for many years due to many reasons such as: it is the cheapest mode of disposal, less time consuming and less difficult to prepare the land for further farming. Open burning of wheat and rice crop residue after harvesting is a common practice performed by farmers in Punjab, India as well as other northwest regions of the country (Mittal *et al* 2009; Singh *et al* 2010; Sahai *et al* 2007, 2009, and 2010). In Punjab, the extensive burning period of rice and wheat crop residues usually starts in

the first or second week of October and April, respectively and lasts over four weeks. Though straw burnings are barred by the local administration still farmers find these practices economical and suitable for the removal of residues. Crop residue burning in the fields also kills friendly pests and bacteria which increase the fertility of soil (PAU, 2006).

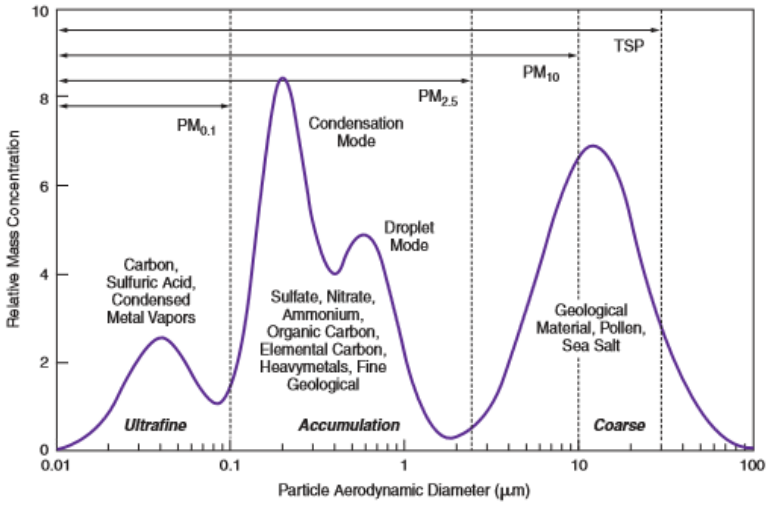
Crop residue burning (CRB) practices generate an immense amount of smoke containing particulate matter and gaseous species which decline the quality of ambient air and affect public health (Dennisa *et al*., 2002; Wiedinmyer *et al*., 2006). These activities involve the partial burning of organic materials under sub-optimum combustion conditions .Mittal *et al* (2010) studied the contribution of ACRB on the concentration of SPM (suspended particulate matter), sulfur oxide and nitrogen oxide.

Fig 1.1 Crop Residue Burning during harvesting months [3]

Particulate Matter (PM) is one of the six criteria pollutants and the most noteworthy in terms of undesirable effects on human health. Particulate Matter (PM) is the name used for a mixture of solid droplets suspended in the air. These particulates originate from a collection of sources such as power plants, biomass burning, industrial processes and diesel trucks and they are produced in the atmosphere by conversion of gaseous emissions. Their chemical and physical composition depends on location, time of year and weather. Particulate Matter is composed of both coarse and

fine particles. Particle size is regarded as one of the chief physical characteristics. The emitted particle have a certain falling velocity (depending on size of particles) due to the downward acting force of gravity , which is opposed by aerodynamic drag of the atmosphere. The balance between these forces is readily attained and particles remain suspended in the air for extensive time. Hence, lesser is the magnitude of particles, the larger the residence time. The aerodynamic diameter of coarse particles (PM_{10}) lies in between 2.5 µm and 10 µm. PM_{10} are formed by mechanical disruption (e.g. crushing, grinding, abrasion of surfaces), evaporation of sprays and suspension of dust. PM_{10} is composed of aluminosilicate and other oxides of crystal elements, and key sources including fugitive dust from roads, industry, agriculture, construction and demolition and fly ash from fossil fuel combustion. PM_{10} is also called Respirable Suspended Particulate Matter (RSPM) as they are able to reach the respiratory tract.

In an analysis reported in 1979, EPA scientists endorsed the need to measure fine and coarse particles separately. PM_{10} has a life time of minutes to hours, and its travel distance varies from <1 Km to 10 Km. The aerodynamic diameter of fine particles is less than 2.5 µm ($PM_{2.5}$). They are produced from gas and condensation of high temperature vapors during combustion, and they are composed of various combinations of sulfate compounds, nitrate compounds, carbon compounds, ammonium, hydrogen ion, and organic compounds, metals (Pb, Cd, V, Ni, Cu, Zn, Mn, and Fe). The fossil fuel combustion, vegetation burning, and the smelting and processing of metals are major sources of $PM_{2.5}$.



ESMAP Report (2011)

The lifetime of $PM_{2.5}$ is from days to weeks and travel distance ranges from 100s to > 1000s Km. The nature of particulate matter (PM) in climate change has long been recognized (IPCC , 2007) and aerosols can also negatively affect human health via inhalation ; especially in the urban environment (Khan *et al* ,2010 ;Kim *et al*, 2011). Aerosols act as carrier of pollutants such as polycyclic aromatic hydrocarbons (PAH), toxic gases, metal particles, etc. which have injurious effects on human health (Freeman and Cattell, 1990; Godoi *et al*., 2004). Biomass burning and cooking fuel combustion are likely sources of PAH in the Indian urban and rural environment.

PAHs known as polyarenes are one of the largest classes of organic molecules found in nature. PAHs are chemical compounds with a related structure comprising two or more (up to seven) condensed aromatic and other cyclic rings and exist under environmental conditions as gases, volatile liquids, semi volatile substances and solids. They include at least two fused benzene (six sided) rings. These are formed by the deficient combustion of coal, oil, petrol, wood, tobacco, charbroiled meats, garbage, or other organic materials. Sources of PAHs in the urban ambient air of developed countries include automobiles, re-suspended soils, refineries and power plants (Venkataraman and Friedlander, 1994a; Harrison *et al*; 1996). Although PAH are mainly concentrated in urban and industrial zones, they can also be found in rural areas (Gevao *et al*., 2000; Garban *et al*., 2002) or even in remote regions (Kallenborn *et al*., 1998; Migaszewski, 1999) because of their persistence in the environment and their ability to transported over long distances (Aamot *et al*., 1996; Halsall *et al*., 2001).

Aromatic hydrocarbons also referred as arenes are derived from benzene. The emissions of PAHs from incomplete combustion are of special environmental concern because of the potential carcinogenicity for some of these compounds. In 1997, Sixteen PAHs were identified as priority pollutants by US Environmental Protection Agency. These compounds are : naphthalene (Nap), acenaphthene (Acp), acenaphthylene (Acpy), fluorine (Flu) ,phenanthrene (PA) ,anthracene (Ant) , fluoranthene (FL) ,pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (Bap), benzo(g,h,i) perylene (BghiP), dibenzo(a,h)anthracene (DBA) and indeno(1,2,3-c,d)pyrene.

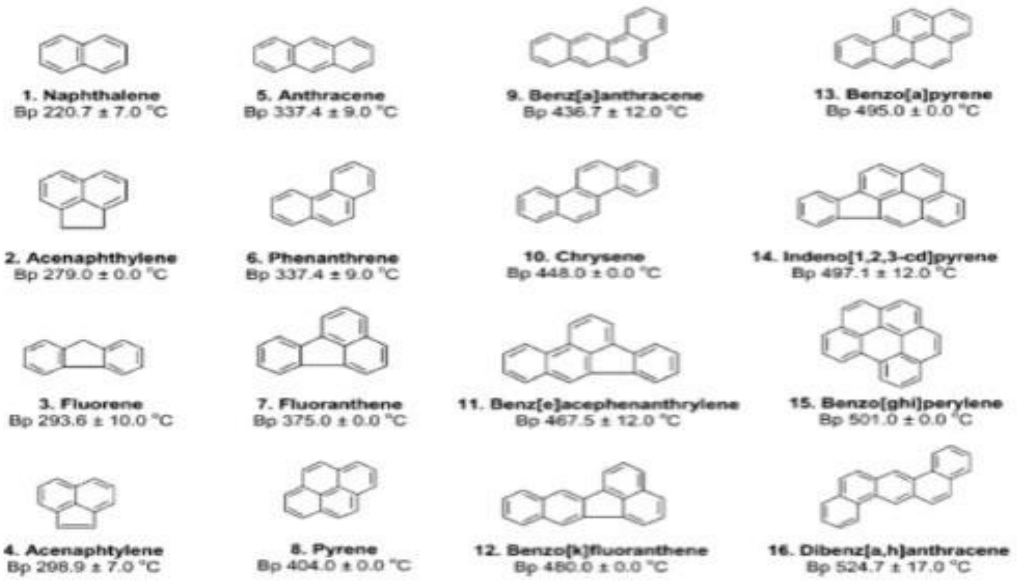


Fig 1.3 Structures of polycyclic aromatic hydrocarbons [44]

The physico-chemical properties of the PAH largely determine their environmental behavior. They are semi-volatile substances at atmospheric conditions and frequently occur both in the vapor-phase and as attached to particles depending on the vapor pressure of each PAH (Wingfors *et al*., 2001; Basheer *et al*., 2003). Low molecular weight PAH, containing two or three fused rings are more water soluble and volatile and are found predominantly in vapor phase. High molecular weight PAH containing more than three fused rings which are primarily associated with particles are found mainly adsorbed on particulate material. Polycyclic aromatic hydrocarbons have been measured in higher concentrations in smoke from solid-fuel stoves burning wood, coal and dried cattle manure (Raiyani *et al*., 1993a) which along with kerosene stoves (Saksena *et al*., 1996) are used as the primary cooking device by urban slum residents.

In India, ambient concentrations of particulate benzo (a) pyrene have been measured in Mumbai (Mohan Rao *et al*., 1983) and Ahmadabad (Aggarwal *et al*., 1982) with a view to evaluate the carcinogenic risk from PAH exposure. Studies of PAH concentrations in ambient aerosol shows that total PAH concentrations in Indian cities like Ahmadabad (90-195 ng m^{-3}) Mumbai (20-95 ng m^{-3}), Nagpur (125-190 ng m^{-3}) and Kanpur are significantly higher than those reported internationally (Raiyani *et al*., 1993b; Pandit et al., 1996; Vaishali *et al*., 1997; Thakre *et al*., 1997; Kulkarni, 1997). PAH concentration in indoor studies from Lucknow were found high for cow dung cake combustion ranging from 2.23-46.07 μg m^{-3} and lowest for liquefied petroleum

gas (LPG) combustion ranging from 0.86-4.76 μg m^{-3} (Bhargava *et al*., 2004). Studies carried out at Mumbai revealed higher concentrations in winter compared to summer (Kulkarni and Venkataraman, 2000). The aerosol PAHs emissions during sugarcane burning were studied in Brazil and Indonesia and the levels were found to be comparable with some urban centers (Fang *et al*., 1999; Godoi *et al*., 2004). Larkin *et al*. (1986) estimated that 1.26 million ha of land was burnt in UK during 1884, resulting in emission of 18,000 tones of black smoke. Based on this and the Freeman and Cattell (1990) study, approximately 6.3 tones of total particulates containing PAHs were released (Wild and Jones, 1995).

In the last decade, more and more data on airborne concentrations of PAH have become available from many industrialized countries around the world such as Brazil, 84.5ng m^{-3} (Tavares *et al*., 2004), China, 170-490ng m^{-3} (Simoneit *et al*., 1991), UK, 20-164ng m^{-3} (Coleman *et al*., 1997; Gardner *et al*., 1995), USA, 48.3-58.3ng m^{-3} (Simick *et al*., 1997), urban Malaysia, 7-9 ng m^{-3} (Fang *et al*., 1999; Omar *et al*., 2002), urban Heraclion 21.4-59 ng m^{-3} (Gogou *et al*., 1996). Few PAH have been identified as markers for various sources in urban atmosphere (Daisey *et al*., Li and Kamens, 1993; Rogge *et al*., 1993; Venkataraman *et al*., 1994; Khalili *et al*., 1995). Pyrene and Chrysene are emitted from industrial oil burning. Fluoranthene and Pyrene are emitted from both petrol and diesel vehicles. PAH profile of diesel bus emissions have also shown a large predominance of phenanthrene along with small amounts of chrysene and benzo (e) pyrene (Shankar, 1990). Wood burning in cooking stoves shows a predominance of benzo (a) pyrene (Li and Kamens, 1993).

Emissions from dried cattle-manure show a predominance of the low molecular weight species (fluoranthene, pyrene and chrysene), possibly because of the lower combustion temperature than wood, and of benzo (a) pyrene. The fossil-cooking fuel emissions show a predominance of pyrene and benzo (a) pyrene, while coal and kerosene show additional predominance of dibenz-anthracene, benzo (ghi) perylene and indeno (123-cd) pyrene. The increase in particulate PAH concentration during the winter and the dependence of concentration on atmospheric temperature have been reported in a number of previously published studies (Sanderson *et al*., 2004; Tsapakis and Stephanou, 2005; Li *et al*., 2006). The seasonal distribution of particle associated PAH is controlled by a combination of emission factors, dispersion conditions and chemical mechanisms (Carricchia *et al*., 1999; Menichini *et al*., 1999). This balance depends on the relative importance

of degradation processes and emission sources (Guo *et al*., 2003). During the cold season, PAH emissions from automobile exhaust are also higher because of low ambient temperature and increased cold start impacts (Ludykar *et al*., 1999). Low atmospheric temperature can affect the distribution of PAH between the gas and particle phases and result in a relatively larger portion of PAH partitioning to the particles phase. Other factors known to contribute to higher wintertime PAH concentration include reduced atmospheric dispersion resulting from lower atmospheric mixing heights and decreased photochemical oxidation. In summer, the lower PAH levels are likely attributed to the combination of easier atmospheric dispersion of pollutants, photo-degradation (Baek *et al*., 1991) and a higher percentage in the vapor phase and to lesser extent, by wash out effects by intermittent rains.

Measurements of aerosol levels in ambient air has always been important, as it one of the true indices of ambient air quality (Baek *et al*., 1997, 1991). The major components of aerosol in urban environments are organic compounds and the second most abundant fraction after sulphates at background and rural sites. The necessity to study the chemical composition of organic aerosols is well described in the literature (Jacobson *et al*., 2000; Jacobson 2001). Various organic markers have been identified in organic extracts of biomass smoke samples collected worldwide (Wang *et al*., 2009; Fartas *et al*., 2009 ;Mazzoleni *et al*., 2007; Simoneit, 2002). The composition data of smoke particulate matter is important for understanding the organic component contribution of biomass burning emissions to atmospheric chemistry and complements existing work on the characterization of direct organic emissions from biomass sources (Abas *et al*., 1995; Simoneit *et al*., 1983, 1988, 1991, 1990, 1993).

