

**MONITORING OF AMBIENT AIR QUALITY OF
PATIALA CITY WITH SPECIAL REFERENCE TO
CROP RESIDUE BURNING**

(PhD Thesis)

By

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MONITORING OF AMBIENT AIR QUALITY OF PATIALA CITY WITH SPECIAL REFERENCE TO CROP RESIDUE BURNING

**A thesis submitted in fulfillment of the requirements
for the award of the degree of**

DOCTOR OF PHILOSOPHY

**in
CHEMISTRY**

**by
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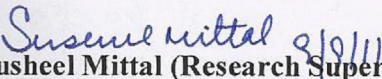
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Patiala (Punjab), India**

2011

CERTIFICATE

This is to certify that the thesis entitled “**Monitoring of Ambient Air Quality of Patiala City with special reference to Crop Residue Burning**”, being submitted by Mr. Nirankar Singh in fulfillment of the requirement for the award of degree of Doctor of Philosophy in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonafide work carried out by him during March 2006 to January 2011 under the supervision of Dr. Susheel Mittal, Senior Professor & Head, School of Chemistry & Biochemistry, Thapar University, Patiala and Mr. Prabhat Kumar Gupta, Scientist ‘G’ and Head, Analytical Chemistry Division, National Physical Laboratory, New Delhi, India.

To the best of our knowledge, the work presented in this thesis is an original contribution and has not been submitted either in partial or full to any other University or Institute for the award of any degree.

 Dr. Susheel Mittal (Research Supervisor) Senior Professor & Head, School of Chemistry & Biochemistry, Thapar University, Patiala, India	 Mr. Prabhat K. Gupta (Research Supervisor) Scientist G & Head, Analytical Chemistry Division, National Physical Laboratory (CSIR), New Delhi, India
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DECLARATION

I hereby declare that the work being presented in the thesis entitled “Monitoring of Ambient Air Quality of Patiala City with special reference to Crop Residue Burning”, in fulfillment of the requirements for the award of the degree of Doctor of Philosophy in Chemistry at School of Chemistry and Biochemistry, Thapar University, Patiala, is my own authenticated work carried out by me during the period of March 2006 to January 2011, under the supervision of Senior Professor (Dr.) Susheel Mittal, Head, School of Chemistry & Biochemistry, Thapar University, Patiala and Mr. Prabhat K. Gupta, Scientist G & Head, Analytical Chemistry Division, National Physical Laboratory, New Delhi, India. I have not submitted the matter embodied in this thesis anywhere for the award of any other degree.

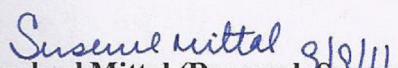
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(NIRANKAR SINGH)

This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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***“Put your heart, mind, intellect and soul even to your smallest acts.
This is the secret of success”.***

-Swami Sivananda

“In the name of GOD-The most gracious, most merciful”

Dedicated to My Parents

***Whose blessings are a great source of strength
in me in every noble endeavor***



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ABBREVIATIONS

AAS	Atomic absorption spectrophotometer
AWiFS	Advanced Wide Field sensor
BkF	Benzo (k) fluoranthene
CARB	California Air Resource Board
COPD	Chronic obstructive pulmonary disease
CPCB	Central Pollution Control Board
CRB	Crop Residue Burning
DCM	Di-chloro methane
EFs	Emission Factors
FID	Flame Ionization Detector
GC	Gas Chromatography
GHG	Green House Gases
HVS	High Volume Sampler
IGP	Indo-Gangetic Plains
INDOEX	Indian Ocean Experiment
LOI	Loss on Ignition
MAS	Military Area Site
NAAQS	National Ambient Air Quality Standards
NCRB	Non Crop Residue Burning
NO _x	Oxides of Nitrogen
OC	Organic Carbon
OTM	Organic Tarry Matter
PAH	Polycyclic Aromatic Hydrocarbon
PPCB	Punjab Pollution Control Board
PUS	Punjabi University Site
Pyr	Pyrene
RCRB	Rice Crop Residue Burning
RWCS	Rice-wheat cropping system
SAS	Sanauri Adda Site
SOM	Soil Organic Matter

SO _x	Oxides of Sulphur
SPM	Suspended Particulate Matter
SVOC	Semi Volatile Organic Compounds
SVS	Sidhuwal Village Site
TCM	Tetra-chloro mercurate
TUS	Thapar University Site
USEPA	United State Environmental Protection Agency
VOC	Volatile Organic Compounds
WCRB	Wheat Crop Residue Burning

ABSTRACT

Development of an effective agricultural crop residue management plan in the Northwest region of India has been hindered by the lack of awareness and information about the adverse impact of agricultural residue burning practices on regional ambient air quality. These practices emit SPM and gaseous species into the atmosphere influencing health and materials in the area. Open wheat (*Triticum aestivum*) and rice (*Oriza sativa*) crop stubble burning events are observed in and around Patiala city during April-May and October-November every year. A study involving ground level measurements was conducted to analyze the contribution of wheat and rice crop stubble burning practices on concentration levels of suspended particulate matter (SPM), Oxides of sulphur and nitrogen (SO₂ and NO₂) were monitored in the ambient air at five different sites in and around Patiala city covering agricultural, commercial and residential areas. Aerosol samples were collected on GMF/A and QMF/A (Whatman) sheets using High Volume Sampling (HVS) units for a 24 h period throughout the study period covering four rice and three wheat crop harvesting seasons from 2006-2010. Simultaneously, sampling of SO₂ and NO₂ was conducted and results obtained during stubble burning periods were compared with the non-stubble burning periods. Interesting results were obtained during this course of study. Results pointed out a distinct increase in aerosol, SO₂ and NO₂ levels during the crop stubble burning periods.

Further, SPM samples were analyzed for the determination of organic tarry matter (OTM), loss on ignition (LOI), heavy metals and poly aromatic hydrocarbons (PAHs). Results indicated a clear impact of crop residue burning practices in Northern India. Average levels of LOI pointed to the presence of a high content of combustible matter in the ambient air of Patiala. It has been observed that levels of combustible matter content were associated with the levels of SPM integrated with the effect of crop residue burning (CRB) practices in the region. SPM samples were analyzed for Dichloromethane (DCM) soluble fraction and concentration levels of OTM were observed. Levels of LOI and OTM were also associated with the CRB episodes.

SPM samples were further analyzed for the concentration levels of potassium (K) and some heavy metals like copper (Cu), nickel (Ni) and zinc (Zn) and the results are compared with

the crop residue burning (CRB) and non-crop residue burning (NCRB) months. Significant association was obtained in the ambient air levels of SPM and K. High concentration levels of K was obtained during agricultural burning seasons of wheat and rice crops. Heavy metals like Cu, Ni and Zn were associated with the similar range of concentration but no relationship was obtained with CRB episodes. Although, increase in K levels was observed at all the sites, but a strong association in K levels and CRB was obtained at an agricultural area site only.

Higher concentration levels of polycyclic aromatic hydrocarbons like benzo (k) fluoranthene (45.33 ppm in April 2007) and pyrene (0.58 ppm in November 2007) were also observed during episodic crop residue burning events for the duration of April-May and October-November. Significant increase in the concentration levels of PAHs was obtained at commercial and agricultural area sites. However, the existence of variations could be attributed from factors such as site characteristics, topography of surrounding area, types and frequency of vehicles plying on the roads, types of biomass burned, etc. The meteorological factors such as wind speed and direction, relative humidity, atmospheric pressure and temperature have also influenced the levels and flow of air pollutants in the study area.

CHAPTER 1

INTRODUCTION

CHAPTER-1

INTRODUCTION

The sustaining state of our earth is due to its unique atmosphere and air is one of the imperative things essential for life on the planet. The atmosphere which is a gaseous envelope around the earth is divided into several concentric zones. Troposphere is the lowest region of the atmosphere containing 80% of the total mass of air and almost all of the water vapors. In addition to nitrogen and oxygen which make up about 99% of the atmosphere, there are small amounts of other gases, minute droplets of various liquids and tiny particles of varieties of solids. We breathe various gases and particles in addition to nitrogen and oxygen. When due to some natural processes or human activities the concentration of substances other than oxygen is increased in the air, it causes pollution of the atmosphere. Fresh air means the composition of air in the absence of humans and their works. The air may be best described as dilute polluted air at the most remote locations at the poles, mountains, sea and in the deserts. It is approximately unpolluted air. Air pollution is the degradation in the quality of air contaminants in sufficient quantity which may be injurious to human health or may damage property. The contaminants which degrade the quality of air are known as air pollutants.

Air pollutants can be classified as primary and secondary pollutants. The primary air pollutants are harmful chemicals which enter directly into the air due to natural human activities. Complete burning of any carbon containing substance produces CO_2 , whereas carbon monoxide is produced when burned partially. Another primary air pollutant is SO_2 which is emitted to the air by volcanic eruption or burning of fuels which contain sulphur impurities. A secondary air pollutant is a harmful chemical produced in the air due to chemical reaction between two or more components. That is, primary pollutant combines with some component of the atmosphere to produce a secondary pollutant. For example, SO_2 can convert to SO_3 with a series of reactions involving free radical mechanism ($\text{SO}_2 + \text{OH}^\bullet \rightarrow \text{HOSO}_2^\bullet$; $\text{HOSO}_2^\bullet + \text{O}_2 \rightarrow \text{SO}_3 + \text{OH}^\bullet$) (Gilbert 2007). This SO_3 can react quickly with water vapor in the atmosphere to produce sulphuric acid ($\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$).

These various primary air pollutants can be grouped under five major categories viz., oxides of carbon, oxides of nitrogen, sulphur oxides, hydrocarbons and aerosols.

Air pollution is an important factor of environmental degradation. Release of smoke from chimneys of the industries, biomass burning, burning of fuels like coal, wood as well as the exhausts from automobiles leads to air pollution. In the modern times, rapid industrialization and use of automobiles for transport to cope with the growing demand of the growing human population have become a major source of air pollution.

Advances in science and medicine have led to a greater understanding of the different health effects, including heart disease (Pope et al. 2004, Henneberger et al. 2005) and cancer, which result from products of incomplete combustion. Emissions from the burning of agricultural waste are of particular concern due to the low combustion efficiency of open burning, difficulty in regulation, and the fact that emissions are released at ground level. Large-scale crop residue burning takes place in the North-West region of India during April-May and October-November every year. Burning agricultural waste has long been practiced to prepare land for planting, return nutrients to the soil, increase harvests, and control pests. The pollutants that are released into the atmosphere include carbon monoxide (CO), nitrogen oxides (NO_x), sulfur oxides (SO_x), and particulate matter (PM) consisting primarily of ash, polycyclic aromatic hydrocarbons (PAH), and soot (Radke et al., 1988, Crutzen et al., 1990). PAHs are a class of compounds that form by incomplete combustion of hydrocarbons. They attach themselves to PM, primarily soot, and can enter the body through inhalation, ingestion, or the skin. They are classified by the U.S. Department of Health and Human Services as “reasonably anticipated as human carcinogens” and are found in several known carcinogens such as coke oven emissions, coal tars, and soot. To better characterize the emissions from agricultural burning, field measurements are often made.

Despite global significance of biomass burning still very little quantitative information is available about the emission of some of the harmful chemical compounds. Furthermore, much agricultural waste is being combusted, particularly in developing countries. In order

to obtain more information on the effect of crop residue burning on ambient air quality, global air quality monitoring is needed.

Meteorological parameters like wind speed, wind direction, precipitation, temperature, and humidity were monitored during the study period spread over four years. The overall aim of the present thesis is to contribute to an improved understanding of deterioration of ambient air quality due to crop residue burning activities. The thesis particularly focuses on aerosol and gaseous particles produced during crop residue burning (rice and wheat crop residue burning practices).

1.1 Clean air regulations and criteria air pollutants

Criteria pollutants, as designated under the Clean Air Act of 1970 (U.S.A.), include pollutants that are ubiquitous in the United States and are known or strongly suspected to be harmful to public health and the environment. Currently, six pollutants are designated as criteria pollutants: particles with aerodynamic diameters under 10 and 2.5 micron, ozone, sulfur dioxide, nitrogen dioxide, carbon monoxide, and lead. For each of these pollutants, a primary health-based National Ambient Air Quality Standard (NAAQS) under the Clean Air Act has been established, which sets the "safe" amount of the pollutant that can be present in the air (Prevention and Control of Air Pollution Act, 1981, India; Clean Air Act, 33 United States Code Sec. 1241 Et Esq., 1971). Central Pollution Control Board, New Delhi, India has revised some standards for these criteria pollutants (CPCB, 2009).

The Air (Prevention and Control) Act 1981 was enacted by the Parliament of India under Article 253 of the Constitution to take appropriate steps to prevent and control air pollution and fulfill the proclamation adopted by the United Nations Conference on the Human Environment held in Stockholm in June 1972. The main functions of Central Pollution Control Board (CPCB), New Delhi, India as per the Air Act are to improve the quality of air and to prevent, control or abate air pollution in the country.

1.1.1 Oxides of Sulphur (SO_x)

Fossil fuels burned in petroleum refineries, pulp and paper mills, steel mills, electricity generating plants, including coal-fired power plants, non-iron ore smelters, diesel vehicles, volcanoes and hot springs are the major sources of SO_x. Constant exposure inhalation of this gas causes acute respiratory problems and headache. This gas can easily get into plants through their stomata and continuous exposure causes leaf blotching, necrosis and loss of yield. Sulphur dioxide is one of the main ingredients in acid rain. SO₂ creates irritation in nose and throat, breathing problems, lung disease, worsening symptoms in people with asthma, chronic obstructive pulmonary disease (COPD), and other long-term lung diseases, worsening cardiovascular (heart) disease and changes in the lungs natural defense.

1.1.2 Oxides of Nitrogen (NO_x)

Burning fossil fuels in motor vehicles, homes, and industries, oil, gas, and coal-fired power plants, metal production, incineration, forest fires, lightning and decaying vegetation are the possible sources of NO_x. It can lower resistance to lung infections and can cause shortness of breath and irritate the upper airways, especially in people with lung disease, such as asthma and COPD. Both Nitric Oxide (NO) and Nitrogen Dioxide (NO₂) are harmful to plants at low concentration and to animals at higher concentration. Nitric Oxide can combine with atmospheric oxygen to form Nitrogen Dioxide ($2\text{NO} + \text{O}_2 = 2\text{NO}_2$) which can be further dissociated to NO and atomic oxygen by ultraviolet radiation. Nitrogen dioxide can readily combine with water to form nitric acid which forms a part of acid rain.

1.1.3 Suspended Particulate Matter (SPM) or Aerosols

Suspended particulate matter (SPM), alternatively referred to as particulate matter (PM), particulates or aerosols is a combination of tiny solid or liquid particles such as dirt, soil dust, pollens, molds, ashes and soot particles suspended in air. They range from 0.1 micron to 100 microns in diameter. United State Environmental Protection Agency (USEPA) has classified these particles into three categories viz., coarse particles (2.5 microns to less than 10 microns), fine particles (>1 micron up to 2.5 microns) and ultrafine particles (<1 micron). The notation PM₁₀ is used to describe particles of 10 microns or less and PM_{2.5}

represents particles less than 2.5 microns in aerodynamic diameter. For comparison, a human hair is about 75 microns in diameter. The fine fraction (2.5 microns or less) is more harmful to human health than the coarse particles. These fine particles can be breathed deeply into lungs and cause silicosis and other lung problems in humans. Fine particles can stay in the air for longer duration and travel farther than larger particles. National regulatory bodies of environmental protection like Central Pollution Control Board (CPCB), New Delhi, set air quality standards to protect health and environment. The standards define how much air pollution is safe in the outdoor air. Sources of particulate matter can be anthropogenic or natural. Natural dust forms about 50% of the total mass of aerosols in the air. Particulate matter air pollution comes from such diverse sources as motor vehicles, wood-burning stoves and fireplaces, construction activity, agriculture, industrial smokestacks, volcanoes, wildfires and other burning activities, and windblown dust from open lands (Lippmann 2000; USEPA 2001).

1.1.4 Polycyclic aromatic hydrocarbons (PAHs)

These are a group of approximately 10,000 compounds. Most of them are produced from incomplete burning of carbon-containing materials like oil, wood, garbage or coal. PAHs may be attached to dust or ash. Contact of PAHs with skin may cause redness, blistering, and peeling. Some PAHs have caused cancer (lung, stomach, skin) in laboratory animals when they were exposed to them. Furnaces, automobile and other exhausts, fireplaces and woodstoves, cigarette smoke, coal and oil-fired power plants, waste incinerators, steel and asphalt production, aluminum smelting, carbon black production, wood preservation, forest and brush fires, volcanic eruptions and decaying organic matter are the sources of PAHs (www.lung.ca).

Processes behind formation and behavior of particles during biomass burnings are complex and still not completely understood and solved. There is a need for knowledge and research in order to further develop the utilization of biomass combustion technology, as well as to reduce particulate emissions and to understand their environmental impact.

1.2 Agricultural crop residue and open field burning

A massive amount of agricultural residues are generated each year in the developing and urbanized countries. Wheat, rice, maize, barley, millet and sorghum are the main crops contributing in the global crop residue generation. Geographical distribution of crop residue is imprecise by large crop productions in India and China. Some countries of Southeast Asia have rice and sugar cane as dominant crops while in the Middle East, the crop mixture is more diverse. In the dry lands of the Near East and Mediterranean northern Africa, wheat and barley predominate. Farther south in the sub-humid and humid regions, maize is important. In Latin America, the crop residues of maize and sugar cane provide significant field and factory waste, with Brazil as the foremost contributor (FAO, 1986).

Open crop residue burning is a truly global practice to dispose of leftover crop residues (rice, wheat, barley, corn, sugarcane and oats) after harvest for land clearing and hinder pest infestations. It has been estimated that humans are responsible for about 90% of biomass burning with merely a small percentage of natural fires contributing to the total amount of vegetation burned. Compared to other types of biomass, crop residue has a relatively high content of inorganic compounds, and especially potassium compounds, that are released during combustion and contribute to particle formation as the flue gases cool down (Nielsen et al., 2000, Jenkins et al., 1998).

1.3 Rice wheat cropping system in India

The rice-wheat cropping system is the process of growing rice after wheat and then again rice. This forms a cycle of rice and wheat crops and known as rice-wheat cropping system (RWCS). The system is well practiced from last more than three decades in North Indian states like Punjab, Haryana, and western Uttar Pradesh. RWCS now occupies 12.33 million hectares (m ha) of which about 10 m ha is in the Indo-Gangetic plains, where it covers 75% of the total rice area and 63% of the total wheat area (Kumar, et al., 1998). A decline in yield has been observed and there are signs a decline in factor productivity of fertilizers also (Yadav, 1998) asking for higher and higher amounts of plant nutrients to obtain the same yield. This is due to declining soil fertility, specially its content of organic matter. RWCS removes 300-400 kg/ha/hr of N, P₂O₅ and K₂O at a moderate level of production (6-

8 t/ha/yr). Nutrient removal is much higher on farmers fields where productivity is 10 t/ha/yr or more. In addition, large amounts of secondary and micronutrients are also removed. Widespread Zn and S deficiencies have been reported in the RWCS belt. Farmers generally go on increasing the level of nitrogen application without adequate supply of other plant nutrients and this is mainly responsible for the observed low factor productivity of fertilizers.



Figure 1.1 Green wheat crop in field



Figure 1.2 Labourers performing wheat crop harvesting by sickle

Besides declining soil fertility, low wheat yields in RWCS are also obtained due to a short turnover period between rice harvest and delayed wheat sowing due to a number of factors, including delayed rice transplanting resulting in delayed rice harvests, high soil moisture content after the rice harvest, delay in removal of rice straw (a large part of it is being burned in situ, which besides the loss of precious organic C creates environmental and health problems), etc. Incorporation of wheat straw asks for additional nitrogen fertilization to prevent immobilization of native soil N.

In past years, the harvesting of crops was carried out by sickle involving a lot of man power. The harvested wheat crop was then brought to mechanical thrashers for crushing and removing seeds from the plants. These practices did not leave a lot of residue in fields behind to dispose involving no waste residue burnings. Thus, there was no problem of air pollution due to crop residue burning. In recent years, the development in agricultural technologies has made a lot of equipment for farmers. Mechanical harvester is one of the products of those technological researches. Crop harvesting by mechanical harvesters requires very less manpower as well as less time but leave behind a lot of waste residue in fields after harvest creating a waste residue management problem. Farmers find crop residue burning as an easy, less manpower and time consuming process and use to go for it.

The manufacture of zero-till machines in the country and their availability at an affordable price is the call of the time. Although RWCS has been a boon from the food security viewpoint for a majority vegetarian nation, it being an intensive cropping system is heavily taxing the two most important natural resources, namely soil and water, which are essential for the survival of human life. Rice is a water consuming crop; about 5000 liters are needed to produce 1 kg rice. The cultivation of rice in the non-traditional rice belt (Punjab, Haryana and western UP), where monsoon rains are not as heavy as in the traditional rice belt in the eastern India, forces the farmers to heavily rely on the groundwater through tubewells. This has considerably lowered the water table in this region.

RWCS has also adverse effects on the environment, mainly due to the application of high rates of fertilizer nitrogen (Prasad, R., 1998). About 5-10% of the nitrogen applied to rice

may be lost through ammonia volatilization. Ammonia volatilization could increase atmospheric levels of N, resulting in increased acid rain (Marshall et al. 1998). Production of N₂O due to denitrification is also likely to be more under alternate wetting and drying conditions obtained under irrigated rice culture. Furthermore, burning of rice residue is so rampant in the RWCS belt that it produces large amounts of CO₂, which adds to the global warming. Hence, well-planned steps are necessary to make it sustainable as well as more productive without adverse effects on the natural resources and the environment.

1.4 Crop residue burning in Punjab, India

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 region of the country (Mittal et al. 2009; Singh et al 2010; Sahai et al 2007, 2009, 2010). Though straw burnings are banned by the local administration still farmers find these practices economical and convenient for the removal of residue and quick seedbed preparation for the next crop and avoids the risk of reduced crop yields associated with late drilling. Crop residue burning (CRB) practices generate a huge amount of smoke containing particulate matter and gaseous species which deteriorate quality of ambient air and affect public health (Dennisa et al., 2002; Wiedinmyera et al., 2006). These activities involve the incomplete burning of organic materials under sub-optimum combustion conditions. Aerosol is one of the criteria pollutants emitted during crop residue burnings (Handa et al., 1980). It acts as a carrier of pollutants such as polycyclic aromatic hydrocarbons (PAH), toxic gases, metal particles, etc. which have deleterious effects on human health (Freeman and Catell, 1990; Godoi et al., 2004). The aerosol associated PAHs emissions during sugarcane burning have been reported by various scientists (Fang et al., 1999; Godoi et al., 2004).

1.5 Smoke from open biomass burning

Besides being an irritant, smoke contains many hazardous chemicals potentially harmful to human health. These mainly include: acrolein, formaldehyde, carbon monoxide, nitrous oxides, particulate matter, polycyclic aromatic hydrocarbons (PAH's), volatile organic compounds (VOCs) and dioxins. Long exposure to these components has been linked to

cause a variety of health problems like risk of cancer, developmental problems in children, heart disease, diabetes and harm to the immune system.



Figure 1.3 Crop residue burning in field at roadside near Patiala after wheat crop harvesting



Figure 1.4 Crop residue burning in Sidhuwal Village sampling site after rice harvesting

In South and Southeast Asia, large amounts of crop residue are burned or removed after harvest (Nguyen et al., 1994; Smil, 1999). This results in loss of organic matter and nutrients and causes atmospheric pollution due to emissions of toxic and greenhouse gases such as CO, CO₂, and CH₄, which pose a threat to human and ecosystem health (Andreae,

M.O., 1991; Nguyen et al., 1994). Demand for crop residue for cooking fuel and animal feed is high in South Asia (Bronson et al., 1998)

1.6 Monitoring of the extent of CRB smoke events and health impacts

It is very difficult to estimate the extent of crop residue burning across the state. The actual amount varies dramatically from year to year, depending upon amounts of rainfall, cropping patterns and weather conditions during and after the harvest season. Burning is a regular method of rice and wheat residues (stubble) management in rice-wheat cropping systems in Punjab, India. This has an extensive impact on soil quality, air quality, biodiversity, water and energy efficiency and human and animal health. Air pollution is particularly severe, directly impacting on health, and also indirectly contributing to accidents through reduced visibility. Burning is not a recommended practice to manage crop residue. Burning may seem like a simple method of managing crop residue, but it is actually expensive and damaging. Fine particulate matter is a major air pollutant that has been shown to cause a number of health symptoms and complications. People will have difficulties breathing polluted air depending on their age and health. People most sensitive to air pollution include: Infants and children, the older adults (those 65 and older), people with lung and heart disease, stroke, diabetes, or those with a current respiratory infection. People sensitive to air pollution may experience problems sooner and at lower levels of pollution. When people are active they breathe more air into their bodies. If air pollution levels rise, they will take in more pollutants (Awasthi et al., 2010).