In India, studies were carried out mainly in the central (Pandey *et al*., 1999; Samal and Santra, 2002) and southern parts of the country. Very few studies (Sandhu and Gehlan, 1991, 1992) are reported on aerosols in the Northwestern region of India. Due to wheat and rice crop residue fires air pollution has become a serious environmental problem in this northwest region, especially Punjab and Haryana provinces of India. In 1999, an international team of scientists conducted an intensive field campaign called the Indian Ocean Experiment (INDOEX) to study the air pollution and its possible impacts on regional and global climate.

The organic fraction may be further divided in to “primary and “secondary materials while searching for the origins of atmospheric aerosols (Stern, 1968) .The carbonaceous material

present in atmospheric aerosols is a mixture of elemental carbon, organic (including polymeric) and inorganic compounds (e.g., carbonate salts). Extensive research efforts have been made to describe the nature and origins of organic particulate constituents known to be hazardous (e.g., PAHs) and some studies of carbonaceous matter have primarily examined organic solvent soluble fractions of aerosols (Mader *et al*., 1952; Ciaccio *et al*.,1974). A large carbonaceous (84%, w/w) content has been reported from the solvent extraction of PM samples from simulated rice crop residue burnings (Hays *et al*., 2005). Numerous techniques have been explored, including column chromatography, high resolution mass spectroscopy, thermal analysis, and multiple solvent extractions with total carbon analyses of the various solvent extracts (Williamson, 1973). After conducting studies on different solvents, Grosjean accomplished that solvent extraction could be used for the extraction of organic compounds in atmospheric particulate matter (Grosjean, 1975).

Availability of detailed organic aerosol data greatly enhances the ability of receptor models to categorize the emission sources (Schauer *et al*., 1996; Schauer and Cass, 2000). A study conducted in Beijing to identify and estimate the contribution of biomass burning to the urban aerosol organic carbon concentration indicated a high aerosol organic carbon concentration during wheat straw open fires (Duan *et al*., 2004). Building an effective air quality management system (AQMS) requires a method of continual improvement, and the source apportionment techniques can contribute in a cost effective manner in improving existing systems or even as the first step to begin an AQMS. Source apportionment is a mathematical method for determining contributions of various sources to a given sample of air. SA aims to elucidate the chemical composition of ambient PM samples as a combination of contribution from different sources. SA is a suitable way to extract information on pollutant sources from routinely collected ambient data (Bottom up Vs Top down approach).

Present study aimed at determining the concentrations of Polycyclic aromatic hydrocarbons in aerosol samples collected previously in Patiala during crop residue burning episodes by using the gas chromatography (GC) to determine the contribution of crop residue burning which may be helpful in source apportionment.

CHAPTER 2

REVIEW OF LITERATURE

A **literature review** is a content written by someone to reflect on the critical points of current knowledge including substantive findings, as well as theoretical and methodological contributions to a particular topic. In this review of literature, the papers related to emission of aerosols (containing PAHs) and gaseous species during crop residue burning episodes and the articles related to source apportionment are included.

Freeman et al., (1990) collected airborne particulate matter containing polycyclic aromatic hydrocarbons derived from burning natural vegetation and paper products in a variety of ways and analyzed by HPLC. Higher concentrations of benzo[a]pyrene and coronene in the polycyclic aromatic hydrocarbons resultant from bush fires than from other sources. Bush fires are expected to be a chief source of exposure of the Sydney population to polycyclic aromatic hydrocarbons.

Jenkin *et al*., (1996) measured emission factors for 19 polycyclic aromatic hydrocarbons during wind tunnel simulations of open burning for agricultural and forest biomass fuels including cereal grasses, agricultural tree prunings, and fir and pine wood (slash). Yields of total PAH varied from 5 to 683 mg kg^{-1} depending chiefly on burning conditions and to a minor extent on fuel type. Barley straw and wheat straw loaded at 400-500gm^{-2} emitted much higher levels of PAH, including benzo[a]pyrene, than other cereal and wood fuel types burning under more vigorous conditions.

Schauer *et al*., (1996) developed chemical mass balance receptor model based on organic compounds that relates source contributions to airborne fine particle mass concentrations. By applying this model, source contributions to the concentrations of specific organic compounds are revealed as well.

Marr *et al*., (1999) quantified PAH concentrations in gasoline and diesel fuel samples collected in summer 1997 in northern California. Naphthalene was the predominant PAH in both fuels, with concentrations of up to 2600 mg L^{-1} in gasoline and 1600 mg L^{-1} in diesel fuel. Emission

factors were determined separately for light-duty vehicles and for heavy-duty diesel trucks, based on measurements of PAHs, CO, and CO_2. Particle-phase emission factors, expressed per unit mass of fuel burned, ranged up to 21 μg kg^{-1} for benzo[ghi]perylene for light-duty vehicles and up to ~1000 μg kg^{-1} for pyrene for heavy-duty diesel vehicles. Light-duty vehicles were found to be a significant source of heavier (four- and five-ring) PAHs, whereas heavy-duty diesel engines were the dominant source of three-ring PAHs, such as fluoranthene and pyrene.

Kulkarni *et al.*, (2000) measured atmospheric particulate PAH concentrations at two locations in Mumbai, India. Total PAH concentrations (seven compounds) at Saki Naka and Indian Institute of Technology (IIT) were 38.8 and 24.5 ng m^{-3}. In ambient samples, the large amount of pyrene indicated its source is cooking-fuel combustion (animal manure, kerosene and liquefied petroleum gas) in addition to vehicular emissions. Pyrene and chrysene are also emitted from industrial oil burning while the low concentrations of benzo(a)pyrene indicated that wood burning is not a significant source.

Zha *et al.*, (2002) developed the new procedure for the extraction of polycyclic aromatic hydrocarbons (PAHs) from the particulate phase of cigarette smoke. The efficiency of the cleanup procedure is verified using a gas chromatographic (GC)–high-resolution mass spectrometric (MS) technique, proving that no interference occurs in the PAHs determination.

Hays *et al.*, (2003) implemented a direct thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS) method to determine the polycyclic aromatic hydrocarbon (PAH) composition (MW = 202–302 amu) in size-segregated aerosols from residential wood combustion.

Lemieux *et al.*, (2004) observed that biomass open burning sources typically emitted less VOCs than open burning sources with anthropogenic fuels on a mass emitted per mass burned basis, particularly those where polymers were concerned. Significant amounts of PAHs produced in burning pools of crude oil and diesel fuel relative to other types of open burning. During combustion of polymers PAH emissions were highest.

Mandalakis *et al.*, (2005) performed radiocarbon analysis of atmospheric polycyclic aromatic hydrocarbons (PAHs) from three background areas in Sweden, Croatia, and Greece to apportion their origin between fossil and biomass combustion. The wood and coal combustion was

relatively more important in the northern European site, while combustion of fossil fuels was the dominant source of PAHs to the two central-southern European background sites by implementing diagnostic ratios.

Poster *et al.*, (2006) concluded that gas chromatography (GC), rather than liquid chromatography (LC), is often the preferred approach for separation, identification, and quantification of polycyclic aromatic hydrocarbons in environmental samples because GC generally affords greater selectivity, resolution, and sensitivity than LC.

Wang *et al.*, (2007) measured chemical compositions of volatile organic compounds and particulate matter were collected in August 2005 in Beijing and in October 2004 in Guangzhou city. Estimation of the impact of biomass burning on air quality was done using acetonitrile and levoglucosan as tracers.

Li bin *et al.*, (2007) described systematically the different sample collection, pretreatment and analytical methods for polycyclic aromatic hydrocarbons (PAHs) in airborne particulates, and the applications of these pretreatment and analytical methods for PAHs are compared in detail.

Lee *et al.*, (2007) identified and quantified major sources of ambient particulate PAHs in Seoul based on measurements made between August 2002 and December 2003. The chemical mass balance (CMB) model was applied. Biomass burning and coal (residential and coke oven) contributed highly in fall and winter, accounting for 63% and 82% of the total concentration of PAHs, respectively.

Seng *et al.*, (2007) characterized hydrocarbons emitted from the burning of two wood samples that is kulim *(Scorodocarpus spp.)* and seraya *(Shorea spp*.). The extraction of hydrocarbons was carried out using dichloromethane as solvent and the extracts fractionated on silica-alumina column. The GC-MS was used for the detection and quantification of aliphatic hydrocarbons and PAHs compounds. The major aliphatic hydrocarbons characterized from the smoke particles were straight n-alkanes in the range of C18-C36. Results also showed that burning resulted in the formation of significant amount of PAHs compounds in both the wood samples; the major PAHs compound exhibited in both wood samples were four rings PAHs (e.g. fluoranthene and pyrene) with lesser amount of two to three (e.g. acenaphthylene) and five to six rings PAHs (e.g. benzo(a)pyrene and benzo(g,h,i) perylene).

HaiLin *et al*., (2008) collected ambient particulate PAH samples ($PM_{2.5}$ and PM_{10}) during both cooking and non-cooking periods. Source emission monitoring was also conducted for both improved and traditional cooking stoves used in the area. During the cooking periods, ambient PAHs had a significant increase and varied from 72.1 to 554.4 ng/m^3. During the supper cooking time the highest total PAH levels were found, in which five- and six-ring species accounted for a large proportion. The experimental PAH levels during cooking periods at this rural site were even higher than those in urban areas. A fine correlation was found between the benzo[a]pyrene level and the total PAH concentration (r=0.98), making benzo[a]pyrene, a probable molecular marker for PAH pollution in the rural areas, where bio- mass burning is typical.

Singh *et al*., (2008) conducted source apportionment of polycyclic aromatic hydrocarbons (PAHs) in particulate depositions on vegetation foliages near highway in the urban environment of Lucknow city (India) using the principal components analysis/absolute principal components scores (PCA/APCS) receptor modeling approach. The multivariate method enabled identification of major PAHs sources along with their quantitative contributions with respect to individual PAH. Three major sources of PAHs by PCA viz. combustion, vehicular emissions, and diesel based activities were identified. The PCA/APCS receptor modeling approach discovered that the combustion sources (natural gas, wood, coal/coke, and biomass) contributed 19–97% of various PAHs, vehicular emissions 0–70%, diesel based sources 0–81% and other miscellaneous sources 0–20% of different PAH.

Zhang *et al*., (2008) developed a regression model based on the provincial energy consumption data to calculate the monthly proportions of residential energy consumption compared to the total year volume. With this model, a PAHs emission inventory with seasonal variation was developed. The seasonal variations of diverse sources in different regions of China and the spatial distribution of the major sources in different seasons were also achieved. The PAHs emissions were enhanced in the winter than in the summer, with a difference of about 1.3-folds between the months with the largest and the smallest emissions. Residential solid fuel combustion dominated the pattern of seasonal variation with the winter-time emissions as much as 1.6 times as that in the summer, while the emissions from wild fires and open fire straw burning was mainly determined during the spring and summer.

Lai *et al*., (2009) measured atmospheric particulate and polycyclic aromatic hydrocarbons (PAHs) size distribution at Jhu-Shan (a rural site) and Sin-Gang (a town site) in central Taiwan during the rice straw burning and non-burning periods. On average, low-weight PAHs (about 87%) symbolize the largest fraction of total PAHs, followed by medium-weight PAHs (7%) and high-weight PAHs (6%). Rice-straw burning is identified as a largest source of atmospheric PAHs during burning periods at the two sites. Open burning of rice straws was probable to contribute approximately by 14-23% to total atmospheric PAHs at the two sites.

Mittal *et al*., (2009) collected aerosols on GMF/A and QMF/A (Whatman) sheets for a 24 h period throughout the year in 2007. A study was done to analyze the contribution of wheat and rice crop stubble burning practices on concentration levels of aerosol, SO_2, and NO_2 in ambient air at five different sites of in and around Patiala city and results clearly showed a distinct increase in aerosol,SO_2 and NO_2 levels during the crop stubble burning periods.

Zhang *et al*., (2009) compiled a database for emission factors, their geometric means and frequency distributions applied for emission calculation and uncertainty analysis, respectively. A comparison was done, the results for 37 countries were compared with other PAH emission inventories. It was expected that the total global atmospheric emission of these 16 PAHs in 2004 was 520 giga grams per year (Gg y^{-1}) with biofuel (56.7%), wildfire (17.0%) and consumer product usage (6.9%) as the major sources, and China (114 Gg y^{-1}), India (90 Gg y^{-1}) and United States (32 Gg y^{-1}) were the top three countries with the highest PAH emissions. The PAH sources in the individual countries varied remarkably.

He. J *et al*., (2010) collected 17 atmospheric samples to investigate the composition of organic compounds in both gaseous and particulate phases during the period of August to early November 2006 in Singapore. These samples were extracted with a mixture of dichloromethane and acetone and separated into functional group fractions for analyses by GC/MS. Over 180 organic compounds belonging to three major fractions (n-alkanes, polycyclic aromatic hydrocarbons – PAHs, and polar organic compounds – POCs) were identified and quantified. The characteristics and abundance of the n-alkanes, PAHs, mono and dicarboxylic acids, methoxylated phenols and other POCs were determined.The composition of these organic compounds relatively higher in October than those in other months of the sampling period.

Demir *et al*., (2010) used chemical mass balance (CMB) and principal component analysis (PCA) together for source identification and source apportionment in this air pollution modeling study. Evaluating overall outcome from the analyses, PCA–CMB combination formed satisfactory results in the aspect of source identification and source apportionment.

Shen *et al*., (2010) studied emissions of polycyclic aromatic hydrocarbons (PAHs) from coal combustion in a typical stove. In anthracite and bituminous, emission factors (EFs) of 16 EPA priority PAHs from tested coals ranged from 6.25 ± 1.16 mg kg^{-1} to 253 ± 170 mg kg^{-1} with NAP and PHE dominated in gaseous and particulate phases, respectively. Size distributions of particulate phase PAHs from tested coals showed that they were mostly associated with particulate matter (PM) with size either between 0.7 and 2.1 μm or less than 0.4 μm ($PM_{0.4}$). In the latter category, not only were more PAHs present in $PM_{0.4}$, but also contained higher fractions of high molecular weight PAHs. Generally, there were more than 89% of total particulate phase PAHs associated with $PM_{2.5}$.

Singh *et al*., (2010) collected aerosol samples at three diverse locations (urban –commercial, semi-urban and rural-agricultural) in Patiala. High levels of LOI (loss on ignition) and OTM (organic tarry matter) obtained at all these sites during rice and wheat crop residue burning periods. During rice crop residue burning period, levels of LOI and OTM found higher than that of wheat crop residue burning.