Crop residue burning causes problems in many ways. Crop residue or straw is a source of soil nutrients and organic material. Decomposition releases these resources to build and maintain the soil. Soil resources, in turn, enhance crop production. Most of the organic material and nutritional content of straw is lost upon burning and resulting in economic loss. During high wind speed, agricultural waste fires can easily get out of control. Smoke can play an important role in road accidents if it drifts across roads and impairs visibility. While smoke may only be a nuisance to some people, it can be a serious health risk for those with respiratory problems, such as asthma or emphysema. Statistics show that 10% - 15% of the general population suffers with some type of respiratory condition. Moreover,

smoke is a source of air pollution. Carbon from the straw is released through burning as carbon dioxide. Many other gases are also released during crop residue burning episodes. Stubble fires generally do not burn soil organic matter. However, the contribution of the straw to the soil organic matter will be lost. Piles of crop residue burning partially decompose organic material in that localized area. Study conducted in Brazil has shown the adverse impact of sugar cane burning emissions on the health of the population. Increased levels of fine particulate matter were associated with the child and elderly respiratory hospitals admissions. (Cancado et al., 2006).

When burning takes place on calm days with no wind. The particles and gases produced can build to levels that are harmful for days. A haze may cover whole communities and reduce visibility. Calm days are often the times that people choose for open burnings. Closing doors and windows do not help. Smoke can easily waft through small cracks and holes, resulting in polluting indoor air as well as the outdoor air. Even smoke from burning can irritate the eyes, nose and throats of healthy adults; it can be much more harmful to small children, the elderly, and people with lung problems such as asthma or chronic obstructive pulmonary disease (COPD). This is because the visible smoke is made up almost entirely of tiny particles that can reach deep into lung tissue and cause symptoms such as coughing, wheezing, chest pain and shortness of breath. These symptoms may occur until several days after exposure to large amounts of smoke.

The crop residue smoke is a health issue for all persons downwind of this activity. All burning activities create harmful by-products, resulting in air pollution. It really does not matter whether oil, gas, wood or stubble is burned, there will be combustion products formed. The difference will be the amount of particles and gases formed. Oil and gas, for example burn much more cleanly and more closely achieve complete combustion, stubble burning is a dirty procedure that produces large amounts of fine particles that can be carried for long distances suspended in the wind.

People with lung diseases and COPD are more quickly affected by these tiny particles entering their breathing system. Children and the elderly are particularly sensitive. Symptoms that can come from stubble burning can be identified as follows: More cases of

lung disease, coughing and shortness of breath; decreased lung function, increase in emergency visits to the hospitals, sore eyes, sinus congestion.

Crop residue burning remains a controversial issue due to the resulting air pollution and real or perceived threats to human health. Alternatives to open burning have long been investigated and debated. In recent years, several feasible alternatives have emerged, including new markets for residual crop biomass. Principal among these markets is the independent power generation industry developed over the last decade. In India, companies like Orient Green Power and Greenko are the largest green utility in India with more than 200 MW of renewable energy capacity mostly in wind and biomass. Another company A2Z is also one of the country's fast-growing enterprises operating in power generation and distribution services, renewable energy and solid waste management. A2Z in cooperation with New Holland has taken an initiative to provide a viable alternative to Indian farmers to burning paddy straw by using crop residues for power generation. In California, about 60 plants have been constructed and now generate roughly 700 megawatts of power through combustion of biomass fuels. Because they also emit pollutants, such new facilities must reduce or "offset" the emission of similar pollutants elsewhere in the region. Agricultural residues that are normally burned in the field can be claimed in determining the offset requirements. The ability to reduce the emission offset requirements from other sources represents an economic incentive to the power generation sector to utilize agricultural residues as fuel (Jenkins et al. 1998).

1.7 Worth of agricultural crop residue

Crop residue is an important source of organic matter for the soil. Many farmers are experimenting with better ways of returning to the soil the parts of the crop that are not destined for human or animal use. Although it has been part of agriculture for many years, it is a relatively recent practice used by farmers. Crop residue or stubble can be used as an alternative energy source. Energy stored in plant material can be converted into usable power by combustion. Wood is one commonly used source of biomass energy. Similarly, crop stubble can be used for heating purposes in Industries. Biomass can also be converted into liquid fuels such as ethanol which can be used to run motor vehicles.

Crop residue is an imperative natural resource for conserving and sustaining soil productivity. It can be incorporated into the soil as it is the prime substrate for replenishment of soil organic matter (SOM). Upon mineralization, crop residue supplies essential plant nutrients (Walters et al., 1992). Additionally, residue incorporation can improve physical and biological conditions of the soil and prevent soil degradation (Nyborg et al., 1995). Annual rice-wheat double-crop systems occupy 21 million ha in the Indo-Gangetic plains of South Asia and China (Woodhead et al., 1994). On-station data from long-term experiments in China (Byerlee, 1992), Nepal (Regmi, 1994) and India (Nambiar, 1995) indicate that productivity of rice and wheat has been declining. Inadequate or imbalanced nutrient management and decreasing SOM are probably the factors in the declining trend in this cropping system (Abrol et al., 1997). There is a need, therefore, to develop agronomic strategies for efficient utilization of crop residue while also sequestering organic C in the soil.

Most of the indicators of population and health trends are inseparable from global environmental conditions. According to the Population Reference Bureau (PRB), World Population Data Sheet-2009, global population will reach 7 billion in 2011, just 12 years after reaching 6 billion in 1999. Virtually all of the increase is in developing countries. This increase will shape the scenario of the environment of different regions and countries over the next half century.

1.8 Alternatives of crop residue burning and crop residue management

Some alternatives of crop residue burning can be identified as follows:

- (i) Return crop residue into the soil using cropping devices and harrowing
- (ii) Bale straw for livestock use (whenever recommended).
- (iii) Sell excess straw for industrial use such as straw particle board, ethanol production, etc.
- (iv) Chop and spread - The combine is the most effective tool for managing residue. Even without grain to harvest, running a combine equipped with a straw chopper and chaff spreader will effectively distribute the residue. All nutrients and organic material are retained.

- (v) Seed into standing stubble - Disc openers can seed into tall, unharvested stubble. The ability of disc openers to go through tall stubble may eliminate the need for the residue to be managed. If the crop is trampled or lodged, other management techniques will have to be used.
- (vi) Proper timings of incorporation of residue into the soil, rotating crops, and composting the residue away from the field and then returning the finished compost are possible ways of overcoming the problem with potential pest or disease organisms that residue may harbor and pass on to a subsequent crop.
- (vii) Residues should be incorporated into the soil soon after harvest is complete so that a cover crop can be seeded. This practice reduces weeds, insects and disease, minimizes erosion, captures excess nutrients and reduces the potential for odor.

1.9 Less polluting new agricultural technologies and policies

Research on crop residue management strategies are helping to transform crop residue from a problematic by-product into a valuable part of soil organic matter management (Franzluebbers, 2004). A device known as 'Happy Seeder' has been developed for direct drilling of wheat into heavy rice residue loads without prior burning. Preliminary financial evaluation of this technology indicated that it is financially viable for farmers, and financially preferable to alternative residue management practices. Researchers at ACIAR in association with National Council of Applied Economic Research, India, are working on the project which will evaluate the economic, policy and social impact of the Happy Seeder (<http://www.aciar.gov.au/project/CSE/2006/132>). This type of projects focus on environmental policy issues associated with rice residue burning and the role of the Happy Seeder in addressing these issues.

1.10 Provincial legislation regulating crop residue burning

The Clean Air Act regulates sources of air pollutants. Under the Act, permits are not required for “a fire for the purpose of burning grain stubble or grain straw.” However, this exemption is only from the requirement to obtain a permit. The individual who sets the fire can be charged and may also face a civil lawsuit if the fire causes property damage, a traffic

accident or aggravates health problems. The Agriculture Operations Act provides a mechanism for resolving disputes from agricultural nuisances. The nuisance provisions of this Act also provide for the development of guidelines for normally accepted agricultural practice (www.agriculture.gov.sk.ca). The Clean Air Washington Act of 1991 (Chapter 70.94 RCW) states that those who contribute to air pollution will share the job of protecting air quality. While it is legal to burn for approved agronomic reasons, it is not legal to allow smoke to impact others (Chapter 173-430 WAC - Agricultural Burning). The agricultural burning of field crop residue and orchard tear out residue can directly impact the safety and health of citizens breathing the smoke-filled air.

1.11 Rationalization of the proposed work

The main focus of the thesis work is to study the effect of crop residue burning events on the quality of ambient air of Patiala city. To establish that the ambient air quality is affected by crop residue burning, some important parameters like SPM, SO₂, NO₂, etc were monitored during the burning episodes and are compared with those monitored in the absence of such events. Some parameters like ground level ozone concentration and PM fine particles were not monitored as; these were of priority lower than the former ones, in the present context. Although, it is desirable to monitor these two parameters, as well, but due to limitations of resources and scope of the present study, these two parameters were not undertaken.

References

- Abrol, I.P., K.F. Bronson, J.M. Duxbury, Gupta, R.K., 1996. Long-term soil fertility experiments in rice-wheat cropping systems: Proceedings of a workshop. Surajkund, Haryana, India. 15-18 Oct. 1996. Rice-Wheat Consortium Indo-Gangetic Plains, New Delhi, India
- Andreae, M.O., 1991. Biomass burning: Its history, use, and distribution and its impact on environmental quality and global climate. p. 3-21. In J.S. Levine (ed.) Global biomass burning: Atmosphere, climate, and biospheric implications. MIT Press, Cambridge, MA.

Awasthi, A., Singh, N., Mittal, S.K., Gupta, P.K., Agarwal, R., 2010. Effects of Agriculture Crop Residue Burning on Children and Young on PFTs in North West India. *Science of the Total Environment* 408 (20), 4440-4445.

Bronson, K.F., Cassman, K.G., Wassmann, R., Olk, D.C., van Noordwijk, M., Garrity, D.P., 1998. Soil carbon dynamics in different cropping systems in principal ecoregions of Asia. p. 35-57. In R. Lal et al. (ed.) *Management of carbon sequestration in soil*. Adv. Soil Sci., CRC Lewis Publishers, Boca Raton, FL.

Byerlee, D., 1992. Technical change, productivity, and sustainability in irrigated cropping systems of South Asia: Emerging issues. *J. Int. Dev.* 4:477-496

Cancado, J.E.D., Saldiva, P.H.N., Pereira, L.A.A., Lara, L.B.L.S., Artaxo, P., Martinelli, L.A., Arbex, M.A., Zanobetti, A., Braga, A.L.F., 2006. The Impact of Sugar Cane-Burning Emissions on the Respiratory System of Children and the Elderly, *Environmental Health Perspectives* 114(5) 725-729.

Clean Air Act 1970, United States Code, by the United States Government Title 42, Chapter 85. Air Pollution Prevention and Control.

Crutzen, P.J., Andreae, M.O., 1990. Biomass Burning in the Tropics: Impact on Atmospheric Chemistry and Biogeochemical Cycles, *Science*, 250(4988) 1669-1678.

Dennisa, 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.

Fang, M., Zheng, M., Wang, M., To, K.L., Jaafar, A.B., Tong, S.L., 1999. The solvent extractable organic compounds in the Indonesian biomass burning SPM characterization studies. *Atmospheric Environment* 33, 783-795.

Food and Agriculture Organization (FAO), *Production Yearbook*, 1985, vol. 39, Food and Agriculture Organization of the United Nations, Rome, 1986

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

Godoi A.F.L., Ravindra, K., Godoi, R.H.M., Andrade, S.J., Santiago-Silva, M., Vaeck, L.V., Grieken, R.V., 2004. Fast chromatographic determination of polycyclic aromatic hydrocarbons in SPM samples from sugar cane burning. *Journal of Chromatography A* 1027 (1-2) 49-53.

Handa, T., Kato, Y., Yamamura, T., Ishii, T., Suda, K., 1980. Correlation between the concentrations of polynuclear aromatic hydrocarbons and those of particulates in an urban atmosphere. *Environmental Science & Technology* 14 (4) 416-422.

Jenkins, B.M., Baxter, L.L., Miles, Jr, T.R., Miles, T.R., Combustion properties of biomass, Fuel Processing Technology, 1998, 54, 17- 46.

Lippmann, M., ed. (2000). Environmental Toxicants, 2nd edition. New York: Wiley.

Masters, Gilbert M., 2007. Introduction to environmental engineering and science. 2nd Edition, ISBN: 0131553844, published by Pearson Education, Inc, Copyright © 1998.

Nguyen, B.C., Putaud, J.P., Mihalopoulos, N., Bonsang, B., 1994. CH₄ and CO emissions from rice straw burning in South East Asia. Environ. Monitor. Assess. 31, 131-137

Nielsen, H.P., Baxter, L.L., Schluppab, G., Morey, C., Frandsen, F.J., Dam Johansen, K., 2000. Deposition of potassium salts on heat transfer surfaces in straw-fired boilers: A pilot scale study. Fuel, 79, 131-139.

Regmi, A.P., 1994. Long-term effects of organic amendment and mineral fertilizers on soil fertility in a rice-wheat cropping system in Nepal, M.S. thesis, Univ. of the Philippines, Los Banos, Philippines

U.S.EPA (2001). Air Quality Criteria for Particulate Matter. EPA 600/p.99/002. Washington, DC: Author, Lippmann, M.

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

Woodhead, T., Huke, R., Huke, E., 1994. Areas, locations, and ongoing collaborative research for the rice-wheat systems of Asia. p. 126-130. In R.S. Paroda et al. (ed.) Sustainability of rice-wheat production systems in Asia. Food and Agriculture Organization of the United Nations, Regional Office for Asia and the Pacific, Bangkok, Thailand.

Yadav, R.L., Prasad, K., Gangwar, K.S., 1998. Analysis of ecoregional production constraints in rice-wheat cropping system. PDCSR Bulletin No. 98-2.

Sahai, S., Sharma, C., Singh, D.P., Dixit, C.K., Singh, N., Sharma, P., Singh, K., Bhatt, S., Ghude, S., Gupta, R.K., Tiwari, M.K., Garg, S.C., Mitra, A.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.

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

Singh, N., Mittal, S.K., Agarwal, R., Awasthi, A., Gupta, P.K., 2010. Impact Assessment of Rice Crop Residue Burning on Levels of SPM, SO₂ and NO₂ in ambient air of Patiala city in India. *International Journal of Environmental Analytical Chemistry*, 90(10) 829-843.

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.

CHAPTER 2
REVIEW OF LITERATURE

CHAPTER 2

REVIEW OF LITERATURE

In order to ascertain the current state of knowledge with regard to emissions data from open biomass burning sources, a computer-aided literature search was performed to locate articles related to emissions of air toxics from open burning. Publications from technical journal articles, conference proceedings, and government reports since 1974 to 2010 are included in this chapter. There may be some references that might have been missed inadvertently. In this review of literature, the articles related to the emission of aerosols and gaseous species during biomass fire (forest fires and agricultural residue burning) episodes and the articles associated with the characterization of aerosols are included.

2.1. Biomass burning and emission of pollutants

Open burning of biomass has been used as a common procedure for crop and forest residue disposal and land clearing but it is a considerable source of atmospheric pollutants. Open burning is defined as the unenclosed combustion of materials in an ambient environment. This includes unintentional fires such as forest fires (Lemieux et al., 2004) and planned combustion activities such as the burning of waste crop residue in agricultural fields in preparation for the next crop. Although, biomass burning has been overlooked to some extent in urban air quality management, but it has drawn global concerns in the past decades for its effects on visibility, human health and global climate by emitting aerosols and trace gases. Particulate matter, CO, CO₂, hydrocarbons (volatile organic compounds and polycyclic aromatic hydrocarbons) with smaller amounts of NO_x and SO₂ are some principally emitted pollutants during these operations leading to generous changes in biogeochemical processes of earth's atmosphere (Fang et al., 1999; Radojevic et al., 1997; Koe et al., 2001; Crutzen et al., 1979, 1985; Crutzen and Andreae, 1990; Radke, 1989; Cofer et al., 1991; Levine, 1995; Andreae and Merlet, 2001; Andreae et al., 1988; Andreae, 1991). Many polycyclic aromatic hydrocarbons (PAH) are toxic and some of them are known as suspected carcinogens. Various compounds identified in smoke particles emitted during biomass combustion of several plant species have been reported by researchers

(Hawthorne et al. 1988, Lee et al. 2005, Oros and Simoneit, 1999, 2001; Fine, 2001, 2002; Sheesley et al. 2003; Hays et al. 2002). They consist of natural and combustion alteration products, whose emissions vary by plant species. Biomass smoke includes both vapor and particulate phase material with much of the particulate matter (PM) in the PM_{2.5} size range.

Savanna fires and forest fires are two major types of biomass burning and are reported in many studies (Allen and Miguel, 1995; Andreae, 1991; Lacaux et al., 1993; Cachier et al., 1995). Nevertheless, agricultural residue burning during the harvest season is another type of biomass burning which might be important for the regional point of view. Such burning practices are likely to affect global air quality as well. Estimation of the extent to which they contribute to the degradation of air quality in urban areas becomes important in such conditions. Agriculture is under scrutiny as a source of airborne particulate matter, but the relative lack of research documenting the emissions of fine (PM_{2.5}) and coarse (PM_{2.5-10}) particulate matter from agricultural operations leads to uncertainty in agricultural contributions. Studies that quantified agricultural particulate emissions represent short monitoring periods. The majority of the published data on emissions from open burning sources has been of criteria pollutants, including CO, SPM and oxides of nitrogen and sulfur (NO_x and SO_x).

As a natural phenomenon, fire serves an important ecological role but in terms of air quality, fires are significant sources of various gases and aerosols. There are numerous examples in the literature of the role that fires play on short-term air quality (Carrico et al. 2005, Mc Meeking et al., 2005; Westerling, 2004; Robinson, et al. 2004; Ward, et al. 2004). There are also multiple examples of a significant influence from fires on air quality at great distances from the source region for both particulate matter and gases (Colarco, et al. 2004; DeBell, et al. 2004; Wotawa, et al. 2000; McKeen, et al., 2002; Jaffe, et al., 2004; Bertschi and Jaffe, 2005). Emissions of air pollutants from the open burning of various materials is of concern to the public as well as local, state, national, and foreign environmental regulatory agencies.

Because of the diverse set of materials that are commonly burned in uncontrolled settings and the difficulties in acquiring representative environmental samples for estimation of emission factors (EFs), there is a considerable uncertainty in the estimated emissions from open burning activities. The overall emissions from a source depend on both the emissions and the activity level. Open burning, due to its less than ideal combustion conditions, typically produces soot and particulate matter (PM) that are visible as a smoke plume, carbon monoxide (CO), methane (CH₄) and other light hydrocarbons, volatile organic compounds (VOCs) such as benzene, and semi-volatile organic compounds (SVOCs) including polycyclic aromatic hydrocarbons (PAHs) such as benzo[a]pyrene. Depending on the source, varying amounts of metals such as lead (Pb) or mercury (Hg) may be emitted. Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) or polychlorinated biphenyls (PCBs) can be emitted as well. Organic carbon (OC) and water-soluble potassium (K⁺) are primary components of the aerosols emitted by biomass fires. Elemental carbon (EC) to organic carbon ratio has been found to be a good tracer of smoke from fires (Ames et al., 2004; McDonald et al. 2000 ; Andreae and Merlet, 2001, Spracklen, et al. 2007 ; Malm, et al. 1994, Park, et al. 2003; Cachier et al., 1995). K⁺ has been used as a tracer element for the qualitative identification of biomass burning (Sahai et al., 2007; Cachier et al., 1991; Chow et al., 1995), in source apportionment study (Lewis et al., 1988), as well as for wood smoke in receptor models (Echalar et al., 1995).

Jenkins et al. (1996c, 1996d, 1996e) published several papers and reports for the California Air Resources Board that discussed a detailed series of laboratory tests on emissions from burning cereal crop residues in the U.C. Davis wind tunnel facility. Gullett and Touati (2003) have performed laboratory simulations to estimate emissions from rice and wheat straw from two US States. Guyton and coworkers (1986) performed sampling from sugar cane field burning, but no emission factor units were presented. Several VOC and SVOC compounds were qualitatively identified but not quantified.

2.2 Health effects of biomass burning smoke

Toxic air pollutants emitted during crop residue burnings can travel long distances affecting thereby the distant regions. Due to these emissions air quality of the region

worsens, which results in nose and throat itching and burning, and irritation of the airway tract (Prasad, 2008). Aerosol particles of biomass burning smoke can have a potentially harmful impact on human health from both chronic and acute exposures. Chronic exposure to biomass smoke can reduce lung function, depress the immune system, and increase the risk of respiratory diseases (Long et al., 1998; Sutherland and Martin, 2003; Sutherland, 2004). Short-term exposures to high levels of PM_{2.5} result in acute health effects in susceptible people, including chronic obstructive pulmonary disease (COPD) patients and asthmatic children (Romieu et al., 1996; Pekkanen et al., 1997; Peters et al., 1997). In an extreme case, smoke emitted from crop residue open burning reduced visibility drastically and led to the temporary closing of an airport and highways. Open burning emissions are troubling from a public health perspective because of several reasons:

- a) Open burning emissions are typically released near ground level instead of through tall stacks which aid dispersion;
- b) Emissions are typically episodic in time or season (regional) and do not spread evenly throughout the year.
- c) Open burning sources are non-point sources, therefore, regulatory approaches such as mandated flue gas cleaning devices, cannot be applied to these sources.
- d) Open burning is a transient combustion phenomenon, frequently with heterogeneous biomass; it is difficult to attribute emissions to a single component of the biomass.

Air quality standards for PM have been established in many countries. The earliest standards were based on threshold models and use of a margin of safety. Initially, standards were based on the mass of total suspended material. In the 1980s a shift to a size-specific standard, PM₁₀, began. In the late 1990s, standards were proposed for PM_{2.5}, which is captured with 50% efficiency at 2.5 µm. The standards for PM are based almost exclusively on human epidemiological data, with laboratory animal and in vitro data used in a supporting role. During the 1990s, new statistical tools began to be used and demonstrated an association between increased PM and an increase in cardio-respiratory morbidity and mortality. The analyses are complicated by the effects of other pollutants such as ozone. Effects have been observed down to 10-20 µgm⁻³ of PM₁₀, levels equal to or below

background in many parts of the world. In many studies there has been no evidence of a threshold limit. In the absence of a threshold limit, it becomes difficult how to determine that the air quality of the area is safe or not. To meet the standards prescribed by the pollution control agencies, sources of both primary and secondary particles need to be listed and controlled. Control of primary particles involves emissions prevention or collection at the source while control of secondary particles require reducing emissions of precursor constituents such as ammonia and oxides of sulfur and nitrogen (Tucker, 2000).

Determining human exposure to suspended particulate concentrations requires measurements that quantify different particle properties in ambient as well as microenvironments where people live, work, and play. Particle mass, size and chemical compositions are important exposure variables and these are typically measured with time-integrated samples on filters. However, newer technologies are being developed that allow in-situ, time-resolved measurements for mass, carbon, sulfate, nitrate, particle size, and other variables but these are much costly and require great care during sampling. These are large measurement systems more suitable for fixed monitoring sites than for personal applications.

There is a need to understand the impacts of large-scale anthropogenic processes which could influence climate. One of the most important of such processes is agricultural trash burning. The Global Land Project (GLP 2005) has identified the need to understand better the impact of land-use-cover change on the atmosphere. In particular, there is a need to quantify the impact of carbonaceous aerosol emissions from spatial processes operating at a local scale (e.g., biomass burning). In order to combat undesirable environmental and health effects from aerosols, a better understanding of regional land use and aerosol relationships is always required. Knowledge about expected changes in the patterns and types of land-use patterns associated with biomass burning will also be an advantage for policy makers.

2.3 International status with respect to crop residue burning (CRB)

Crop residue burning (CRB) practices are worldwide (Andreae, 2001; Yongtaohu et al., 2009; Prasad, 2008). In countries like Mexico, neighbouring United States, nearly 20% of land is used for agriculture and residues from rice, wheat, corn, sugar cane, cotton, soybean and horticultural crops are usually burned in these areas. In addition to burning crop residues both during and after harvest, fire is also used in cropland areas for pest and weed control. Several American states including California, Washington, Arkansas, Colorado, Florida, Idaho, Kansas, Louisiana, North and South Dakota, Oklahoma, Oregon and Texas experience high levels ($> 3 \times 10^4$ ha yr⁻¹) of CRB (McCarty et al., 2009). CRB helps growers stay competitive as it is a less expensive and effective method to remove excess residue. It also provides a short-term ash fertilization effect. Annual cropland burning (1,239,000 hectares) have been observed equivalent to 43% of the annual average area of wild land fires in the United States (United States Forest Service; McCarty et al., 2009). Several other countries of Africa and Asia (Philippines, Australia, China, Pakistan, Nepal, Bangladesh etc.) also face the severe pollution problem due to the open burning of different types of crop residues every year.

The introduction of the new National Ambient Air Quality Standard (NAAQS) for various pollutants in any country may face controversy, not only with respect to the stringent limit selected, but also due to the many problems associated with ensuring compliance with a standard for a pollutant if it is poorly understood. Many countries still have no standards for PM_{2.5} (Sloss and Smith, 2000).