Rajput *et al*., (2010) collected samples of particulate matter at an urban and industrial cum residential site in Agra (India) from Dec 2005 to Dec 2006 for measuring the 16 PAH. The reported average total PAH concentration was 115 ± 17 ngm^{-3} which was found to be lower than those from other cities like Mumbai, Delhi, Chennai and Kolkata. The seasonal cycle was shown by PAH during the year with greater concentration in cold months.

Dogan *et al*., (2010) collected particulate matter samples from rural sites of Canada for measuring polycyclic aromatic hydrocarbons (PAHs) with 24 h integrated samples analyzed at 6 day intervals. Sources were identified using positive matrix factorization (PMF).

Oanh *et al*., (2011) conducted in situ experiments (11 spread field burning) and laboratory hood experiments (3 pile and 6 spread burning) during 2003–2006 in Thailand. The largest fractions of PM, EC and OC were associated with $PM_{1.1}$. The major components in $PM_{2.5}$ and PM_{10} include

OC, water soluble ions and levoglucosan. Great quantity of some methoxyphenols (e.g., acetylsyringone), PAHs (e.g., fluoranthene and pyrene), organochlorine pesticides and PCBs may also serve as additional signatures for the PM emission.

Kanabkaew *et al.*, (2011) invented a multipollutant emission inventory for crop residue field burning in Thailand. In the base year of 2007, the best emission estimates in Gigagrams were as follows: particulate matter as $PM_{2.5}$, 128; particulate matter as PM_{10}, 143; sulfur dioxide (SO_2), 4; carbon dioxide (CO_2), 21,400; carbon monoxide (CO), 1,453; oxides of nitrogen (NOx), 42; ammonia (NH_3), 59; methane (CH_4), 132; non-methane volatile organic compounds (NMVOC), 108; elemental carbon (EC), 10; and organic carbon (OC), 54. Rice straw burning was largest contributor to the total emissions, especially during the dry season and in the central part of the country.

Awasthi *et al.*, (2011) conducted a study on eight stage size segregated mass distribution of RSPM for wheat 2and rice crop seasons at rural and agricultural sites of Patiala (India). During winter months concentration levels of PM_{10} and $PM_{2.5}$ were higher during the winter months as compared to that in the summer months. Background concentration levels of PM_{10}, $PM_{2.5}$ and $PM_{10\text{-}2.5}$ were found to be around 97 ± 21, 57 ± 15 and 40 ± 6 mg m^{-3}, respectively. During rice season the levels increased up to 66, 78 and 71% and 51, 43 and 61% during wheat crop residue burning, respectively. The pair t-test was used for extensive statistical analysis of the data.

Rajput *et al.*, (2011) described an analytical method for the quantitative determination of 16-polycyclic aromatic hydrocarbons (PAHs) using accelerated solvent extraction (ASE), followed by purification on a silica cartridge, and subsequent measurement by gas chromatograph coupled to a mass spectrometer (GC-MS). The parameters of solvent extraction (T = 100 ˚C, P = 1500 psi, t = 30 min, V = 30 ml) are optimized with dichloromethane (DCM) in order to avoid fractionation effect, thereby achieving quantitative mass recovery of PAHs. The matrix effect was eliminated by purification of PAHs on silica cartridge facilitated their enrichment from extracted solution and quantitative determination in presence of an internal-standard (Pyrene-D10). In quantification of 16-PAHs and their isomer ratios the analytical protocol has been successfully used in atmospheric aerosols collected from northern India dominated by agricultural- waste (post-harvest paddy and wheat residue) burning emissions. The overall

recovery efficiency for 2- to 3-ring PAHs is 85% and near 100% recovery for 4- to 6-ring compounds based on the analysis of ambient aerosols, collected from different sites.

Shen *et al*., (2011) measured emission factors of PAHs for nine commonly used crop residues burnt in a typical Chinese rural cooking stove in simulated kitchen. The gaseous and particulate phase PAHs emission factors were 27 ± 13 and 35 ± 23 mg/kg, respectively. Isomer ratios and composition profiles of emitted PAHs were characterized. Modified combustion efficiency and fuel moisture were the most important factors affecting the emissions found by stepwise regression. PAHs (80 ± 6 %) were associated with $PM_{2.5}$ and the mass percentage of PAHs in fine particles increased as the molecular weight increased.

Chiu *et al*., (2011) demonstrated that during rice field open burning event, the PM concentration in the ambient air of rice field is over 17 times higher than that of the non-open burning period. It was found that during an open burning event, the mean total PAH and total toxic equivalence (BaPeq) concentrations in the ambient air of a rice field were 7206 ng m^{-3} and 10.3 ng m^{-3}, respectively, whereas after the open burning event, they were 376 ng m^{-3} and 1.50 ng m^{-3}, respectively. Total PAH and total BaPeq concentrations increased by 19-fold and 6.8-fold, respectively during open burning. Due to the increased amount of PM in the ambient air resulting from rice straw open burning, particle-bound PAHs contributed more to dry deposition fluxes of total PAHs than they do during non-open burning periods. Biomass (rice straw) open burning is an important PAH emission source that significantly increases both PM and PAH concentration levels and PAH dry deposition in ambient air as shown by results.

Nagarajappa *et al*., (2012) collected air samples for the analysis of benzo(a)pyrene in suspended particles (as 24 h sample once in a month) at selected monitoring sites within the Peenya industrial monitoring network between February 2011 and April 2011. The Benzo(a)pyrene concentrations of the eight sampling sites ranged from zero to 0.0490ng/m^3. At Kongovi Monitoring Station site the total benzo(a)pyrene concentrations was higher than those at other seven sites during monitoring period. The results obtained during the period of a whole year, it was concluded that, the concentrations of BaP were much higher during winter season at almost all measuring sites.

Gugamsetty *et al*., (2012) collected samples simultaneously using a dichotomous sampler (Andersen Model SA-241) and a MOUDI (MSP Model 110) over a 24-h period from May 2011 to November 2011 at Shinjung station. Samples were monitored for metallic trace elements using ion coupled plasma mass spectroscopy (ICP-MS) and ionic compounds by ion chromatography (IC). The average concentrations of PM_{10}, $PM_{2.5}$ and $PM_{0.1}$ were found to be 39.45 ± 11.58, 21.82 ± 7.50 and 1.42 ± 0.56 ng/m^3, respectively. Positive matrix factorization (PMF) was used to identify PM sources. Five source types were identified, including soil dust, vehicle emissions, sea salt, industrial emissions and secondary aerosols, and their contributions were expected using PMF.

Yang *et al*., (2012) collected day and night from three sites in Tanggu District at Tianjin Binhai New Area, China**)** during the November 2008 by using the filter samples. In PM_{10} and $PM_{2.5}$ samples sixteen polycyclic aromatic hydrocarbons (PAHs) were analyzed .The total PAHs concentrations in $PM_{2.5}$ and PM_{10} are in the range of 8.47– 113.94 ng/m^3 with average of 62.88 ng/m^3 and 21.07– 118.23 ng/m^3 with average of 73.42 ng/m^3, respectively. During sampling time the light ring PAHs (2–4 rings) are dominant in both $PM_{2.5}$ and PM_{10} compared with the heavy ring (5–6 rings) PAHs. The correlation of PAHs and $PM_{2.5}$ ($r = 0.689$, $p<0.05$) was stronger than PAHs and PM_{10} ($r = 0.570$, $p<0.05$), illustrated PAHs tend to adsorb in $PM_{2.5}$.

Singh *et al*., (2013) determined experimentally the emission factors and emission estimates of PAH emitted from biomass fuels (dung cake, fuel wood and crop residue) from rural household of six states (Delhi, Uttar Pradesh, Punjab, Haryana, Uttarakhand and Bihar). Determination of gaseous phase and particulate phase PAHs emissions was done simultaneously from various biomass fuels. The particulate phase PAHs emission factor (56.5 mg kg^{-1}, 45.3mg kg^{-1} and 35.8 mg kg^{-1}) was found higher as compared to 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. Anthracene, fluoranthene, pyrene, benzo[a]anthracene and chrysene are chief PAHs in all biomass fuels.

Kaur *et al*., (2013) analyzed PAHs in air particulate matter (PM10) from different geographical locations by high-volume air sampler. Pyrene, naphthalene, acenaphthene, acenaphthylene, fluoranthene, fluorene, and dibenzo(a,h)anthracene accounted for 80% of 16 PAH concentrations and the contribution of seven carcinogenic PAHs accounted for 12 % of 16PAHs. The probable carcinogenicity of PAHs in terms of benzo(a)pyrene toxic equivalency (BaPTEQ) was assessed

and confirmed that dibenzo(a,h)anthracene was the dominant PAH contributor (88.7 %) followed by benzo(a)pyrene (6.67 %). Mixed pyrogenic sources including biomass burning, coal combustion, and petrogenic sources, such as vehicular emissions are dominant PAH sources in Amritsar calculated by homolog pattern and diagnostic ratios of PAHs.

Callén *et al*., (2013) collected samples by using high volume air sampler with a PM2.5 cut off from June 2011-May 2012 in the city of Zaragoza, Spain. The particle phases PAH were extracted by Soxhlet and 19 PAH were analyzed by gas-chromatography with mass spectrometry mass spectrometry detection (GC-MS-MS). Chrysene, benzo(b)fluoranthene, fluoranthene, pyrene and benzo(e)pyrene represented the 47% of the average total PAH.

Singh *et al*., (2013) collected samples of SPM in ambient air of Patiala during 2006-2007 at selected urban and rural locations and analyzed for the K concentration using flame photometry. At the urban site, the monthly average of SPM levels ranged between 100±30-446±94 μgm^{-3} and 111±22-491±173μgm^{-3} at rural site in ambient air of Patiala during 2006-2007 at selected urban and rural locations. During the crop residue burning (CRB) periods an increase in SPM levels was observed at the rural as well as urban area site. At the urban area site, monthly average K concentration varied between 3.3±0.58μgm^{-3} to 12.74±4.82 μgm-3 while levels varied between 3.42±1.33 μgm^{-3} to 31.81±14.19 μgm^{-3} at the rural site. The concentration of K and SPM was significantly higher at rural area site as compared to the urban area site during CRB months.

Tripathi *et al*., (2013) observed that burning of crop residues emit gases like sulphur dioxide (SO_2), oxides of nitrogen (NOx), carbon dioxide (CO_2), carbon monoxide (CO), black carbon (BC), organic carbon (OC), methane (CH_4), volatile organic compounds (VOC), non-methane hydrocarbons (NMHCs), ozone (O_3), and aerosols etc which affect the global atmospheric chemistry and climate.

Chuesaard *et al*., (2014) collected total suspended particulates (TSP) and ten polycyclic aromatic hydrocarbons (PAHs); 19 nitropolycyclic aromatic hydrocarbons (NPAHs); and levoglucosan (LG), a marker for biomass burning, were quantified in total suspended particulates (TSP) in Chiang Mai during the dry, transition, and wet seasons in 2010. In the dry season the concentrations of PAHs and NPAHs were significantly higher than in the wet season. The indicator of traffic, the benzo[a]pyrene(BaP)-benzo[ghi]perylene(BghiPe) ratio, and the

correlations of PAHs and NPAHs with LG showed that biomass burning significantly contributes to air pollution in the dry season. The most abundant NPAH Nitroanthracene (9-NA) which suggested that 9-NA is generated from biomass burning. In dry season the biomass burning was a major source of PAHs and NPAHs in the dry season, whereas vehicle exhaust was the main contribution in the wet season.

Jain *et al*., (2014) prepared a state-wise inventory of crop residue burnt in India and the air pollutants emitted was prepared using the Inter-Governmental Panel on Climate Change (IPCC) national inventory preparation guidelines for the year 2008–09. The generation of total amount of residue in 2008–09 was 620 Mt out of which ~15.9% residue was burnt on farm. The contribution of rice straw was 40% of the total residue burnt followed by wheat straw (22%) and sugarcane trash (20%). The crop residues burning emitted 8.57 Mt of CO, 141.15 Mt of CO_2, 0.037 Mt of SOx, 0.23 Mt of NOx, 0.12 Mt of NH_3 and 1.46 Mt NMVOC, 0.65 Mt of NMHC, 1.21 Mt of particulate matter for the year 2008–09.

Jamhari *et al*., (2014) collected PM_{10} samples on glass fiber filter paper using a High Volume Sampler (HVS) for 24 h between September 2010 and April 2011 at two sites within the Klang Valley, Kuala Lumpur (urban, KL) and Petaling Jaya (industrial, PJ), and one site outside the Klang Valley, Bangi (semi-urban, BG). The extraction of filter papers with PM_{10} was done by using dichloromethane-methanol (3:1), and analysis of 16 USEPA priority PAHs was determined using gas chromatography with mass spectra (GC–MS). Total PAHs (more than 80%) consisted of 5-ring and 6-ring PAHs such as benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcP), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF) and benzo[g,h,i]perylene (BgP). The high concentration of benzo[g,h,i]perylene (BgP) at all locations suggested a source indicator for traffic emission.

2.1 Purpose of review

The purpose of this review is to report on open agricultural burning activities especially on rice and wheat crop residues and the availability of particulates emission data. Literature survey was also conducted to compare emissions of air toxic pollutants (polycyclic aromatic hydrocarbons) from the burning of different crop residues.

2.2 Summary of findings

A detailed literature search was performed to collate available data reporting emissions of air toxics from crop residue burning sources. Availability of data varied according to the source and the class of air toxics of interest. Studies suggest that crop residue burning is a potential source of air pollution such as suspended particulate matter, SPM (coarse, fine, and ultrafine), gases like CO_2, CO, CH_4 and NOx, SOx, and VOC and PAH. Most of the studies are based on the extrapolation of the old data sets. Very less ground based studies are reported. There exist potentially important data gaps in the studies that should be filled by additional research based on ground based experiments. Continuous monitoring of air is needed in the areas where crop residue is burned in open fields.

CHAPTER 3

MATERIALS AND METHODS

3.1 Study plan

Design of the ambient air quality monitoring programme depends on the monitoring specific objectives specified for the air quality management in the chosen area of interest. The main objectives stated for the progress of an air quality measurement and surveillance programme was to: ease the background concentration(s) measurements, observe current levels as a baseline for assessment, verify the air quality relative to standards or limit values, identify the importance of individual sources.

In the present study, concentrations of polycyclic aromatic hydrocarbons were determined in already collected aerosol samples in Patiala during crop residue burning episodes, by using gas chromatography (GC) to determine the contribution of crop residue burning in polluting the air.