2.3.1 Crop residue burning practices in United States of America and United Kingdom

In the past decade, agricultural field burning has been the subject of analysis and public debate in several countries. In eastern Washington and northern Idaho, farmers prepare their fields for seeding, their practices involve the use of fire to dispose waste residue. In North America and Europe, deliberate agricultural and silvicultural burning for the purpose of rapid residue and vegetation clearing operations largely contribute in the emission of pollutants after wildfires. These sources constitute roughly 30% of known sources of

atmospheric carbon monoxide (CO). Recent reductions in atmospheric CO concentrations in these regions have been attributed in part to a slowdown in the rate of tropical biomass burning (Levine, 1991; Khalil and Rasmussen, 1994). The characteristics and mutagenic activities of biomass-derived PAH from a number of sources are described in the literature but there are less reports on open burning (Bjorseth and Ramdahl, 1985; Ramdahl et al., 1982; Nielsen et al., 1992; Elomaa et al., 1991; Mast et al., 1984). In the United States, estimates suggest that about 35% of the primary fine particulate matter (PM_{2.5}) emissions come from biomass burning and a large portion of these emissions are carbonaceous (70-95%). (USEPA, 1996, 2000, 2001; Barber et al., 2003). In response to the adverse effects of particulate matter, the U.S. Environmental Protection Agency (USEPA) has publicized National Ambient Air Quality Standard (NAAQS) in 1997 for PM_{2.5} and designated nonattainment areas in April 2005.

Barley, rice and wheat straw, corn stover, almond and walnut tree prunings, and Douglas fir and Ponderosa pine slash are commonly burned throughout the world. Rice and wheat straw, alongwith almond and walnut prunings comprise 95% of the agricultural biomass, exclusive of wildfires and prescribed forest fires, openly burned in the state of California (Jenkins et al., 1992). Production of total PAH varied from 5 to 683 mg kg⁻¹ depending principally on burning conditions and to a lesser extent on fuel type. Barley straw and wheat straw loaded at 400-500 gm⁻² emitted much higher levels of PAH, including benzo[a]pyrene, than other cereal and wood fuel types burning under more robust conditions. As anticipated, total PAH emission rates increased with increasing particulate matter emission rates and with declining combustion efficiency (Jenkins et al., 1996).

In a Georgia case study (Yongtaohu et al., 2009), biomass burning was identified as a major and growing contributor to PM_{2.5}. Individual impacts from each burning source were quantified using the Community Multiscale Air Quality (CMAQ) Model, a chemical transport model (CTM). Impacts of prescribed burning dominate biomass burning impacts, contributing about 55% and 80% of PM_{2.5} in January and March, respectively, followed by land clearing and agriculture field burning. Significant impacts of wildfires in May and

residential wood combustion in fireplaces and woodstoves in January were also experienced.

The contribution of fires to aerosol depends on the size and duration of the fire, as well as the burning conditions. Local fires are responsible for short term increases in $PM_{2.5}$ concentration, while long time large fires are responsible for broader increases in $PM_{2.5}$ over much larger regions. Recent studies show that fires in the Western U.S. and Canada have been increasing, both in frequency and duration, over the last few decades. These fires are linked to global climate change, which has resulted in warmer temperatures and reduced winter snow packs (Westerling et al., 2006; Gillett et al., 2004). If fires continue to increase in severity, the downward trend in $PM_{2.5}$ concentrations may close down and concentrations in some regions will increase. In 1999, the USEPA has issued the Regional Haze Rules (RHR) to address visibility impairment in Class I areas of the United States (National Parks and designated wilderness). Visibility is impacted by the aerosol loadings, chemistry, and humidity (USEPA Part II, 40 CFR Part 51, 1999). However, it is difficult to distinguish whether a fire is natural or human-caused. Nonetheless, quantification of the $PM_{2.5}$ influence from fires remains important to our overall understanding of air pollution.

Limited numbers of studies are reported on wheat and rice crop residue waste burnings. Jenkins and Turn developed a wind tunnel to simulate agricultural burning and measured its particulate and gaseous emissions (Turn et al., 1997; Jenkins, 1996). Hays and coworkers (2005) simulated agricultural fire in an enclosure and presented the physical and chemical characterization of particulate emissions. Similarly, Zarate et al. (2000) performed combustion chamber experiments and a field burning experiment to estimate emission factors from cereal waste burning in Spain. Nguyen et al. conducted field experiments and measured CO_2 , CO and CH_4 emissions from rice straw burning in Vietnam (Nguyen et al., 1994). Dhammapala et al. (2006) performed wheat and bluegrass stubble burn experiments at the USEPA open burning test chamber and measured $PM_{2.5}$, CO_2 , CO, and total hydrocarbon emissions.

Anthropogenic emissions from some open burning sources can be major contributors to overall emission inventories. Open burning of household waste in barrels is one of the largest airborne sources of PCDDs/Fs in the United States (USEPA, 2000). As industrial sources reduce their emissions in response to environmental regulations, non-industrial sources such as open burning begin to dominate the emissions inventory. Air emissions from open burning can also have impacts to other environmental media such as surface water and the sensitive species that occur in these media (Barber et al., 2003). The USEPA database (1996) contains a significant amount of information on emissions of criteria pollutants from open burning sources, mainly from the agriculture industry.

In a study conducted in United Kingdom (Harrison et al., 2001), a strong correlation between fine and coarse particles concentrations was observed at different monitoring locations. Notably lower proportion of coarse particles was observed at rural site as compared to the urban and suburban sites. Appreciable weekday-to-weekend and day-to-night differences between coarse particle concentrations were obtained which were most marked at the urban sites indicative of anthropogenic activities being a source of coarse particles. In an another study conducted in United Kingdom, it has been observed that the emission of ammonia declined from 20 Gg N per year in 1981 to 3.3 Gg N per year in 1991, as a result of changes in agricultural practices because of an imposed ban on the burning of crop residue (Samara et al., 2003).

2.3.2 Crop residue burning practices in China

Rice-wheat cropping system is widely practiced in China producing a huge amount of crop residue in the fields. This residue is burned openly and is an important source of air pollution in China. Epidemiological studies indicate that the health effects of outdoor air pollution may be more severe in Asia than in Europe or North America due to the magnitude of the air pollution, the amount of exposure to pollution, and the underlying health status of the population. The biomass burning occurs in small patches, covering larger area, for the purpose of land clearing.

Through hasty financial growth, China has faced severe air pollution problems especially in urban areas with particulate matter (PM) as the principal pollutant in most cases. Field burning of agriculture residues is a common way to eliminate waste after harvesting and a significant type of biomass burning over there. Many studies have been conducted in China in last one decade to estimate the contribution of biomass burnings in air pollution. Some studies estimated that 17-26% of the total agricultural residue production, or 110-157.5 Tg of crop wastes are burned in the fields in China every year (Street et al., 2003; Cao et al., 2006; Yan, 2006). During harvest seasons, open burning of agricultural residues releases a large amount of pollutants to the atmosphere, including particulate matter (PM), CO, hydrocarbons, and others, which cause serious local and regional environmental impact (Guo et al., 2004; Duan et al., 2004). In June 2006, wheat straw field burning caused serious air pollution in Beijing (The Global Fire Monitoring Center, GFMC).

Fuel wood and crop residue burned as fuel and in the field are the foremost types of biomass burning in China, accounting for nearly 90% of the total biomass burning on dry weight base. Due to indoor burning of biofuel, the majority of biomass burning in China is not accessible from satellite. Statistical data showed that the occurrence of forest fire in China has decreased dramatically since the 1980s. Grassland fires are a minor source of biomass burning in China. The estimated carbon monoxide (CO) emission from open biomass burning (field burning of crop residue and forest and grassland fires) was 16.5 Tg in 2000, with a 90% uncertainty range of 3.4-34 Tg. Uncertainties in CO emission factors, especially for field burning of crop residue, contributed much more to the variance than those in the activity data (Yan et al., 2006).

Gaseous and particulate emissions from the burning of three major agricultural crop residues (rice, wheat and corn straws) have been investigated in China, using a self-built burning stove and an aerosol chamber. Emission factors of CO₂, CO, NO, NO₂ and NO_x are reported. The percentages of CO, CO₂, and NO_x to the total emissions were highest for corn straw followed by wheat straw and rice straw, respectively (Zhang et al., 2008). In another study, emission factors of particulate matter (PM), element carbon (EC), organic carbon (OC), SO₂, NO_x, CO, CO₂, and some common ions were estimated from the

domestic burning of some commonly produced crop residues in rural China. To measure the emission factors, a combustion tower was designed to simulate the cooking conditions under which the growers burned their crop residues in rural China. Wheat straw had the highest emission factor for the total PM (8.75 g/kg) among the four crop residues, whereas, corn stover and wheat straw have the highest emission factor for EC (0.95 g/kg) and OC (3.46 g/kg), respectively. Corn stover showed the highest emission factors of NO, NO_x, and CO₂, whereas, wheat straw, rice straw and cotton stalk had the highest emission factors of NO₂, SO₂, and CO, respectively. The water soluble ions, K⁺ and Cl⁻, had the highest emission factors from all the crops. Wheat straw had a relatively higher emission factor of cation species and some anions like F⁻, Cl⁻, NO₂⁻ than other residues. (Cao et al., 2008).

Wheat-rice double cropping system is widely adopted in Suqian, China with 4523 km² of total area under cultivation. Based on the data of crop output from 2001 to 2005, the annual average amount of crop residue generated was estimated as 3.04×10⁶ t. About 82% of wheat straw and 37% of rice straw is burned in the field, so the proportion of crop residue burned in the field is about 43%. According to the field survey, it is regarded that combine harvester acts as an important role in crop residue burning in the field (Yang et al., 2008). Estimates of emissions from field burning of crop residues in China (Street et al. 2003; Yan et al. 2006) mainly adopted emission factors given by Andreae and Merlet (2001). Andreae and Merlet synthesized a large body of information on emissions from various types of biomass burning and presented a set of emission factors for separate species emitted from different types of biomass burning. Air quality is significantly affected because of agricultural field burning during the harvest period. To determine its contribution to ambient air quality, PM source profiles from agricultural fire are needed (Zhang et al., 1998).

Oxides of Nitrogen (NO_x) play crucial roles in tropospheric chemistry, terrestrial ecosystems and in the earth's radiation budget. These are key species regulating ozone and hydroxyl radical production. In many regions, deposition of nitrogen compounds affects surface acidity and nutrient status (IPCC, 1995; Galloway, 1995; Graedel et al., 1995, Pelley, 1998). Biomass burning is an important source of NO_x, accounting for some 15%

of the total global annual NO_x source (Martin et al., 2003). This source is characterized by seasonal increases (June to October) in NO_x columns over several regions including South America, which provides a major fraction of the global total NO_x. Tropospheric chemistry models for global NO_x distribution show an encouraging correspondence with satellite observations, but the models are limited where information on emission factors and quantity of biomass burned are poorly constrained (Andreae and Merlet, 2001).

Previous studies have suggested that China is one of the most important contributors to global carbonaceous aerosol emissions (Bond et al., 2004, Chameides and Bergin, 2002) and bio-fuel combustion is currently responsible for a large fraction of carbonaceous aerosol emissions in China accounting for 30% of black carbon and 55% of organic carbon of the total national emissions, respectively (Bond et al., 2004, Streets et al., 2001, Cao, 2006, Ohara et al., 2007, Zhang et al., 2007). Due to the global climate effects and the scale of China's carbonaceous aerosol emissions, it is important to have more accurate estimates of emissions (Roden et al., 2006).

Under the ideal conditions of complete combustion, the burning of biomass material produces CO₂ and water vapour (H₂O) (Levine, 1991). Since the complete combustion is not achieved under any conditions of biomass burning, other carbon species including carbon monoxide (CO), methane (CH₄), and nonmethane hydrocarbons (NMHCs) and particulate carbon result through the incomplete combustion of biomass material. Particles emitted from the biomass burning, which are composed primarily of organic and black carbon, play an important role in earth's radiation balance through their direct scattering and absorption properties and their effects on micro-physical structure of clouds (Hobbs and Radke, 1969; Christopher et al., 1996). Interaction of aerosols with the radiation passing through atmosphere also produces significant spectral deformation in the satellite images.

2.3.3 Crop residue burning practices in Brazil and Australia

Sugar cane is the main agricultural crop affected by agricultural crop residue burning. Pre-harvest burning of the cane reduces trash biomass by 80-90%, and increases the efficiency

of labor by 30% (Arbex et al., 2000). Burning is applied widely and this greatly increases tropospheric concentrations of particulate matter, CO, O₃, and other trace gases, though to uncertain levels (Kirchhoff et al., 1991; da Rocha, 2003). Brazil is the largest sugar cane exporter, followed by India and Australia, and responsible for 25% of the global 19.5-106 ha harvest. About half (52%) of Brazil's harvest comes from Sao Paulo, making the state a globally significant agricultural biomass burning emissions source. In rural Sao Paulo State of Brazil, the composition of the lower troposphere represents a tropical and subtropical region having an agriculture based economy and low population density. Here sugar cane production constitutes the single largest agricultural entrepreneur with more than 75% of the area planted. Farmers perform in situ burning of the crop prior to harvest which emits huge amount of gases and aerosols to the atmosphere (da Rocha et al., 2003; Allen et al., 2004, Oppenheimer et al., 2004).

The size distribution of atmospheric dust particles typically includes coarse ($>2\ \mu\text{m}$), accumulation mode ($0.1\text{-}2\ \mu\text{m}$), and nuclei mode ($< 0.1\ \mu\text{m}$) particles (Finlayson-Pitts et al., 2000). Knowledge of particle composition according to size can provide valuable insights into likely origins as well as subsequent behavior and impact on atmospheric processes. Once formed, particles provide an environment for a variety of secondary surface or aqueous phase processes acting to transform their physical and chemical properties. Water-soluble material, which can constitute much of the mass of tropospheric aerosols (Yin et al., 2005; Yamasoe et al., 2000), is a key component influencing gas-particle partitioning, rates of aqueous phase reactions, and ability of the particles to act as cloud condensation nuclei (Feingold et al., 2001; Teinila et al., 2004; Chebbi and Carlier, 1996 ; Krivacsy and Molnar, 1998; Kerminen, 2001; Hazi, 2003; Eldering and Glasgow, 1998; Hughes et al., 1998; Hughes et al., 1999; Chung et al., 2001, Xiu et al., 2004 ; Parmar et al., 2001). Data on the influence of widespread rural biomass burning in the tropics on aerosol size distribution, dry deposition and transport is very much limited or not available.

Methods of waste management most widely used in the developed world are land filling and controlled combustion. Recent surveys show that 16-48% of rural population practice open burning in the United States, and 54% of all population does so in Mexico (Neurath,

2003) The European Union Dioxin Emission Inventory document (European Commission, 2000) assumes that only 0.25% of total domestic waste is burned illegally in former EU countries. At the same time these authorities admit that there are no data on the frequency with which this activity is performed. The emissions from open burning are released at the ground level, possibly resulting in decreased dispersion, raises concerns about the human exposure to a range of pollutants (organic, inorganic and particulate matter).

2.3.4 Crop residue burning practices in Philippines and Thailand

Rice is widely grown crop in Asia. China (30%) and India (21%) contribute to about half of the world's total rice production while Thailand and the Philippines are contributing 4% and 2% of the world's rice production respectively. Rice straw is one of the main field based residues produced extensively in the region. While rice production practices vary from one country to another, open burning of straw is a common practice in these countries. It has been estimated that about 95, 22, and 11 Mt of rice straw residue is produced in India, Thailand, and the Philippines, respectively. In India, 23% of rice straw residue produced is leftover and largely burnt in open fields. About 48% of this residue produced is subjected to open-field burning in Thailand. In Philippines, about 95% leftover residue is burned in open agriculture fields. The GHG emissions contribution through open-field burning of rice straw in India, Thailand, and the Philippines were estimated as 0.05%, 0.18%, and 0.56% (Gadde et al., 2009)

In an another crop residue field burning study in Thailand conducted in the year 2007, the emission of PM_{2.5}, PM₁₀, SO₂, NO_x and non-methane volatile organic compounds (NMVOC) were estimated at 128, 143, 4, 42 and 108 Giga grams respectively along with other emission estimates. Rice straw burning was the largest contributor to the total emissions, especially during the dry season in the central part of the Thailand. Only a limited number of studies are reported for crop residue open burning for the country with significant discrepancy (Kanabkaew et al., 2010).

2.3.5 CRB practices in India, Pakistan, Bangladesh and Nepal

The rice-wheat cropping system has been practiced by farmers in Indo-Gangetic Plains (IGP) of South Asia (specially India, Pakistan, Bangladesh and Nepal) etc for more than 1000 years and is an imperative source of food security and livelihood for millions of rural and urban people of the world. It has since expanded and is currently estimated at 23.5 million hectares. It represents 32% of the total rice area and 42% of the total wheat area in these countries. Rice and wheat straw is the main crop residue that is largely burnt in these regions due to introduction of mechanical harvesters. Burning of crop residue creates diversified pollution problems like atmospheric pollution and loss of soil nutrients.

Rice, wheat and sugarcane are three major crops in Northern India. The harvesting of these crops leaves a huge amount of crop residue in the fields. Punjab produces around 23 million tons of rice straw and 17 million tons of wheat straw annually. More than 80% of paddy straw (18.4 million tons) and almost 50% wheat straw (8.5 million tons) produced in the state is being burnt in fields every year. Burning of wheat and rice straw has contributed to loss of soil fertility and air pollution due to emission of large amounts of SPM besides gases like CH_4 , CO , NO_x , SO_x , etc. leading to various health hazards like respiratory, skin and eye diseases. Intensive agriculture is also a contributor to greenhouse gasses (GHG) like, CO_2 , CH_4 and N_2O causing climate change. At an all India level, emissions from the agriculture sector are reported to be 28% of the aggregate national emissions. These include emissions from fermentation in livestock, manure management, rice cultivation and burning of agricultural crop residues (Economic and Statistical Advisor, 2005). Punjab state of India produces around 23 million tons of rice straw and 17 million tons of wheat straw, annually. This straw is rich in nitrogen, phosphorus and potassium contents. However, instead of its recycling into the soil by mulching, it is burnt in the fields. This raises the temperature of the soil (top 3 inches) and consequently the carbon, nitrogen equilibrium in soil changes rapidly. The carbon as CO_2 is lost to atmosphere, while nitrogen is converted to nitrate. This leads to a loss of about 0.824 million tons of NPK from soil. This is about 50 percent of total fertilizer consumption in the state. Considering that 90% of rice and 30% of wheat straw is available for recycling, it will be equivalent to recycling of 0.56 million tons of worthy nutrients. According to the agriculture experts, residue burning in the fields also

kills friendly pests and bacteria (which increase the fertility of soil) (PAU, 2006). Thus, more than 20 million tons of wheat and paddy straw are lost every year, which could have otherwise been used as feed for cattle or ploughed back into the soil to improve some of its characteristics. Carbon loss due to straw burning in state is more than 1.83 million tons per year, which is of concern not only for soil fertility but also for the environment of this area (Sidhu, 2002). The smoke is also a major problem for vehicular traffic in the state as it hampers the movement of vehicles on highways and link roads. The calculated total emissions in Punjab suggested that wheat crop residue burning contributes about 113 Gg (Giga Gram: 10 billion gram or 10 million kg) of CO, 8.6 Gg of NO_x, 1.33 Gg of CH₄, 13 Gg PM₁₀ (smoke) and 12 Gg of PM_{2.5} during May 2005 (Badrinath et al., 2006). The classified remote sensing images for wheat and paddy indicate that some districts of Indian Punjab are more affected than the rest. The extent of paddy crop residue burning during October 2005 has been estimated to be in 12,685 sq km area, which is much higher than the wheat crop residue burning that occurs during May each year. Emissions from paddy fields burning were estimated to be 261 Gg of CO, 19.8 Gg of NO_x, 3 Gg of CH₄, 30 Gg of PM₁₀ and 28.3 Gg of PM_{2.5} during October 2005. As per Gupta et al. (2004), one ton straw on burning releases 3 kg particulate matter, 60 kg CO, 1460 kg CO₂, 199 kg ash and 2 kg SO₂. These gases and aerosols consist of carbonaceous matter and play an important role in altering the atmospheric chemistry.

Although there are vast data with respect to laboratory and field studies on the gaseous species emitted during biomass burning in different types of ecosystems all over the globe, there are relatively very less field-based studies in India quantifying gaseous and aerosols emissions. Streets et al. (2003) report that the emissions of carbonaceous aerosols are largely uncertain in Southeast Asia, because limited information is available regarding the pattern of biomass burning practices and fossil fuel emissions (e.g., through increased use of automobiles). The emission rates and transport process of black carbon over Southeast Asia also are not well understood and are given a key research priority (Ramanathan et al., 2001). To assess the atmospheric impact of biomass burning, accurate data on aerosol emissions from fires are needed. Regional scale studies should be a key research priority in order to reconcile some of the uncertainties in global models. In Southeast Asia, the

estimation of aerosol emissions from biomass burning is confounded by the significant fossil fuel combustion and industrial pollution; therefore, analyses linking carbonaceous aerosols concentrations to the spatial and temporal patterns of biomass burning would reduce these uncertainties (Chin et al. 2002). Aerosols are removed from the atmosphere by precipitation, but if precipitation is suppressed by aerosols, they remain in the atmosphere for longer duration, furthering their impact. Drier conditions from suppressed aerosols also increase dust and smoke (from drier vegetation). These direct and indirect effects can significantly disrupt the regional hydrological cycle (Ramanathan et al., 2001; Jacobson, 2001). Finally, biomass burning and the associated release of aerosols into the atmosphere have potentially serious effects on both the locations where the pollution is created and the locations to which it is transported (Pfister et al., 2005).

Studying the extent and pattern of aerosols is an empirically challenging work. The extent and severity of biomass burning is affected by several factors, including density of the vegetation, humidity, temperature, and wind speed (Schultz 2002). Numerical transport models of carbonaceous aerosols have demonstrated key uncertainties in sources and sinks of black carbon (Uno et al., 2003). Aerosols differ from greenhouse gases, which are distributed uniformly, in that they generally remain in the atmosphere for only a short time, and thus large spatial and temporal variations in their concentration are evident (Ramanathan et al., 2001). To understand the spatial and temporal patterns of aerosols, it is necessary to develop spatial and temporal emission profiles relating these patterns to land-use processes.

Various land-use practices have different expected emission rates, but it remains an empirical question what the exact amount and spatial and temporal pattern of these emission rates will be on an intra-regional scale (Streets et al. 2003). Finally, because aerosols are highly mobile and complex physical and chemical interactions among particulates can occur in the atmosphere, changes in biomass burning associated with evolving land-use systems can also interact with other sources of aerosols (including the burning of fossil fuels). As a primary example, while it is clear that the brown haze over Southeast Asia and the Indian Ocean has significant implications for the regional energy

balance, it is unclear to what degree biomass burning and fuel combustion are responsible for the haze (Uno et al. 2003).

Synchronous satellite measurements on aerosol optical depth and ground reaching solar irradiance carried at an urban location in central region of India have shown elevated aerosol layers up to 3 km on certain days during October 2007. Observations on aerosol properties suggested transport of particles from agriculture crop residue burning in Indo-Gangetic Plains over large regions (Badarinath et. al., 2009). In the year 2000, major crops subject to open field burning of crop residue generated an estimated 284 Tg of residue in India, of which 40% was contributed by wheat crop. About 7.5% of this total generated wheat stubble was subjected to on-site burning, that is expected to emit large amounts of trace gases and particulate matter (PM) to the atmosphere. The Emission Factors (EFs) reported in an in-situ experiment for wheat stubble burning undertaken for India addressed important information gap on open crop stubble burning in the region (Sahai et. al., 2007; Gupta et al., 2004).

Most double-crop grain farmers in South Asia remove or burn crop residue to facilitate seedbed preparation and to avoid possible yield reductions. This results in loss of soil organic matter (SOM) and nutrients. Studies demonstrate that incorporation of crop residue in a rice-wheat system has potential to increase soil organic matter while maintaining high grain yields. (Aulakh et al., 2001)

2.4 Purpose of review

The purpose of this review is to report on open agricultural burning activities especially on rice and wheat and the availability of inorganic and organic air toxics emissions data. Literature survey was also conducted to compare emissions of different air toxic pollutants from the burning of different crop residues.

2.5 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 pollutants such as suspended particulate matter, SPM (coarse, fine and ultrafine), gases like CO₂, CO, CH₄ and NO_x, SO_x, 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 in 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.