3.2 Study region and characteristics of sampling sites

Patiala district is one of the eminent princely states of erstwhile Punjab forming the south-eastern part of the state. It lies between 29°49’ and 30°47’ north latitude, 75°58’ and 76°54' east longitude. It is surrounded by the districts of Fatehgarh Sahib & Rupnagar and the Union Territory of Chandigarh in the north, Sangrur district in the west, Ambala and Kurukshetra districts of neighboring state of Haryana in the east and Kaithal district of Haryana in the south. No point source of air pollution is found in Patiala city because there is no industry in the vicinity. Due to sub -tropical latitude of Punjab the temperature difference from month to month is very high. Though the lowest temperature rarely drops below 0^{o} C, ground frost is a common event in mid -winter. The rise in temperature is steady when the moisture content is high; the rise is however steep when the sky is clear and there is little moisture content in the air. The maximum day time temperature is observed during May and June months. The minimum temperature is recorded during the month of January. In Patiala, the wind direction is North-West (NW) for most of the time period (Mittal *et al*., 2009). Wheat and Rice (paddy) are the two major

crops in Punjab covering 86% of the total cultivated land. Burning of crop residues occurs during April-May (wheat crop harvesting period) and October-November (rice crop harvesting period) each year.

Samples from Thapar University site were selected for the monitoring of polycyclic aromatic hydrocarbons (PAHs) in the ambient air. Thapar University is a key institute in the 250-acre (1.0 km^2) Thapar Technology Campus (TTC) in Patiala having around 6,000 populations. Total suspended particulate matter (TSPM) present in the air were collected using sampling device (High Volume Sampler) installed on the roof top of PG hostel were extracted using Soxhlet extractor in dichloromethane medium. The organic tarry matter so collected was further analyzed for PAH contents using Gas chromatography fitted with FID detector.

3.3 Collection of SPM samples

SPM samples collected previously were used for their analysis for polycyclic aromatic hydrocarbons content in the organic tarry matter. SPM samples collection was done previously followed the procedure as detailed below:

Total suspended particulate matter (TSP) monitoring measures the total amount of particles suspended in the atmosphere. High volume air sampler is an instrument used to collect TSP samples. A large known volume of air is passed through a High volume air sampler (pre-weighed filter paper for 24 hours). High and low volume air samplers are instruments used to collect samples of air particles. The difference between high and low volume air samplers lies in the amount of air sampled. More than 1500 m^3 of air over a 24-hour period are drawn by High volume air samplers while low volume air samplers sample only 24 m^3 of air, or less.

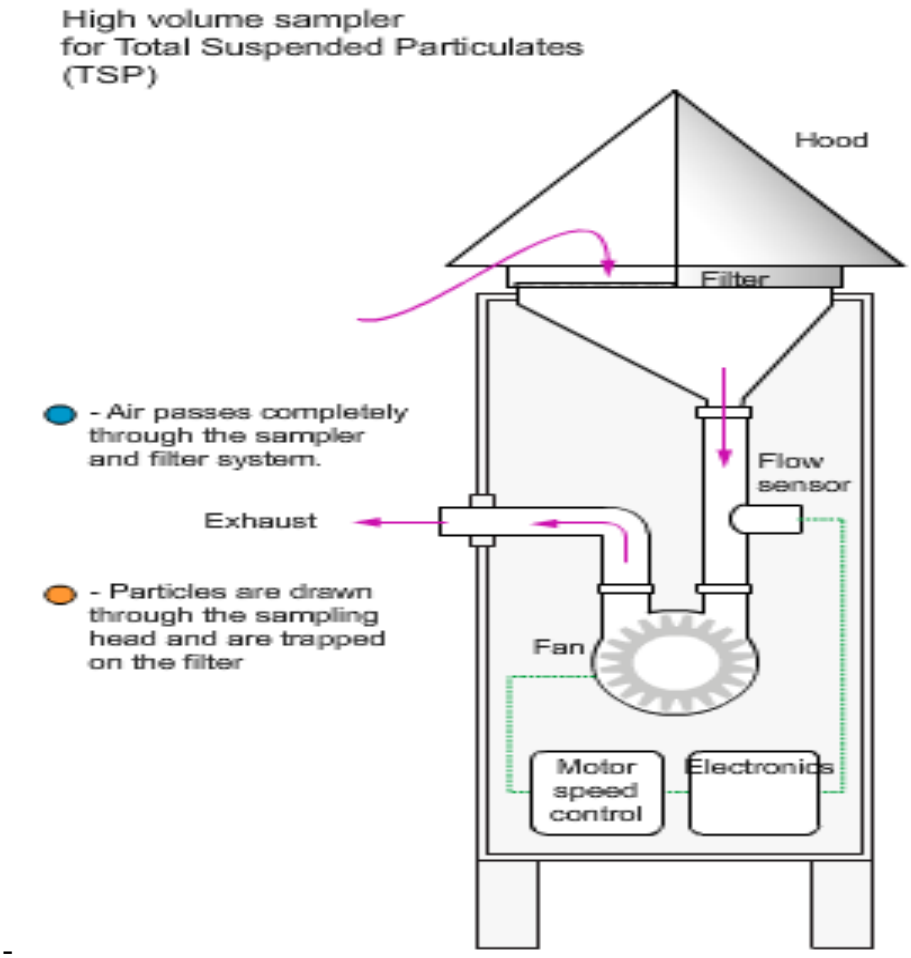


Fig 3.1 Diagrammatic view of High Volume Sampler [42]

The high-volume (Hi-Vol) sampler is the workhorse of air sampling and monitoring. The sampler employs a continuous duty blower to suck in an air stream. The air stream is then drawn through a filter to collect particles lesser than 10µm size (PM_{10}). The pre-weighed Glass Micro Fiber Filter Sheets (GMF/A, 20×25cm^2) were used for the collection of SPM samples (particles of less than 100µm size) at an average flow rate of 1.5 m^3min^{-1}. Each filter sheet was removed after 24 hours continuous sampling, placed in clean polythene bag and carried into laboratory for conditioning and weighing. Weekly sampling was done during both crop and non-crop burning months.

3.4 Characterization of aerosol samples

Previously collected SPM samples were extracted by solvent extraction method and the organic matter was analyzed for the determination of polycyclic aromatic hydrocarbons (PAHs) in the ambient air.

Sample processing and extraction

Cut or punched the 25% of exposed filter in to small strips or circular pieces in a flask of 250 mL capacity. Added about 100 mL of dichloromethane (DCM) for extraction and sonicated the sample for 30 min. Filtered the extracts by using Whatman filter paper no. 40. Repeated the extraction procedure twice and combined the extract and dried its moisture by using anhydrous sodium sulphate.

Sample concentration

Evaporated the extract by using Rotary Evaporator at approximately 40℃. Do not evaporate up to total dryness. Added 2 mL of dichloromethane to rinse the walls of evaporation flask and transfer extracts into a beaker of 5 mL capacity.

Clean-up and enrichment

It was performed using silica gel column having length 200 mm and inner diameter of 5 cm. The column was packed by using 5g of deactivated silica gel (60-100 mess size). Then dichloromethane was eluted through the column for conditioning. The extract was then loaded (concentrated 2 or 3 ml) on the top of silica column and fraction of PAH was collected with dichloromethane. The eluent was collected into a round bottom flask and solvent was evaporated to 1 mL by using Rotary Evaporator. Then it was transferred to 5 ml amber vials for further analysis.

3.5 Gas chromatographic analysis

The analytical instrument that measures the content of various components in a sample known as Gas chromatograph (GC) and the analysis performed by a gas chromatograph is called gas chromatography.

Principle of gas chromatography: The sample solution injected into the instrument enters a gas stream which transports the sample into a separation tube known as the "column." The various components are separated inside the column.

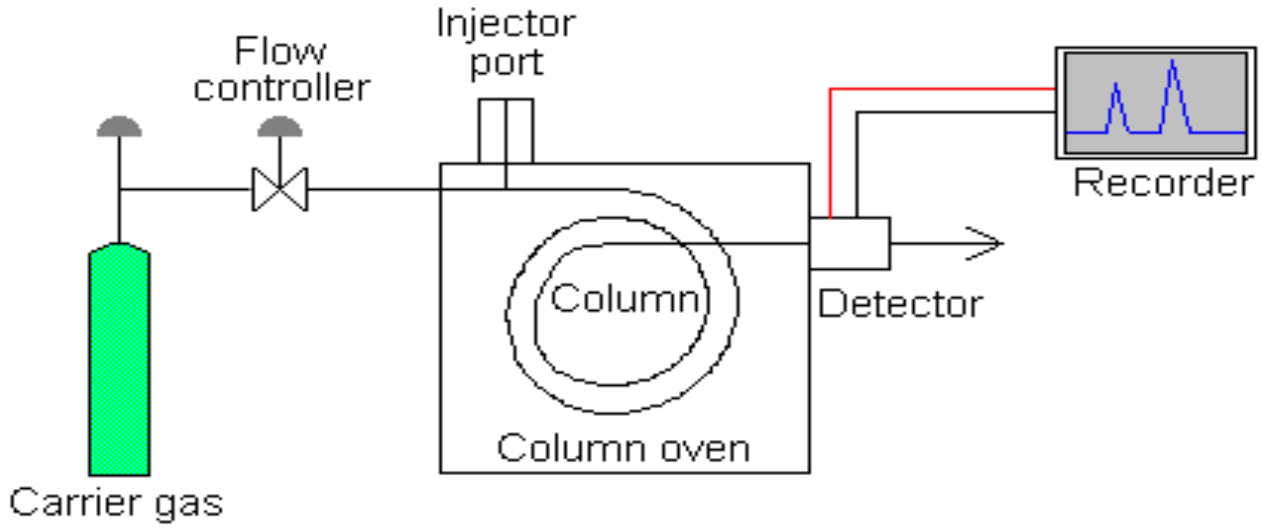


Fig 3.2 Diagrammatic view of Gas Chromatography [43]

The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The option of carrier gas is often dependent upon the type of detector which is used. To remove water and other impurities the carrier gas system also contains a molecular sieve. The detector measures the quantity of the components that exit the column.

3.6 Quantification of polycyclic aromatic hydrocarbons (PAHs)

PAHs were determined in SPM samples using a gas chromatograph (NUCON 5765) with a flame ionization detector (FID) in a split mode. The chromatograph was equipped with a 30m long, 0.25mm i.d., 0.25µm film thickness capillary column (dimethyl polysiloxane). Each SPM sample (extracted) was prepared in DCM (HPLC grade, Merck, India) for the analysis. Each prepared sample (volume of 1µL) was injected in Gas Chromatograph (NUCON 5765) fitted with FID and the corresponding peaks were obtained according to their retention times.

3.7 Optimization of GC-FID parameters

Optimization of GC-FID parameters was done prior to the analysis of samples. For optimization and standardization of GC-FID conditions a standard mixture of 16-PAHs (Supelco) containing 16 PAH compounds (EPA 610 PAH mixture) was used. A standard PAH solution (1µL) was injected frequently for studying the reproducibility of the detector and determined the retention times of different PAHs. The peaks were resolved of all the 16 PAHs. The optimum condition shown in Table 3.1 was obtained for determination of different PAHs in the ambient samples.

Table 3.1 Conditions for Gas Chromatograph with FID (GC-FID)

Parameters	**Specification/operating conditions**
GC column	Supelco 28089-U , Equity-5, 30m ,0.25mm i.d.,0 .25µm film thickness
Liner	Liner Splitless glass liner
Carrier gas	Ultra purified Nitrogen gas, 99.99% pure,(30mL min^{-1})
Injection type	Split (1:10)
Injection port temperature	275^{o}C
Detector (temperature)	FID (280^{o}C)
Oven temperature	60^{o}C(hold 5 min) to 300^{o}C @4^{o}C min^{-1} to 320^{o}C @1^{o}min^{-1}
Injection volume	1µL
Fuel gas and flow rate	Hydrogen gas (30mL min^{-1})
Oxidant gas and flow rate	Air (300 mL min^{-1})

Table 3.2 Retention times (R_t) of 16 PAHs for standard solution (Supelco)

S.No	PAH	Ellipsis	Retention times (R_t) (Minutes)
1	Naphthalene	Nap	10.33
2	Acenaphthene	Acp	12.14
3	Acenaphthylene	Acpy	12.76
4	Fluorene	Flu	18.84
5	Phenanthrene	PA	19.52
6	Anthracene	Ant	21.63
7	Fluoranthene	FL	24.79
8	Pyrene	Pyr	30.56
9	Benzo(a)anthracene	B(a)A	31.3
10	Chrysene	CHR	36.9
11	Benzo(b)fluoranthene	B(b)F	45.55
12	Benzo(k)fluoranthene	B(k)F	49.19
13	Benzo(a)pyrene	B(a)P	57.01
14	Indeno(1,2,3-c,d)pyrene	IND	59.93
15	Dibenzo(a,h)anthracene	DBA	61.03
16	Benzo(g,h,i)perylene	B(ghi)P	67.24

3.8 Identification and quantification of PAHs

The identification of PAHs was done by comparing the retention times of each PAH component in sample with the retention times of standard PAHs and was quantified by considering the area under respective peak. Then calculate the amount of analyte using the equations-:

Response factor = peak area (standard)/PAH amount (standard)

Amount of analyte = peak area/response factor

CHAPTER 4

RESULTS AND DISCUSSION

Quantitative analysis of samples collected from Thapar University Campus in 2008-2009 was done for PAH contents using Gas chromatography. In previous studies, samples were collected using HVS to study quantity of the TSPM in ambient air of Thapar University Campus. The same samples collected in December 2008 till November 2009, 47 in number) were kept preserved under refrigeration. One-quarter of each of the sample was extracted in dichloromethane medium using microwave digestion. After vacuum evaporating, the refluxed material was run through silica gel column to remove impurities. Organic content of the SPM sample so obtained was further evaporated to remove last traces of the solvent and it was stored in borosil vials of 5 mL capacity. Each such sample was injected in Gas chromatograph fitted with capillary column (dimethyl polysiloxane).

Chromatographic analysis of the samples was done to identify and quantify the polycyclic aromatic hydrocarbons (PAHs) according to the procedure as per IS: 5182 (Part12) Methods for measurement of Air pollution, Polynuclear Aromatic Hydrocarbons in Air Particulate Matter Bureau of Indian standards (BIS). Sixteen PAHs were identified as priority pollutants by US Environmental Protection Agency, only four of these were identified for detailed analysis in the present study.

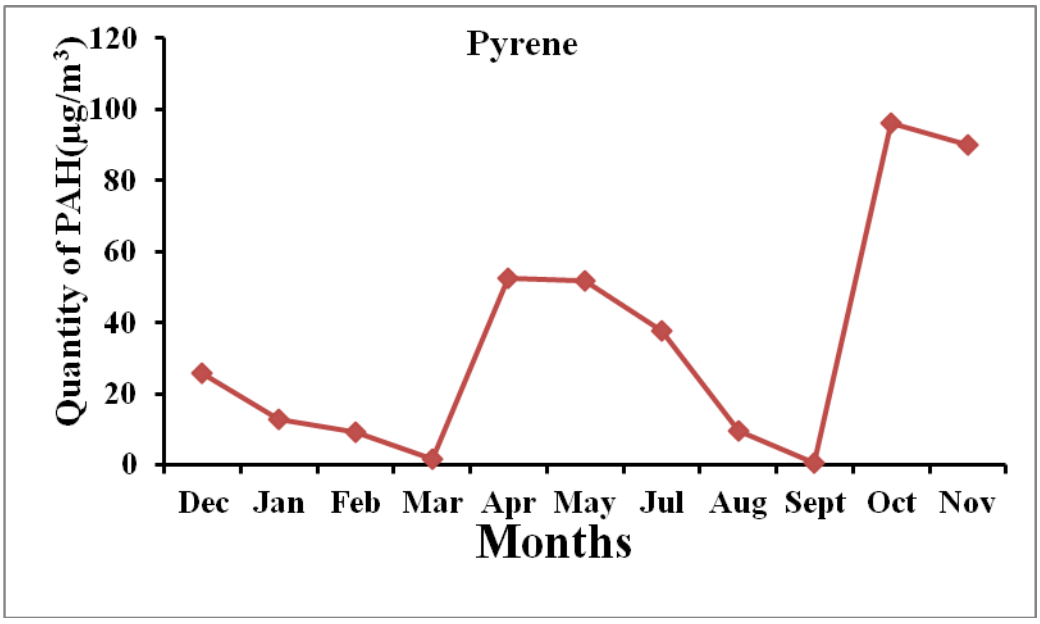
The four identified PAHs namely pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene are named as PAH1, PAH2, PAH3 and PAH4, on the basis of their occurrence in the sample analyzed. These are the four compounds observed frequently and throughout the study.

The concentration levels of individual PAH compounds varied from 0.36 to 625 μgm^{-3} with mean value of total PAH concentration (TPAH) of 275 ± 161 μgm^{-3}. In present study, the concentration levels of each one of these have been correlated with respective concentration levels of TSPM in the ambient air of TUC.

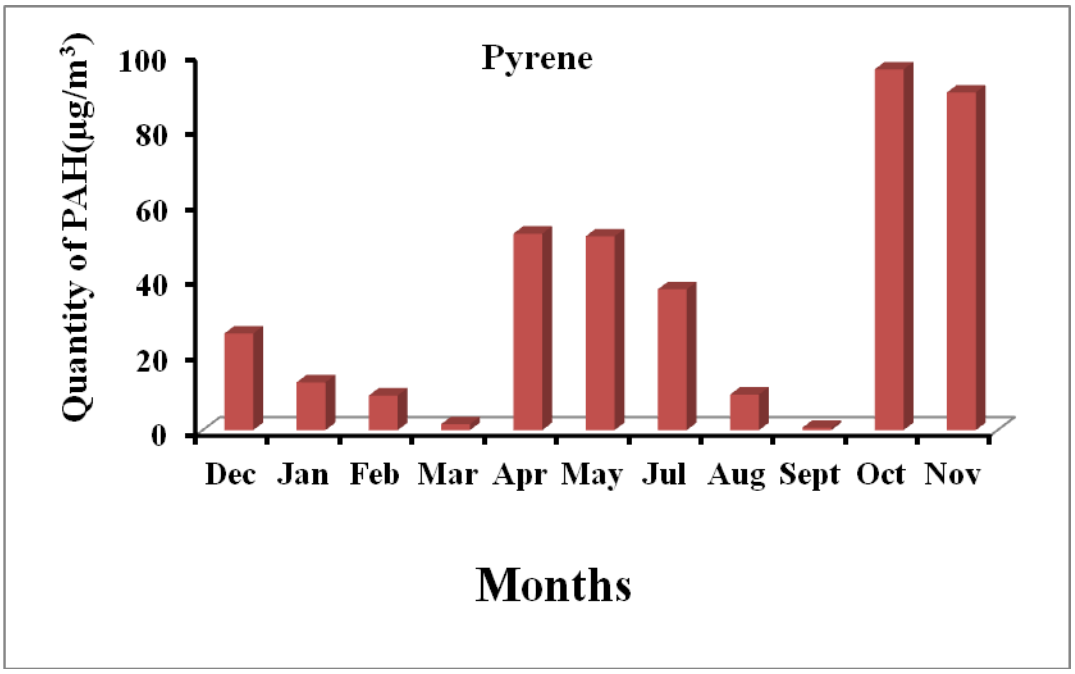
Table 4.1 Statistical summary of PAH concentration (µgm^{-3}) in ambient air of TUC site

PAH	Minimum concentration, µgm^{-3}	Maximum concentration, µgm^{-3}	Mean concentration, µgm^{-3}
Pyrene	0.67	96.29	22.37
Benzo(a)anthracene	1.90	152.96	57.67
Chrysene	0.36	105.69	16.69
Benzo(b)fluoranthene	27.15	625.36	178.67
TPAH	30.07	980.30	275.37

The total PAH1 (pyrene) concentration varies from 0.665 to 96.29 µgm^{-3}. In the months of December 2008, January 2009 till May 2009 (identified as wheat crop non burning months) the PAH1 values vary from 25.77 to 96.29 µgm^{-3} and from 52.44 to 51.73 µgm^{-3} in the months of April and May 2009 (wheat crop burning months), respectively. The concentration levels of PAH vary from 37.6 to 0.66 µgm^{-3} during July 2009 to September 2009 (rice crop non burning months) and 96.29 to 90.13 µgm^{-3} in months of October and November 2009 (rice crop burning months).

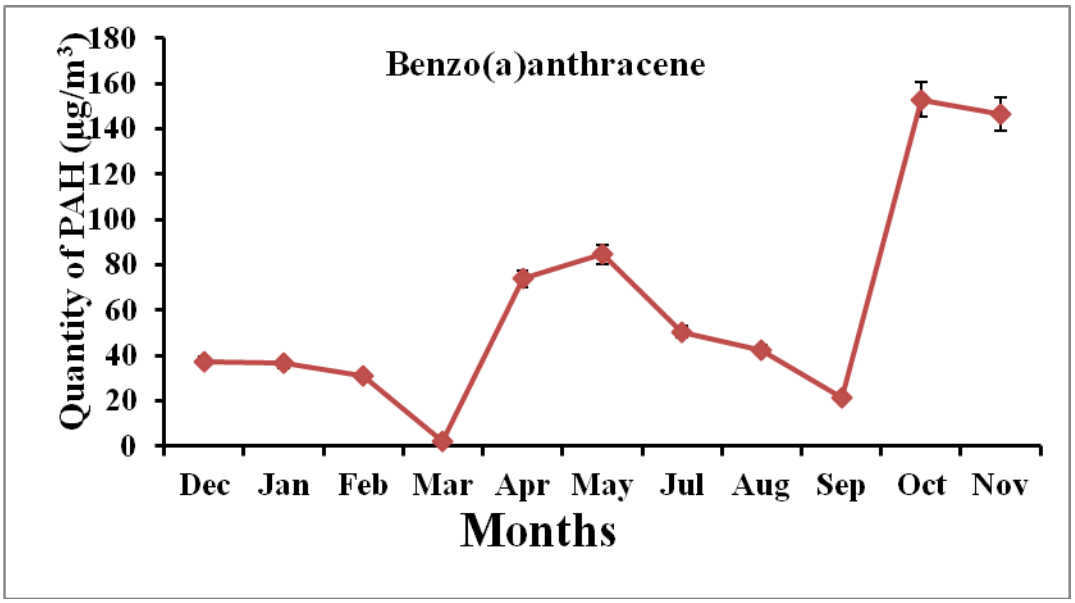


(a)

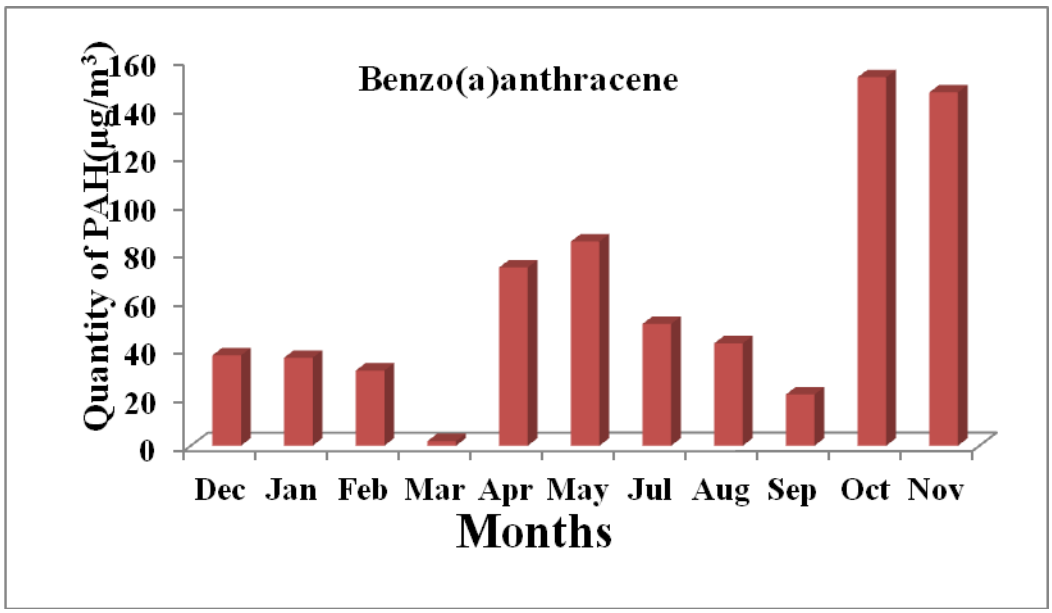


(b)

Figure 4.1 (a) and (b): Pyrene content in ambient air of Thapar University Campus site during Dec 2008-Nov 2009

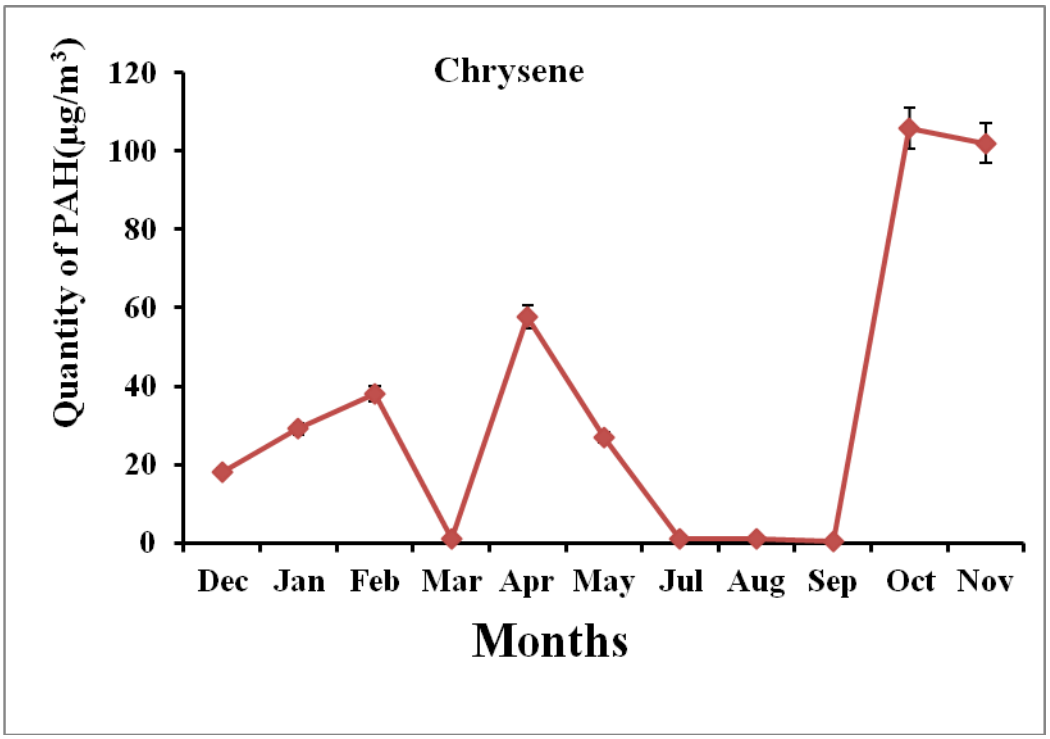


(a)

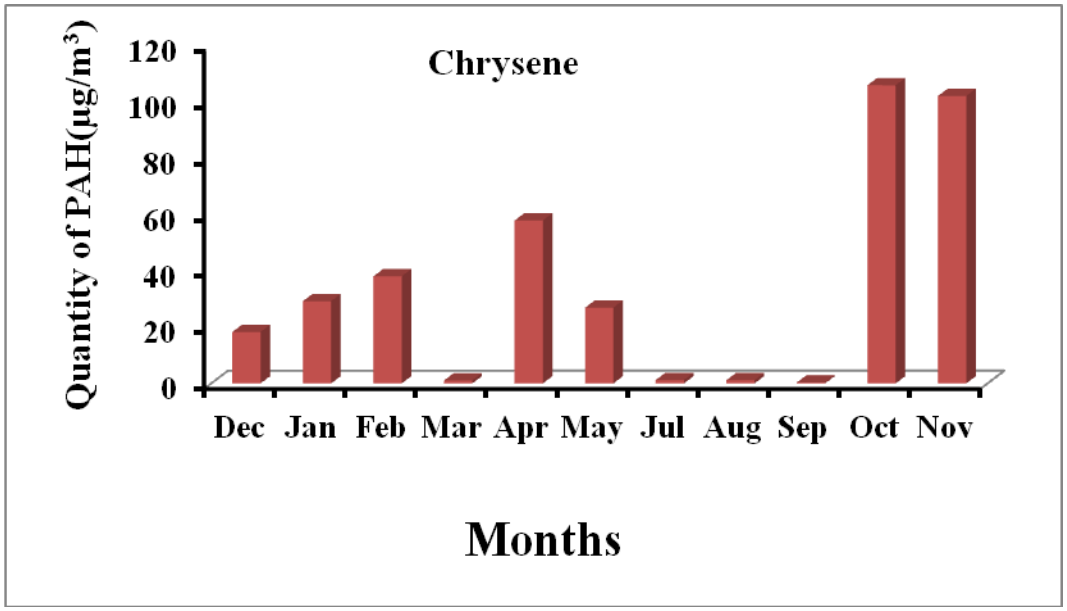


(b)