References

- Allen, A.G., Cardoso, A.A., da Rocha, G.O., 2004. Influence of sugar cane burning on aerosol composition in southeastern Brazil. *Atmospheric Environment*, 38, 5025-5038.
- Allen, A.G., Miguel, A.H., 1995. Biomass burning in the amazon: characterization of the ionic component of aerosols generated from flaming and smouldering rain forest and savannah. *Environmental Science and Technology* 29, 486-493.
- Ames, R., Fox, D. G., Malm, W. C., Schichtel, B. A., 2004. Preliminary apportionments of carbonaceous aerosols to wild fire smoke using observations from the IMPROVE network; Paper #76, Conference on Regional Haze, AWMA, Asheville, NC.
- Andreae, M. O., 2001. Merlet, P. Emission of trace gases and aerosols from biomass burning. *Global Biogeochemical Cycle*, 15 (4), 955-966.
- Andreae, M. O., et al., *Journal of Geophysical Research*, 1988, 93, 1509-1527.
- Andreae, M.O., 1991. In: Levine, J.S. (Ed.), *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implications*. MIT Press, Cambridge, MA.
- Arbex, M.A., Bohm, G.M., Saldiva, P.H.N., Conceicao, G.M.S., Pope, A.C., III, Braga, A.L.F. 2000 Assessment of the effects of sugar cane plantation burning on daily counts of inhalation therapy. *Air Waste Manage. Assoc.*, 50, 1745-1749.
- Aulakh, M.S., Khera, T.S., Doran, J.W. and Bronson, K.F., 2001. Managing Crop Residue with Green Manure, Urea, and Tillage in a Rice–Wheat Rotation, *Soil Science Society of America Journal* 65:820-827.

Badarinath, K.V.S., Kharol, S.K., Sharma, A.R., 2009. Long-range transport of aerosols from agriculture crop residue burning in Indo-Gangetic Plains-A study using LIDAR, ground measurements and satellite data *Journal of Atmospheric and Solar-Terrestrial Physics*, 71(1) 112-120.

Barber, T.R., Lutes, C.C., Doom, M.R.J., Fuchsman, P.C., Timmenga, H.J., Crouch, R.L., 2003. Aquatic ecological risks due to cyanide releases from biomass burning. *Chemosphere*, 50, 343-348

Bertschi, I.T., Jaffe, D.A., 2005. Long-range transport of ozone, carbon monoxide and aerosols to the NE Pacific troposphere during the summer of 2003: Observations of smoke plumes from Asian boreal fires. *Journal of Geophysical Research*, 110 (D5), D05303; doi: 10.10292004JD005135.

Bjorseth, A., Ramdahl, T., *Handbook of polycyclic aromatic hydrocarbons*; Marcel Dekker: New York, 1985.

Bond, T.C., Streets, D.G., Yarber, K.F., Nelson, S.M., Woo, J.H., Klimont, Z., 2004. A technology based global inventory of black and organic carbon emissions from combustion. *Journal of Geophysical Research*, 109(D14203), doi:10.1029/2003JD003697.

Cachier, H., Ducret, J., Bremond, M.P., Gaudichet, A., Lacaux, J.P., Yoboue, V., Baudet, J., 1991. In Levine, J. (Ed.), *Characterization of biomass burning aerosols in a savannah region of the Ivory Coast*. Global Biomass Burning, MIT press, Cambridge, pp. 174-180.

Cachier, H., Lioussé, C., Buat-Menard, P., Gaudichet, A., 1995. Particulate content of savanna fire emissions. *Journal of Atmospheric Chemistry* 22, 123-148.

Cao, G., Zhang, X., Gong, S., Zheng, F., 2008. Investigation on emission factors of particulate matter and gaseous pollutants from crop residue burning, *Journal of Environmental Sciences*, Volume 20 (1), 50-55.

Cao, G., Zhang, X., Zheng, F., 2006. Inventory of black carbon and organic carbon emissions from China. *Atmospheric Environment*, 40, 6516-6527.

CARB, *Atmospheric Pollutant Emission Factors from Open Burning of Agricultural and Forest Biomass by Wind Tunnel Simulations*, Volume 1, California State Air Resources Board, (NTIS PB97-133037).

Carrico, C.M., Kreidenweis, S.M., Malm, W.C., Day, D.E., Lee, T., Carrillo, J., McMeeking, G.R., 2005. Hygroscopic growth behavior of a carbon-dominated aerosol in Yosemite National Park. *Atmospheric Environment*, 39, 1393-1404.

Chameides, W.L., Bergin, M., 2002. Soot takes center stage. *Science*, 297, 2214-2215.

Chebbi, A., Carlier, P., 1996. Carboxylic acids in the troposphere, occurrence, sources, and sinks: A review. *Atmospheric Environment*, 30, 4233-4249.

Chin, M., Ginoux, P., Kinne, S., Torres, O., Holben, B.N., Duncan, B.N., Martin, R.V., Logan, J.A., Higurashi, A.K., Nakajima, T., 2002. Tropospheric Aerosol Optical Thickness from GOCART Model and Comparisons with Satellite and Sun Photometer Measurement, *Journal of the Atmospheric Sciences*, 59, 461-483.

Christopher, S.A., Kliche, D.V., Chou, J., Welch, R.M., 1996. *Journal of Geophysical Research*, 101, 21, 265-273.

Chung, A., Herner, J.D., Kleeman, M.J., 2001. Detection of alkaline ultrafine atmospheric particles at Bakersfield, California. *Environmental Science & Technology*, 35, 2184-2190.

Clausnitzer, H., Singer, M.J., 1996. Respirable-dust production from agricultural operations in the Sacramento Valley, California. *J. Environ. Qual.* 25, 877-884.

Clausnitzer, H., Singer, M.J., 1997. Intensive land preparation emits respirable dust. *Calif. Agric.* 51, 27-30.

Cofer, W. R. III, Levine, J.S., Winstead, E.L., Stocks, B.J., 1991. New estimates of nitrous oxide emissions from biomass burning, *Nature* 349, 689-691.

Colarco, P.R., Schoeberl, M.R., Doddridge, B.G., Marufu, L.T., Torres, O., Welton, E.J., 2004. Transport of smoke from Canadian forest fires to the surface near Washington, DC: Injection height, entrainment, and optical properties. *Journal of Geophysical Research*, 109(D6), Art. No. D06203.

Cowherd Jr., C., Kinsey, J.S.: Identification, assessment and control of fugitive particulate emissions. EPA/600/8-86/023, US EPA, Research Triangle Park, NC (1986)

Cowherd, Jr., C., Axetall, Jr., K., Guenther, C.M., Jutze, G.A.: Development of Emission Factors for Fugitive Dust Sources. NTIS PB-238 262, Midwest Research Institute, Kansas City, MO (1974)

Crutzen, P.J., Andreae, M.O., 1990. Biomass Burning in the Tropics: Impact on Atmospheric Chemistry and Biogeochemical Cycles, *Science*, 250 (4988), 1669-1678.

Crutzen, P.J., Heidt, L.E., Krasnec, J.P., Pullock, W.H., Sieler, W., 1979. Biomass burning as a source of atmospheric gases CO, H₂, N₂O, NO, CH₃Cl and COS. *Nature*, 282, 253-256.

Cuscino Jr., T.A., Kinsey, J.S., Hackney, R., 1984. The Role of Agricultural Practices in Fugitive Dust Emissions. Midwest Research Institute, Kansas City, MO.

da Rocha, G.O., Franco, A., Allen, A.G., Cardoso, A.A., 2003. Sources of atmospheric acidity in an agricultural-industrial region of Sao Paulo State, Brazil. *Journal of Geophysical Research*, 108 (D7), 4207.

DeBell, L.J., Talbot, R.W., Dibb, J.E., Munger, J.W., Fischer, E.V., Frolking, S.E., 2004. A major regional air pollution event in the northeastern United States caused by extensive

forest fires in Quebec, Canada. *Journal of Geophysical Research*, 109(D19), doi:10.1029/2004JD004840.

Dhammapala, R., Claiborn, C., Corkill, J., Gullett, B., 2006. Particulate emissions from wheat and Kentucky bluegrass stubble burning in eastern Washington and northern Idaho. *Atmospheric Environment*, 40, 1007-1015.

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, 1275-1282.

Echalar, F., Gaudichet, A., Cachier, H., Artaxo, P., 1995. Aerosol emissions by tropical forest and savanna biomass burning: characteristic trace elements and fluxes. *Geophysical Research Letters* 22, 3034–3042.

Economic and Statistical Advisor, 2005. *Statistical Abstract of Punjab*. Published by Directorate of Economics and Statistics, Government of Punjab.

Eldering, A., Glasgow, R.M., 1998. Short-term particulate mass and aerosol-size distribution measurements: transient pollution episodes and bimodal aerosol-mass distributions. *Atmospheric Environment*, 32, 2017-2024.

Elomaa, M., Saharinen, E., 1991. Polycyclic aromatic hydrocarbons (PAHs) in soot produced by combustion of polystyrene, polypropylene, and wood. *Journal of Applied Polymer Science*, 42(10), 2819-2824.

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

Feingold, G., Remer, L.A., Ramaprasad, J., Kaufman, Y.J., 2001. Analysis of smoke impact on clouds in Brazilian biomass burning regions: An extension of Twomey's approach. *Journal of Geophysical Research*, 106(D19), 22907-22922.

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2001. Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States. *Environmental Science & Technology*, 35, 2665-2675.

Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2002. Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the southern United States. *Environmental Science & Technology*, 36, 1442-1451.

Finlayson-Pitts, B.J., Pitts, J.N.Jr., 2000. *Chemistry of the upper and lower atmosphere*; Academic Press: Florida.

Flocchini, R.G., Cahill, T.A., Matsumura, R.T., Carvacho, O., Lu, Z.: Study of fugitive PM-10 emissions for selected agricultural practices on selected agricultural soils. SJV Grant File-20960, University of California, Davis, CA (1994)

Gadde, B., Bonnet, S., Menke, C., Garivait, S., 2009. Air pollutant emissions from rice straw open field burning in India, Thailand and the Philippines, *Environmental Pollution*, 157(5)1554-1558

Gadde, B., Menke, C., Wassmann, R., 2009. Rice straw as a renewable energy source in India, Thailand, and the Philippines: Overall potential and limitations for energy contribution and greenhouse gas mitigation, *Biomass and Bioenergy*, 33(11) 1532-1546.

Galloway, J.N., 1995. Acid deposition: perspectives in time and space. *Water, Air Soil Pollution*, 85, 15-24.

Gerstle R.W., Kemnitz DA., 1967. Atmospheric emissions from open burning. *Journal of Air Pollution Control Association* 17(5), 324-327.

Gillett, N.P., Weaver, A.J., Zwiers, F.W., Flannigan, M.D., 2004. Detecting the effect of climate change on Canadian forest fires. *Geophysical Research Letters*, 31, L18211.

GLP (Global Land Project), (2005), Science Plan and Implementation Strategy. International Geosphere-Biosphere Programme (IBGP) Report No. 53/International Human Dimensions Programme (IHDP) Report No. 19. Stockholm, Sweden: IGBP Secretariat, p. 64.

Goldhammer J., *Int Forest Fire News* 2002; 27 (July-Dec).

Graedel, T.E., Benkovitz, C.M., Keene, W.C., Lee, D.S., Marland, G., 1995. Global emission inventories of acid-related compounds. *Water, Air Pollut.*, 85, 25-36.

Gullett, B., Touati, A., 2003. PCDD/F Emissions from Burning Wheat and Rice Field Residue. *Atmospheric Environment* 37, 4893-4899.

Guo, H., Wang, T., Simpson, I.J., Blake, D.R., Yu, X.M., Kwok, Y.H., Li, Y.S., 2004. Source contributions to ambient VOCs and CO at a rural site in eastern China. *Atmospheric Environment*, 38, 4551-4560.

Gupta, P.K., Sahai, S., Singh, N., Dixit, C.K., Singh, D.P., Sharma, C., Tiwari, M.K., Gupta, Raj K., Garg, S.C., 2004. Residue Burning in Rice-Wheat Cropping System: Causes and Implications, *Current Science*, 87 (12) 1713-1717.

Guyton, B., Stephenson, G., Clayton, R., Sampling support for cane field burning. Acurex final report TR-86-010/SR; 1986.

Harrison, R.M., Yin, J., Mark, D., Stedman, J., Appleby, R.S., Booker, J., Moorcroft, S., 2001. Studies of the coarse particle (2.5–10 μm) component in UK urban atmospheres, *Atmospheric Environment*, 35 (21) 3667-3679.

Hashmonay, R.A., Natshke, D.F., Wagoner, K., Harris, D.B., Thompson, E.L., Yost, M.G., 2001. Field evaluation of a method for estimating gaseous fluxes from area sources using open-path Fourier transform infrared. *Environ Sci Technol*, 35(11) 2309-13.