Figure 4.2 (a) and (b): Benzo(a)anthracene content in ambient air of Thapar University Campus site during Dec 2008-Nov 2009

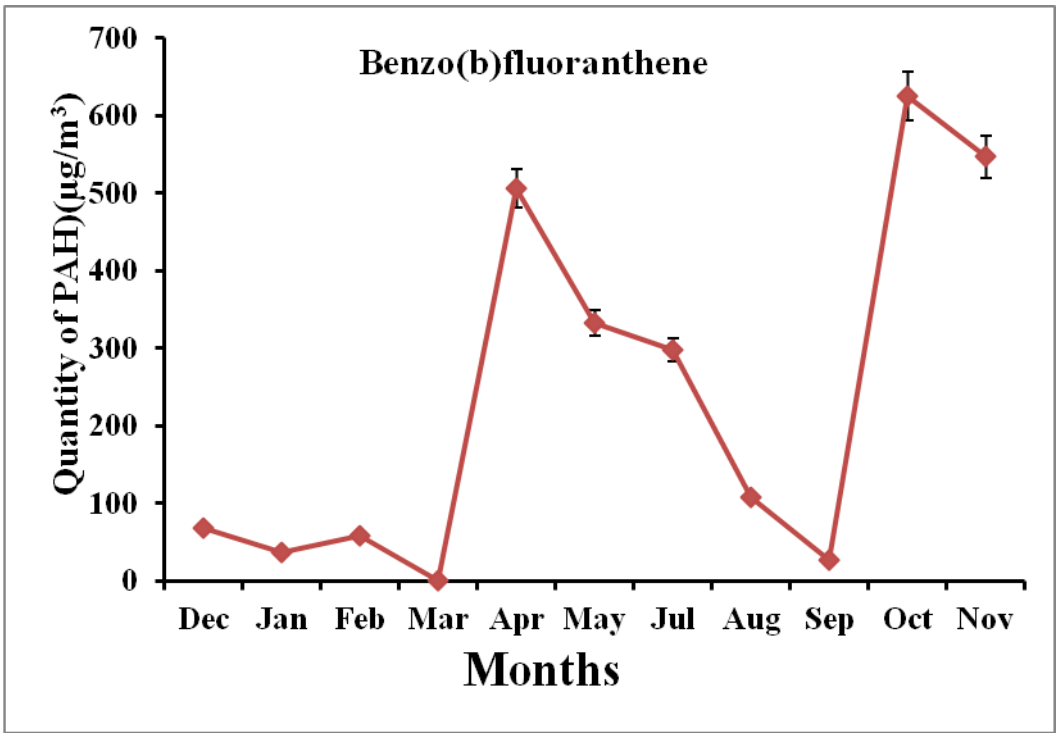


(a)

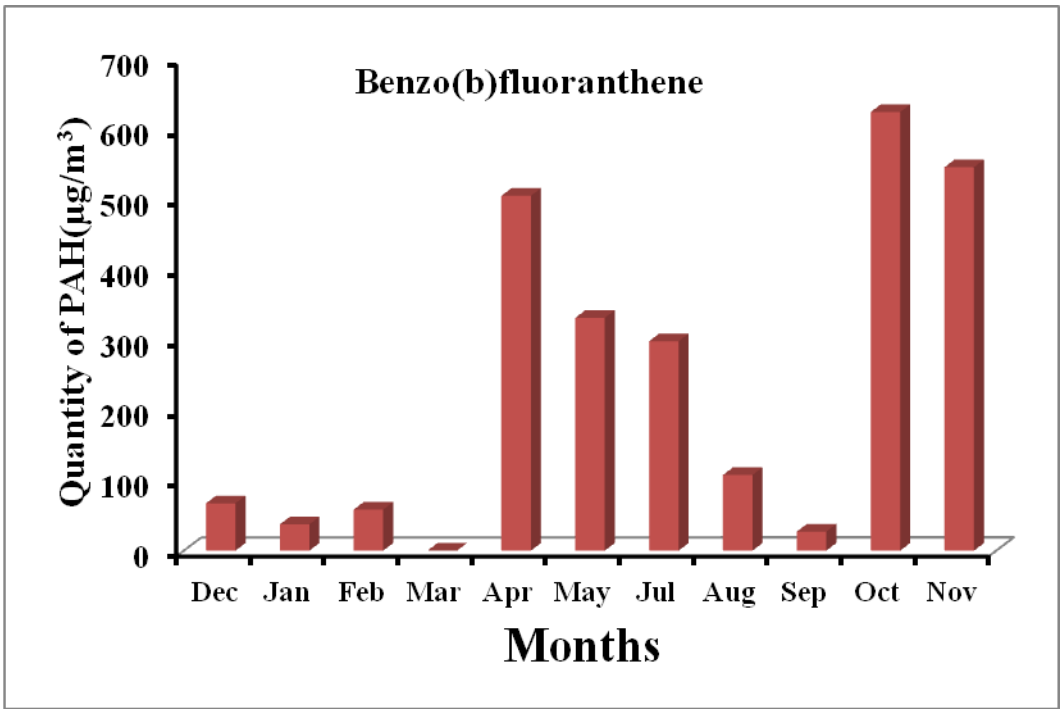


(a)

Figure 4.3 (a) and (b): Chrysene content in ambient air of Thapar University Campus site during Dec 2008-Nov 2009



(a)



(b)

Figure 4.4 (a) and (b): Benzo(b)fluoranthene content in ambient air of Thapar University Campus site during Dec 2008- Nov 2009

The concentration levels of each PAH have been compared with corresponding levels of TSPM. As seen from Figures 4.5 to 4.8 a very good correlation between PAH and TSPM exists. Remarkably high values of PAH1 are seen in the months of April-May when the harvesting followed by burning of crop residue occurs. An exactly similar rise in SPM is also measured. For the similar reason of activities, the concentration levels of both PAH and SPM are exceptionally higher in months of October and November which is also a harvesting period followed by crop residue burning activity for the rice crop season. The above observation is a strong indicator of an intimate correlation between the two parameters i.e., concentration levels of PAH1 and SPM in the ambient air.

Almost similar trends can be seen for other PAHs (i.e. PAH2, PAH3 and PAH4) indicating that field activity of harvesting and crop residue burning are strongly correlated.

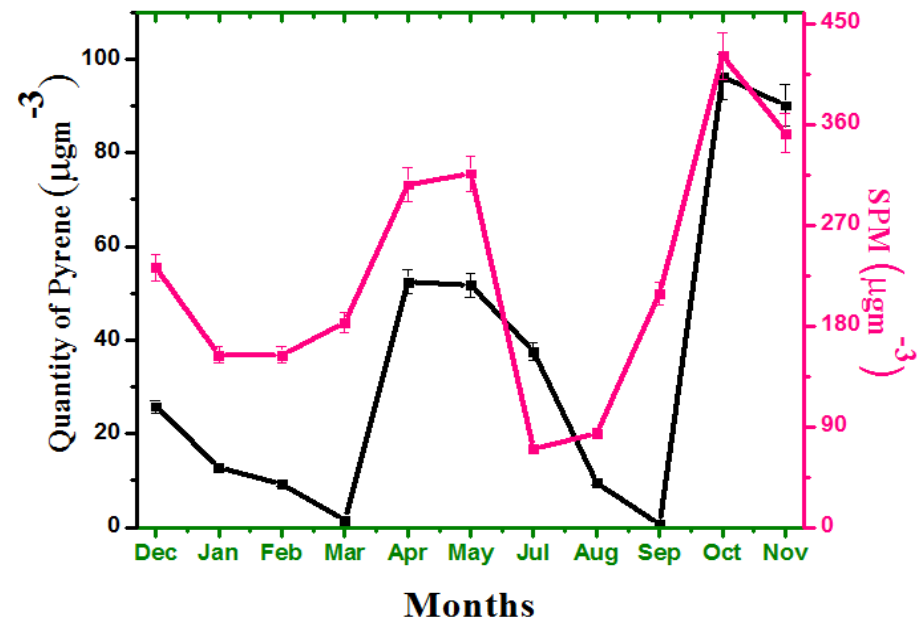


Figure 4.5 Concentration levels of pyrene (PAH1) and suspended particulate matter (SPM) in ambient air of Thapar University Campus site (TUC) over a period of Dec 2008 till Nov 2009

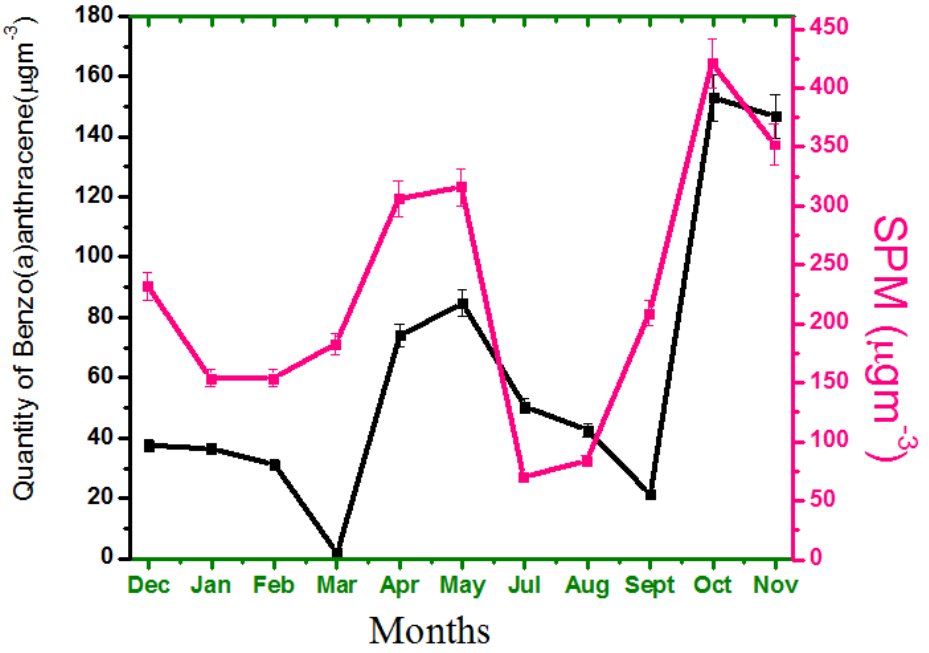


Figure 4.6 Concentration levels of benzo(a)anthracene (PAH2) and suspended particulate matter (SPM) in ambient air of Thapar University Campus site (TUC) over a period of Dec 2008 till Nov 2009

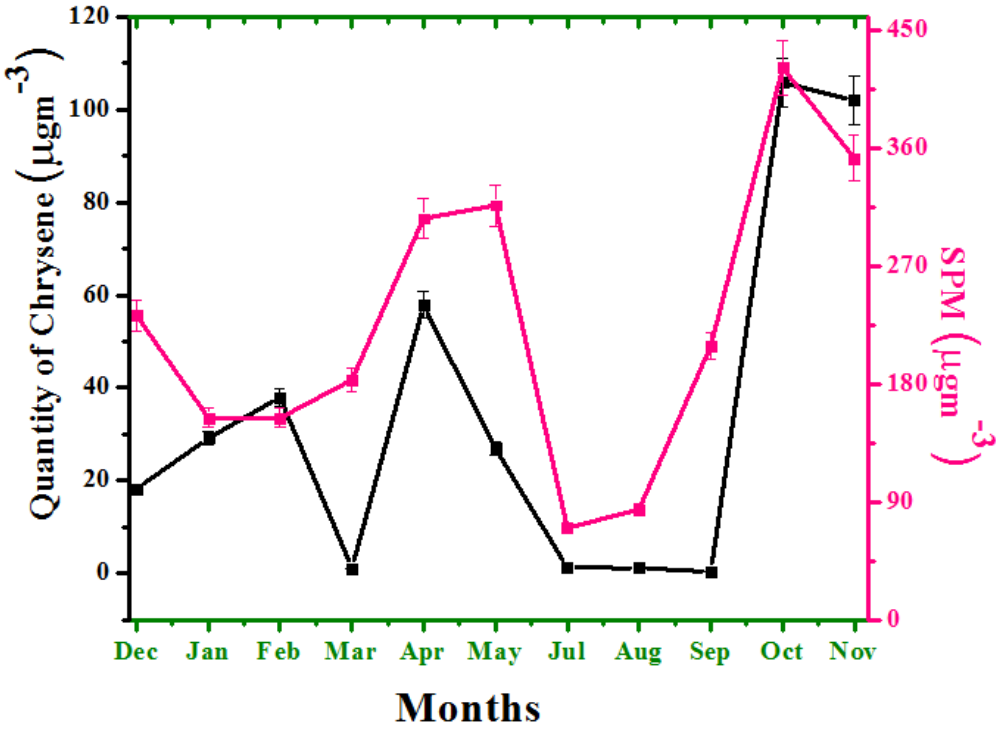


Figure 4.7 Concentration levels of chrysene (PAH3) and suspended particulate matter (SPM) in ambient air of Thapar University site (TUS) over a period of Dec 2008 till Nov 2009

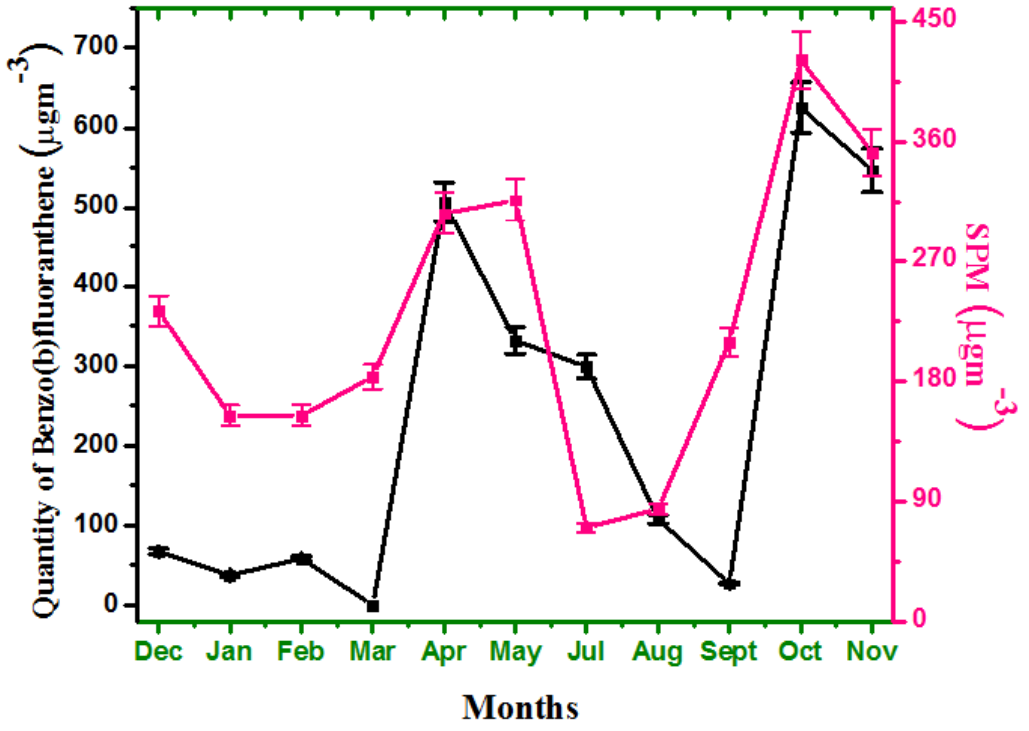


Figure 4.8 Concentration levels of benzo(b)fluoranthene (PAH4) and suspended particulate matter (SPM) in ambient air of Thapar University Campus site (TUC) over a period of Dec 2008 till Nov 2009

Another very important observation can be made from the data that the concentration levels of PAH almost doubled in the month of rice crop season from that of wheat crop season. A seasonal trend was observed for both SPM and the PAH concentration and the concentration of PAH varied inversely with temperature. Hence, the situation of ambient air quality during the months of October and November is much worse than that in the months of April and May. The reason for sharp increase in PAH content in Oct-Nov is that the stubble burning after rice crop harvesting happens at much lower temperature and more humid environment as compared to that in April and May when the dry stubble burns quickly in the peak summer season. Low ambient temperature results in relatively incomplete burning hence leads to more soot formation.

PAHs in SPM samples collected from TUC (semi-urban site) were detected during different sampling months. The concentration levels and the variations are shown in Figures 4.5- 4.8. The maximum concentration of pyrene (155.64μgm^{-3}) was recorded in starting weeks of October and was absent in September.

High quantity of Benzo(a)anthracene (203.48 $\mu g\ m^{-3}$) was observed in month of October and absent in month of September.

The chrysene was found maximum (136 $\mu g\ m^{-3}$) in last weeks of November and a small increase in month of September.

During last weeks of October, the concentration levels of benzo(b)fluoranthene rose at maximum level of 984.25 $\mu g\ m^{-3}$ and was absent in month of February.

There was a distinct increase in the concentration levels of benzo(b)fluoranthene throughout the course of the study.

Correlations analysis was performed to determine relationships between individual PAH and to hypothesize probable sources on the assumption that two or more components may correlate either due to common origin or atmospheric behavior. Correlations between individual PAH were determined by the SPSS software (version 9.0). Concentration levels of TPAH and TSPM have been correlated separately for each of four identified PAHs in Table 4.2.

Table 4.2 Correlations of SPM and PAHs in terms of correlation coefficients(r)

S.No	Months	PAH1	PAH2	PAH3	PAH4
1	May	0.79	0.79	0.17	0.74
2	November	1.00	1.00	1.00	1.00

PAH1=Pyrene PAH2=Benzo(a)anthracene
PAH3=Chrysene PAH4= Benzo(b)fluoranthene

Correlations calculated for the month of May indicate strong correlation for PAH1, PAH2 and PAH4 while less correlated for PAH3. The correlations between the two variables (concentration of PAH and SPM) for the month of November indicate perfect value of 1 for all the PAHs. For the non burning months of wheat crop season the correlations do not follow any pattern and are either negative or positive with lot of variable values. However, during the non burning months of July till September the correlations are either -1 or +1 again indicating an irregular pattern of relationship between the PAH and the SPM concentration levels.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

On the basis of discussions in the preceding chapters, the following salient findings emerged from the present study:

During the study period, the four PAHs were identified prominently, namely pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene , on the basis of their occurrence in the sample analyzed.

Monthly average concentration of SPM and PAH indicate a clear increase during crop residue burning months.

There was a distinct increase in the concentration levels of benzo(b)fluoranthene throughout the course of the study.

Positive correlation was observed between SPM and PAH concentration during burning months i.e. May and November.

Future Scope of Research

Crop residue burning in NW India is a challenging issue linking research disciplines such as sociology, economics, atmospheric science, epidemiology, agriculture, and engineering. To fully understand air quality in Punjab and the best strategies for its improvement, continuing research is needed in each of these areas. A mathematical treatment of the data should be done to formulate models for the prediction of concentration levels of criteria pollutants as a function of the harvesting area undergoing CRB practices. Analysis of SPM samples targeting large number of metals and organic compounds (specially PAH), would better improve understanding of the state of particulate pollution and its associated impacts on human health.

REFERENCES

Aamot, E., Steinnes, E., & Schmid, R. (1996). Polycyclic aromatic hydrocarbons in Norwegian forest soils: impact of long range atmospheric transport. *Environmental Pollution*, *92*(3), 275-280.

Abas, M. R., Simoneit, B. R., Elias, V., Cabral, J. A., & Cardoso, J. N. (1995). Composition of higher molecular weight organic matter in smoke aerosol from biomass combustion in Amazonia. *Chemosphere*, *30*(5), 995-1015.

Aggarwal, A. L., Raiyani, C. V., Patel, P. D., Shah, P. G., & Chatterjee, S. K. (1982). Assessment of exposure to benzo (a) pyrene in air for various population groups in Ahmedabad. *Atmospheric Environment (1967)*, *16*(4), 867-870.

Awasthi, A., Agarwal, R., Mittal, S. K., Singh, N., Singh, K., & Gupta, P. K. (2011). Study of size and mass distribution of particulate matter due to crop residue burning with seasonal variation in rural area of Punjab, India. *Journal of Environmental Monitoring*, *13*(4), 1073-1081.

Baek, S. O., Field, R. A., Goldstone, M. E., Kirk, P. W., Lester, J. N., & Perry, R. (1991). A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior. *Water, air, and soil pollution*, *60*(3-4), 279-300.

Baek, S. O., Choi, J. S., & Hwang, S. M. (1997). A quantitative estimation of source contributions to the concentrations of atmospheric suspended particulate matter in urban, suburban, and industrial areas of Korea. *Environment International*, *23*(2), 205-213.

Basheer, C., Balasubramanian, R., & Lee, H. K. (2003). Determination of organic micropollutants in rainwater using hollow fiber membrane/liquid-phase microextraction combined with gas chromatography–mass spectrometry. *Journal of Chromatography A*, *1016*(1), 11-20.

Bhargava, A., Khanna, R. N., Bhargava, S. K., & Kumar, S. (2004). Exposure risk to carcinogenic PAHs in indoor-air during biomass combustion whilst cooking in rural India. *Atmospheric Environment*, *38*(28), 4761-4767.

Callén, M. S., López, J. M., Iturmendi, A., & Mastral, A. M. (2013). Nature and sources of particle associated polycyclic aromatic hydrocarbons (PAH) in the atmospheric environment of an urban area. *Environmental Pollution*, *183*, 166-174.

Caricchia, A. M., Chiavarini, S., & Pezza, M. (1999). Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples (Italy). *Atmospheric Environment*, *33*(23), 3731-3738.

"Chemistry, Emission Control, Radioactive Pollution and Indoor Air Quality", book edited by Nicolas Mazzeo, ISBN 978-953-307-316-3, Published: July 27, 2011

Chiu, J. C., Shen, Y. H., Li, H. W., Chang, S. S., Wang, L. C., & Chang-Chien, G. P. (2011). Effect of biomass open burning on particulate matter and polycyclic aromatic hydrocarbon concentration levels and PAH dry deposition in ambient air. *Journal of Environmental Science and Health, Part A*, *46*(2), 188-197.

Ciaccio, L. L., Rubino, R. L., & Flores, J. (1974). Composition of organic constituents in breathable airborne particulate matter near a highway. *Environmental Science & Technology*, *8*(10), 935-942.

Chuesaard, T., Chetiyanukornkul, T., Kameda, T., Hayakawa, K., & Toriba, A. (2014). Influence of Biomass Burning on the Levels of Atmospheric Polycyclic Aromatic Hydrocarbons and Their Nitro Derivatives in Chiang Mai, Thailand. *Aerosol and Air Quality Research*, *14*, 1247-1257.

Coleman, P. J., Lee, R. G., Alcock, R. E., & Jones, K. C. (1997). Observations on PAH, PCB, and PCDD/F trends in UK urban air, 1991-1995. *Environmental Science & Technology*, *31*(7), 2120-2124.

Daisey, J. M., Cheney, J. L., & Lioy, P. J. (1986). Profiles of organic particulate emissions from air pollution sources: status and needs for receptor source apportionment modeling. *Journal of the Air Pollution Control Association*, *36*(1), 17-33.

Demir, S., Saral, A., Ertürk, F., & Kuzu, L. (2010). Combined use of principal component analysis (PCA) and chemical mass balance (CMB) for source identification and source apportionment in air pollution modeling studies. *Water, Air, & Soil Pollution*, *212*(1-4), 429-439.

Dennis, A., Fraser, M., Anderson, S., & Allen, D. (2002). Air pollutant emissions associated with forest, grassland, and agricultural burning in Texas. *Atmospheric Environment*, *36*(23), 3779-3792.

Duan, F., Liu, X., Yu, T., & Cachier, H. (2004). Identification and estimate of biomass burning contribution to the urban aerosol organic carbon concentrations in Beijing. *Atmospheric Environment*, *38*(9), 1275-1282.

Doğan, G., Anastasopoulos, A., & Karman, D. (2010) "Source Apportionment of Polycyclic Aromatic Hydrocarbons at Rural Sites of Ontario Canada."(2010).

ESMAP project report, 2011, Review of Top-down SourceApportionment Techniques and Their Application in Developing Countries. Todd M. Johnson, Sarath Guttikunda, Gary J. Wells, Paulo Artaxo, Tami C. Bond.

Fang, M., Zheng, M., Wang, F., To, K. L., Jaafar, A. B., & Tong, S. L. (1999). The solvent-extractable organic compounds in the Indonesia biomass burning aerosols–characterization studies. *Atmospheric Environment*, *33*(5), 783-795.

Fartas, F. M., Othman, M. R., & Latif, M. T. (2009). Qualitative Analysis of Dominant Organic Compounds in PM and Burning Residue of Selected Plants. *Research Journal of Agriculture and Biological Sciences*, *5*(4), 452-457.

Freeman, D. J., & Cattell, F. C. (1990). Woodburning as a source of atmospheric polycyclic aromatic hydrocarbons. *Environmental Science & Technology*, *24*(10), 1581-1585.

Garban, B., Blanchoud, H., Motelay-Massei, A., Chevreuil, M., & Ollivon, D. (2002). Atmospheric bulk deposition of PAHs onto France: trends from urban to remote sites. *Atmospheric Environment*, *36*(34), 5395-5403.

Gardner, B., Hewitt, C. N., & Jones, K. C. (1995). PAHs in air adjacent to two inland water bodies. *Environmental science & technology*, *29*(9), 2405-2413.

Gevao, B., Hamilton-Taylor, J., & Jones, K. C. (2000). Towards a complete mass balance and model for PCBs and PAHs in a small rural lake, Cumbria UK. *Limnology and oceanography*, *45*(4), 881-894.

Gogou, A., Stratigakis, N., Kanakidou, M., & Stephanou, E. G. (1996). Organic aerosols in Eastern Mediterranean: components source reconciliation by using molecular markers and atmospheric back trajectories. *Organic Geochemistry*, *25*(1), 79-96.

Grosjean, D. (1975). Solvent extraction and organic carbon determination in atmospheric particulate matter. Organic extraction-organic carbon analyzer (OE-OCA) technique. *Analytical chemistry*, *47*(6), 797-805.

Guo, H., Lee, S. C., Ho, K. F., Wang, X. M., & Zou, S. C. (2003). Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmospheric Environment*, *37*(38), 5307-5317.

Gugamsetty, B., Wei, H., Liu, C. N., Awasthi, A., Hsu, S. C., Tsai, C. J., ... & Chen, C. F. (2012). Source characterization and apportionment of PM10, PM2. 5 and PM0. 1 by using positive matrix factorization. *Aerosol Air Qual. Res*, *12*, 476-491.

Harrison, R. M., Smith, D. J. T., & Luhana, L. (1996). Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. *Environmental Science & Technology*, *30*(3), 825-832.

Halsall, C. J., Sweetman, A. J., Barrie, L. A., & Jones, K. C. (2001). Modelling the behaviour of PAHs during atmospheric transport from the UK to the Arctic. *Atmospheric environment*, *35*(2), 255-267.

Hays, M. D., Smith, N. D., Kinsey, J., Dong, Y., & Kariher, P. (2003). Polycyclic aromatic hydrocarbon size distributions in aerosols from appliances of residential wood combustion as determined by direct thermal desorption—GC/MS. *Journal of Aerosol Science*, *34*(8), 1061-1084.

He, J., Zielinska, B., & Balasubramanian, R. (2010). Composition of semi-volatile organic compounds in the urban atmosphere of Singapore: influence of biomass burning. *Atmospheric Chemistry and Physics*, *10*(23), 11401-11413.

Jain, N., Bhatia, A., & Pathak, H. (2014). Emission of Air Pollutants from Crop Residue Burning in India. *Aerosol and Air Quality Research*, *14*(1), 422-430.

Jacobson, M. C., Hansson, H. C., Noone, K. J., & Charlson, R. J. (2000). Organic atmospheric aerosols: Review and state of the science. *Reviews of Geophysics*, *38*(2), 267-294.

Jacobson, M. Z. (2001). Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature*, *409*(6821), 695-697.

Jamhari, A. A., Sahani, M., Latif, M. T., Chan, K. M., Tan, H. S., Khan, M. F., & Mohd Tahir, N. (2014). Concentration and source identification of polycyclic aromatic hydrocarbons (PAHs) in PM< sub> 10</sub> of urban, industrial and semi-urban areas in Malaysia. *Atmospheric Environment*, *86*, 16-27.

Jenkins, B. M., Jones, A. D., Turn, S. Q., & Williams, R. B. (1996). Emission factors for polycyclic aromatic hydrocarbons from biomass burning. *Environmental Science & Technology*, *30*(8), 2462-2469.

Kallenborn, R., Oehme, M., Wynn-Williams, D. D., Schlabach, M., & Harris, J. (1998). Ambient air levels and atmospheric long-range transport of persistent organochlorines to Signy Island, Antarctica. *Science of the Total Environment*, *220*(2), 167-180.

Kanabkaew, T., & Oanh, N. T. K. (2011). Development of spatial and temporal emission inventory for crop residue field burning. *Environmental Modeling & Assessment*, *16*(5), 453-464.

Kaur, S., Senthilkumar, K., Verma, V. K., Kumar, B., Kumar, S., Katnoria, J. K., & Sharma, C. S. (2013). Preliminary Analysis of Polycyclic Aromatic Hydrocarbons in Air Particles

(PM10) in Amritsar, India: Sources, Apportionment, and Possible Risk Implications to Humans. *Archives of environmental contamination and toxicology*, *65*(3), 382-395.

Khalili, N. R., Scheff, P. A., & Holsen, T. M. (1995). PAH source fingerprints for coke ovens, diesel and, gasoline engines, highway tunnels, and wood combustion emissions. *Atmospheric Environment*, *29*(4), 533-542.

Kim Oanh, N. T., Ly, B. T., Tipayarom, D., Manandhar, B. R., Prapat, P., Simpson, C. D., & Sally Liu, L. J. (2011). Characterization of particulate matter emission from open burning of rice straw. *Atmospheric Environment*, *45*(2), 493-502.

Kulkarni, P., & Venkataraman, C. (2000). Atmospheric polycyclic aromatic hydrocarbons in Mumbai, India. *Atmospheric Environment*, *34*(17), 2785-2790.

Lai, C. H., Li, H. C., & Chen, K. S. (2009). Source characterization and environment impact of open burning of rice straw residues on polycyclic aromatic hydrocarbons in agricultural county, Taiwan. *J. Environ. Eng. Manage*, *19*(2), 79-88.

Larkin, S. B. C., Lee, M., McInnes, G., Sharp, M., & Simmonds, A. C. (1985). *Measurement of air pollution and other factors relating to the practice of straw and stubble burning* (No. PB-86-182086/XAB; LR-18 (AP) M). Warren Spring Lab., Stevenage (UK).

Lee, J. Y., & Kim, Y. P. (2007). Source apportionment of the particulate PAHs at Seoul, Korea: impact of long range transport to a megacity. *Atmospheric Chemistry and Physics*, *7*(13), 3587-3596.

Lemieux, P. M., Lutes, C. C., & Santoianni, D. A. (2004). Emissions of organic air toxics from open burning: a comprehensive review. *Progress in energy and combustion science*, *30*(1), 1-32.

Li, J., Zhang, G., Li, X. D., Qi, S. H., Liu, G. Q., & Peng, X. Z. (2006). Source seasonality of polycyclic aromatic hydrocarbons (PAHs) in a subtropical city, Guangzhou, South China. *Science of the Total Environment*, *355*(1), 145-155.

Li, C. K., & Kamens, R. M. (1993). The use of polycyclic aromatic hydrocarbons as source signatures in receptor modeling. *Atmospheric Environment. Part A. General Topics*, *27*(4), 523-532.

LIU, L. B., LIU, Y., LIN, J. M., TANG, N., HAYAKAWA, K., & MAEDA, T. (2007). Development of analytical methods for polycyclic aromatic hydrocarbons (PAHs) in airborne particulates: A review. *Journal of Environmental Sciences*, *19*(1), 1-11.

Mader, P. P., MacPhee, R. D., Lofberg, R. T., & Larson, G. P. (1952). Composition of organic portion of atmospheric aerosols in the Los Angeles area. *Industrial & Engineering Chemistry*, *44*(6), 1352-1355.

Mandalakis, M., Gustafsson, Ö., Alsberg, T., Egebäck, A. L., Reddy, C. M., Xu, L., ... & Stephanou, E. G. (2005). Contribution of biomass burning to atmospheric polycyclic aromatic hydrocarbons at three European background sites. *Environmental science & technology*, *39*(9), 2976-2982.

Marr, L. C., Kirchstetter, T. W., Harley, R. A., Miguel, A. H., Hering, S. V., & Hammond, S. K. (1999). Characterization of polycyclic aromatic hydrocarbons in motor vehicle fuels and exhaust emissions. *Environmental science & technology*, *33*(18), 3091-3099.

Mazzoleni, L. R., Zielinska, B., & Moosmüller, H. (2007). Emissions of levoglucosan, methoxy phenols, and organic acids from prescribed burns, laboratory combustion of wildland fuels, and residential wood combustion. *Environmental science & technology*, *41*(7), 2115-2122.

Menichini, E., Monfredini, F., & Merli, F. (1999). The temporal variability of the profile of carcinogenic polycyclic aromatic hydrocarbons in urban air: a study in a medium traffic area in Rome, 1993–1998. *Atmospheric Environment*, *33*(23), 3739-3750.

Migaszewski Z. M. 1999. Determining organic compound ratios in soils and vegetation of the Holy Cross MTS, Poland. *Water, Air Soil Poll.* **III**, 123-138.

Mittal, S. K., Singh, N., Agarwal, R., Awasthi, A., & Gupta, P. K. (2009). Ambient air quality during wheat and rice crop stubble burning episodes in Patiala. *Atmospheric Environment*, *43*(2), 238-244.

Mohan Rao, A. M., Rajgopalan, R., Doshi, M. H., & Vohra, K. G. (1983). Measurement of benzo (a) pyrene in the ambient air for estimation of carcinogenic risk. *Sci. Total Environ*, *27*, 33-42.

Nagarajappa, D. P., Muttagi, S. G., Lokeshappa, B., & Dikshit, A. K. (2012). Study on Evaluvation of Benzo (a) Pyrene Soluble Fraction in Respirable Suspended Particulate Matter in Peenya Industrial Area by GCMS. *American Journal of Environmental Engineering*, *2*(6), 182-187.

Omar, N. Y. M., Abas, M. R. B. A., Ketuly, K. A., & Tahir, N. M. (2002). Concentrations of PAHs in atmospheric particles (PM-10) and roadside soil particles collected in Kuala Lumpur, Malaysia. *Atmospheric Environment*, *36*(2), 247-254.

Poster, D. L., Schantz, M. M., Sander, L. C., & Wise, S. A. (2006). Analysis of polycyclic aromatic hydrocarbons (PAHs) in environmental samples: a critical review of gas chromatographic (GC) methods. *Analytical and bioanalytical chemistry*, *386*(4), 859-881.

Raiyani, C. V., Jani, J. P., Desai, N. M., Shah, S. H., Shah, P. G., & Kashyap, S. K. (1993). Assessment of indoor exposure to polycyclic aromatic hydrocarbons for urban poor using various types of cooking fuels. *Bulletin of environmental contamination and toxicology*, *50*(5), 757-763.

Rajput, N., & Lakhani, A. (2010). Measurements of polycyclic aromatic hydrocarbons in an urban atmosphere of Agra, India. *Atmosfera*, *23*(2), 165-183.

Rajput, P., Sarin, M., & Rengarajan, R. (2011). High-precision GC-MS analysis of atmospheric polycyclic aromatic hydrocarbons (PAHs) and isomer ratios from biomass burning emissions. *Journal of Environmental Protection*, *2*(04), 445.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., & Simoneit, B. R. (1993). Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environmental science & technology*, *27*(4), 636-651.

Sahai, S., Sharma, C., Singh, D. P., Dixit, C. K., Singh, N., Sharma, P., & Gupta, P. K. (2007). A study for development of emission factors for trace gases and carbonaceous particulate species from in situ burning of wheat straw in agricultural fields in India. *Atmospheric Environment*, *41*(39), 9173-9186.

Sahai, S., Sharma, C., Singh, S. K., & Gupta, P. K. (2010). Ambient CO levels during winter and summer agricultural burning seasons of Northern India. *Asian Journal of Water, Environment and Pollution*, *7*(4), 99-104.

Samal, A. C., & Santra, S. C. (2002). Air quality of Kalyani township (Nadia, West Bengal) and its impact on surrounding vegetation. *Indian Journal of environmental health*, *44*(1), 71-76.

Sandhu, R. S., & Gehlan, M. S. (1991). Determination of combustible and organic tarry matter proportions of the suspended particulate matter in the ambient air of Amritsar. *Indian Journal of Environmental Protection*, *11*(12), 895-898.

Sandhu, R. S., & Gehlan, M. S. (1992). Estimation of some metals in the ambient air of Amritsar. *Indian Journal of Environmental Protection*, *12*, 733-733.

Sanderson, E. G., Raqbi, A., Vyskocil, A., & Farant, J. P. (2004). Comparison of particulate polycyclic aromatic hydrocarbon profiles in different regions of Canada. *Atmospheric Environment*, *38*(21), 3417-3429.

Schauer, J. J., & Cass, G. R. (2000). Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. *Environmental science & technology*, *34*(9), 1821-1832.

Schauer, J. J., Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., & Simoneit, B. R. (1996). Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmospheric Environment*, *30*(22), 3837-3855.

Seng, T. H., Tahir, N. M., & Abas, M. R. (2007). Aliphatic and PAHs emissions from open burning of selected tropical woods. *Malaysian J Anal Sci* 11 (2007): 36-41.

Shankar R. V., 1990. Characterization of atmospheric polynuclear aromatic hydrocarbons with special reference to automobile exhaust PhD Thesis. New Delhi, Jawaharlal Nehru University. 112 pp.

Shen, G., Wang, W., Yang, Y., Ding, J., Xue, M., Min, Y., ... & Russell, A. G. (2011). Emissions of PAHs from Indoor Crop Residue Burning in a Typical Rural Stove: Emission Factors, Size Distributions, and Gas− Particle Partitioning. *Environmental science & technology*, *45*(4), 1206-1212.

Shen, G., Wang, W., Yang, Y., Zhu, C., Min, Y., Xue, M., ... & Tao, S. (2010). Emission factors and particulate matter size distribution of polycyclic aromatic hydrocarbons from residential coal combustions in rural Northern China. *Atmospheric Environment*, *44*(39), 5237-5243.

Simoneit, B. R., Sheng, G., Chen, X., Fu, J., Zhang, J., & Xu, Y. (1991). Molecular marker study of extractable organic matter in aerosols from urban areas of China. *Atmospheric Environment. Part A. General Topics*, *25*(10), 2111-2129.

Simcik, M. F., Zhang, H., Eisenreich, S. J., & Franz, T. P. (1997). Urban contamination of the Chicago/coastal Lake Michigan atmosphere by PCBs and PAHs during AEOLOS. *Environmental science & technology*, *31*(7), 2141-2147.

Singh, N., Mittal, S. K., Agarwal, R., Awasthi, A., & Gupta, P. K. (2010). Impact of rice crop residue burning on levels of SPM, SO2 and NO2 in the ambient air of Patiala (India). *International Journal of Environmental and Analytical Chemistry*, *90*(10), 829-843.

Singh, D. P., Gadi, R., Mandal, T. K., Saud, T., Saxena, M., & Sharma, S. K. (2013). Emissions estimates of PAH from biomass fuels used in rural sector of Indo-Gangetic Plains of India. *Atmospheric Environment*, *68*, 120-126.

Singh, N., Mittal, S., Singh, R., Agarwal, R., Awasthi, A., & Gupta, P. K. (2014). Potassium as a Marker in Air Particulate Matter After Crop Residue Burning Events in Patiala, India.

Singh, K. P., Malik, A., Kumar, R., Saxena, P., & Sinha, S. (2008). Receptor modeling for source apportionment of polycyclic aromatic hydrocarbons in urban atmosphere. *Environmental monitoring and assessment*, *136*(1-3), 183-196.

Stephanou, E. G., & Stratigakis, N. E. (1993). Determination of anthropogenic and biogenic organic compounds on airborne particles: flash chromatographic fractionation and capillary gas chromatographic analysis. *Journal of Chromatography A*, *644*(1), 141-151.

Tavares Jr, M., Pinto, J. P., Souza, A. L., Scarmínio, I. S., & Cristina Solci, M. (2004). Emission of polycyclic aromatic hydrocarbons from diesel engine in a bus station, Londrina, Brazil. *Atmospheric Environment*, *38*(30), 5039-5044.

Tsapakis, M., & Stephanou, E. G. (2005). Occurrence of gaseous and particulate polycyclic aromatic hydrocarbons in the urban atmosphere: study of sources and ambient temperature effect on the gas/particle concentration and distribution. *Environmental Pollution*, *133*(1), 147-156.

Tripathi, S., Singh, R N., & Sharma, S. (2013). Emissions from Crop/Biomass Residue Burning Risk to Atmospheric Quality."

Vaishali, R.., Phadke, K. M., Thakre, R., & Hasan, M. Z. (1997). PAHs in respirable particulate matter of Nagpur city air. *J. Indian Assoc. Environ. Manag.* **24**, 11.

Venkataraman, C., Lyons, J. M., & Friedlander, S. K. (1994). Size distributions of polycyclic aromatic hydrocarbons and elemental carbon. 1. Sampling, measurement methods, and source characterization. *Environmental science & technology*, *28*(4), 555-562.

Wang, H., Zhuang, Y., Hao, Z., Cao, M., Zhong, J., Wang, X., & Nguyen, T. K. O. (2008). Polycyclic aromatic hydrocarbons from rural household biomass burning in a typical Chinese village. *Science in China Series D: Earth Sciences*, *51*(7), 1013-1020.

Wang, Q., Shao, M., Liu, Y., William, K., Paul, G., Li, X., ... & Lu, S. (2007). Impact of biomass burning on urban air quality estimated by organic tracers: Guangzhou and Beijing as cases. *Atmospheric Environment*, *41*(37), 8380-8390.

Wang, Z., Bi, X., Sheng, G., & Fu, J. (2009). Characterization of organic compounds and molecular tracers from biomass burning smoke in South China I: broad-leaf trees and shrubs. *Atmospheric Environment*, *43*(19), 3096-3102.

Wild, S. R., & Jones, K. C. (1995). Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget. *Environmental pollution*, *88*(1), 91-108.

Williamson, S. J. (1973). Fundamentals of air pollution. In *Fundamentals of air pollution*. Addison-Wesley.

Wiedinmyer, C., Quayle, B., Geron, C., Belote, A., McKenzie, D., Zhang, X., & Wynne, K. K. (2006). Estimating emissions from fires in North America for air quality modeling. *Atmospheric Environment*, *40*(19), 3419-3432.

www.qld.gov.au/environment/pollution/monitoring/air-pollution/samplers/

www.teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gaschrm.htm

www.pirika.com/NewHP/PirikaE/PAHs.html

Yang, D., Qi, S., Devi, N. L., Tian, F., Huo, Z., Zhu, Q., & Wang, J. (2012). Characterization of polycyclic aromatic hydrocarbons in PM2. 5 and PM10 in Tanggu District, Tianjin Binhai New Area, China. *Frontiers of Earth Science*, *6*(3), 324-330.

Zhang, Y., & Tao, S. (2009). Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. *Atmospheric Environment*, *43*(4), 812-819.

Zhang, Y., & Tao, S. (2008). Seasonal variation of polycyclic aromatic hydrocarbons (PAHs) emissions in China. *Environmental pollution*, *156*(3), 657-663

***