Hawaii. Inventory of Hawaii greenhouse gas emissions; estimates for 1990 by the Energy, Resources, and Technology Division, Department of Business, Economic Development, and Tourism and the Clean Air Branch, Department of Health, State of Hawaii, Honolulu. Greenhouse gases: Hawaii. I. Hawaii. Department of Health, Clean Air Branch; 1997. TD885.5.G73.H38

Hawthorne, S.B, Miller, D.J., Barkley, R.M., Krieger, M.S., 1988. Identification of methoxylated phenols as candidate tracers for atmospheric wood smoke pollution. *Environmental Science & Technology*, 22, 1191-1196.

Hays, M.D., Fine, P.M., Geron, C.D., Kleeman, M.J., Gullett, B.K., 2005. Open burning of agricultural biomass: physical and chemical properties of particle-phase emissions. *Atmospheric Environment*, 39, 6747-6764.

Hays, M.D., Geron, C.D., Linna, K.J., Smith, N. D., Schauer, J.J., 2002. Speciation of gas-phase and fine particle emissions from burning of foliar fuels. *Environmental Science & Technology*, 36, 2281-2295.

Hazi, Y., Heikkinen, M.S.A., Cohen, B.S., 2003. Size distribution of acidic sulfate ions in fine ambient particulate matter and assessment of source region effect. *Atmospheric Environment*, 37, 5403-5413.

Hobbs, P.V., Radke, L.F., 1969. Cloud condensation nuclei from a simulated forest fire, *Science*, 163, 279-280.

http://www.rwc.cgiar.org/Rwc_Crop.asp. Rice-Wheat Consortium for the Indo-Gangetic Plain.

Hughes, L.S., Cass, G.R., Gone, J., Ames, M., Olmez, I., 1998. Physical and chemical characterization of atmospheric ultrafine particles in the Los Angeles area. *Environmental Science & Technology*, 32, 1153-1161.

Jacobson, M.Z., 2001. Strong Radiative Heating Due To the Mixing State of Black Carbon in Atmospheric Aerosols. *Nature*, 409, 695-697.

Jaffe, D., Bertschi, I., Jaegle, L., Novelli, P., Reid, J.S., Tanimoto, H., Vingarzan, R., Westphal, D.L., 2004. Long-range transport of Siberian biomass burning emissions and impact on surface ozone in western North America. *Geophys. Res. Lett.*, 31, L16106.

Jenkins, B.M., Jones, A.D., Turn, S.Q., Williams, R.B., 1996. Emission factors for polycyclic aromatic hydrocarbons from biomass burning. *Environ Sci Technol*, 30(8) 2462-9.

Jenkins, B.M., Jones, A.D., Turn, S.Q., Williams, R.B., 1996. Particle concentrations, gas-particle partitioning, and species intercorrelations for polycyclic aromatic hydrocarbons (PAH) emitted during biomass burning. *Atmospheric Environment*, 30 (22) 3825-35.

Jenkins, B.M., Turn, S.Q., Williams, R.B., Goronea, M., and Abd-el-Fattah, H., (1996d). Atmospheric Pollutant Emission Factors from Open Burning of Agricultural and Forest Biomass by Wind Tunnel Simulations, Volume 2, California State Air Resources Board, (NTIS PB97-126940).

Jenkins, B.M., Turn, S.Q., Williams, R.B., Goronea, M., and Abd-el-Fattah, H., (1996e), Atmospheric Pollutant Emission Factors from Open Burning of Agricultural and Forest Biomass by Wind Tunnel Simulations, Volume 3, California State Air Resources Board, (NTIS PB97-132369).

Jenkins, B.M., Turn, S.Q., Williams, R.B., Goronea, M., Abd-el-Fattah, H., 1996. Atmospheric pollutant emission factors from open burning of agricultural and forest biomass by wind tunnel simulations, vol. 1, California State Air Resources Board, NTIS PB97 133037.

Jenkins, B.M., Turn, S.Q., Williams, R.B., Goronea, M., Abd-el-Fattah, H., 1996. Atmospheric pollutant emission factors from open burning of agricultural and forest biomass by wind tunnel simulations, vol. 2, California State Air Resources Board, NTIS PB97-126940.

Kanabkaew, T., Oanh, N.T.K., 2010. Development of Spatial and Temporal Emission Inventory for Crop Residue Field Burning Environmental Modeling and Assessment, DOI: 10.1007/s10666-010-9244-0

Kerminen, V.M., Hillamo, R., Teinila, K., Pakkanen, T., Allegrini, I., Sparapani, R., 2001. Ion balances of size-resolved tropospheric aerosol samples: implications for the acidity and atmospheric processing of aerosols. *Atmospheric Environment*, 35, 5255-5265.

Khalil, M.A.K., Rasmussen, R.A., 1994. Global decrease in atmospheric carbon monoxide concentration, *Nature*, 370, 639-641.

Kirchhoff, V.W.J.H., Marinho, E.V.A., Dias, P.L.S., Pereira, E.B., Calheiros, R., Andre, R., Volpe, C., 1991. Enhancements of CO and O₃ from burnings in sugar cane fields. *J. Atmos. Chem.*, 12, 87-102.

Koe, L.C.C., Avellano, A.F., McGregor, J.L., 2001. Investigating the haze transport from 1997 biomass burning in Southeast Asia: its impact upon Singapore. *Atmospheric Environment* 35, 2723-2734.

Krivacsy, Z., Molnar, A.A., 1998. Size distribution of ions in atmospheric aerosols. *Atmos. Res.*, 46, 279-291.

Lacaux, J.P., Cachier, H., Delmas, R., 1993. Biomass Burning in Africa: an overview of its impact on atmospheric chemistry. In: Crutzen P.J., Goldammer J. G. (Eds.), *Fire in the Environment*. Wiley, Chichester. Dahlem Workshop Report on Environmental Sciences Research, ES 13, pp. 159-191.

Lee, S., Baumann, K., Schauer, J.J., Sheesley, R.J., Naeher, L.P., Meinardi, S., Blake, D.R., Edgerton, E.S., Russell, A.G., Clements, M., 2005. Gaseous and Particulate Emissions from Prescribed Burning in Georgia. *Environmental Science & Technology*, 39, 9049-9056.

Levine, J. S., Ed. Global biomass burning; MIT Press: Cambridge, MA, 1991.

Levine, J.S., Cofer, W.R., Cahoon, D.R., Winstead, E.L., 1995. Biomass burning: a driver for global change. *Environmental Science & Technology*, 29 (3), 120A-125A.

Lewis, C.W., Baumgardner, R.E., Stevens, R.K., Claxt, L.D., Lewtas, J., 1988. Contribution of woodsmoke and motor vehicle emissions to ambient aerosol mutagenicity. *Environmental Science and Technology* 22, 968-971.

Lioussé, C., Penner, J.E., Chuang, C., Walton, J.J., Eddleman, H., Cachier, H., 1996. A global 3-dimensional model study of carbonaceous aerosols. *Journal of Geophysical Research* 101, 19411–19432.

Long, W., Tate, R.B., Neuman, M., Manfreda, J., Becker, A.B., Anthonisen, N.R., 1998. Respiratory symptoms in a susceptible population due to burning of agricultural residue. *Chest* 1132, 351-356.

Malm, W.D, Sisler, J.F., Huffman, D., Eldred, R.A., Cahill, T.A., 1994. Spatial and seasonal trends in particle concentration and optical extinction in the United States. *Journal of Geophysical Research*, 99 (D1), 1347-1370.

Martin, R.V., Jacob, D.J., Chance, K., Kurosu, T.P., Palmer, P.I., Evans, M.J., 2003. Global inventory of nitrogen oxide emissions constrained by space-based observations of NO₂ columns. *Journal of Geophysical Research*, 108 (D17), 4537.

Mast, T.J., Hsieh, D.P.H., Seiber, J.N., 1984. *Environmental Science & Technology*, 18 (5), 338-348.

McCarty, J.L., Korontzi, S., Justice, C.O., Loboda, T., 2009. The spatial and temporal distribution of crop residue burning in the contiguous United States, *Science of The Total Environment*, 407 (21) 5701-5712.

McDonald, J.D., Zielinska, B., Fujita, E. M., Sagebiel, J. C., Chow, J.C., Watson, J.G., 2000. Fine particle and gaseous emission rates from residential wood combustion. *Environmental Science & Technology*, 34 (11), 2080-2091.

McKeen, S.A., Wotawa, G., Parrish, D.D., Holloway, J.S., Buhr, M.P., Hubler, G., Fehsenfeld, F.C., Meagher, J.R., 2002. Ozone production from Canadian wildfires during June and July of 1995. *Journal of Geophysical Research*, 107(D14), doi:10.1029/2001JD000697.

McMeeking, G.R., Kreidenweis, S.M., Carrico, C.M., Lee, T., Collett, J.L., Malm, W.C., 2005. Observations of smoke-influenced aerosol during the Yosemite Aerosol

Characterization Study: Size distributions and chemical composition. *Journal of Geophysical Research*, 110, D09206; doi:10.1029/2004JD005389.

Mickler R.A., Henderson, B., Smith, S., Crews, T., VanDruten K., Range management of wildland fire fuels, fire risk and prescribed burning of the US air force and navy dare county bombing range and alligator river NWR. Poster presented at the SERDP/ESTCP Partners in Environmental Technology Conference, Washington, DC; December 2002.

Neurath, C., 2003. Open burning of domestic wastes: The single largest source of dioxin to air? *Organohalogen Compd.*, 63, 122-125.

Nguyen, B.C., Mihalopoulos, N., Bonsang, B., 1994. CH₄ and CO emissions from rice straw burning in South East Asia. *Environmental Monitoring and Assessment*, 31, 131-137.

Nielsen, P.A., Grove, A., Olsen, H., 1992. *Chemosphere*, 24 (9),1317-1330.

Ohara, T., Akimoto, H., Kurokawa, J., Horii, N., Yamaji, K., Yan, X., Hayasaka, T., 2007. An Asian emission inventory of anthropogenic emission sources for the period 1980-2020. *Atmos. Chem. Phys.*, 7, 4419–4444.

Oppenheimer, C., Tsanev, V.I., Allen, A.G., McGonigle, A.J.S., Cardoso, A.A., Wiatr, A., Paterlini, W., Dias, C.M., 2004. NO₂ emissions from agricultural burning in Sao Paulo, Brazil. *Environmental Science & Technology*, 38(17), 4557-4561.

Oros, D.R., Simoneit, B.R.T., 2001. Identification and emission factors of molecular tracer in organic aerosols from biomass burning, part 1. Temperate climate confers. *Applied Geochemistry*, 16, 1513-1544.

Oros, D.R; Simoneit, B.R.T., 1999. Identification of molecular tracers in organic aerosols from temperate climate vegetation subjected to biomass burning. *Aerosol Science & Technology*, 31, 433 445.

Park, R.J., Jacob, D.J., Chin, M., Martin, R.V., 2003. Sources of carbonaceous aerosols over the United States and implications for natural visibility. *Journal of Geophysical Research*, 108 (D12), 4355.

Parmar, R.S., Satsangi, G.S., Kumari, M., Lakhani, A., Srivastava, S.S., Prakash, S., 2001. Study of size distribution of atmospheric aerosol at Agra. *Atmospheric Environment*, 35, 693-702.

Pekkanen, J., Timonen, K.J., Ruuskanen, J., Reponen, A., Mirme, 1997. Effects of ultrafine and fine particles in urban air on peak expiratory flow among children with asthmatic symptoms. *Environmental Research*, 74, 24-33.

Peters, A., Dockery, D.W., Heinrich, J., Wichmann, H.E., 1997. Short term effects of particulate air pollution on respiratory morbidity in asthmatic children. *European Respiratory Journal*, 10, 872-879.

Pfister, G., Hess, P.G., Emmons, L.K., Lamarque, J.F., Wiedinmyer, C., Edwards, D.P., Petron, G., 2005. Analysis of the Wildfires in Alaska and Canada in Summer 2004: Sources Estimates and the Impact on Air Chemistry and Composition, *Geophysical Research Abstracts*, 7, 05676.

Prasad, R., 2008. Monitoring air quality on crop residue burning in fields, *Indian Journal of Air Pollution Control*, 8(1) 87-91.

Pyne, S.J., *Fire in America: a cultural history of wild and rural fire*. Seattle: University of Washington Press; 1982.

Radke, L.F., Proceedings of a symposium on the role of clouds in atmospheric chemistry and global climate, American Meteorological Society, Anaheim, Calif, 29 January-3 February 1989, pp. 310–315.

Radojevic, M., 1997. The haze in Southeast Asia. *Environmental Scientist* 6 (6), 1-3.

Ramanathan, V., Crutzen, P.J., Kiehl, J.T., Rosenfeld, D., 2001. Aerosols, Climate and the Hydrological Cycle. *Science*, 7, 2119-2124.

Ramdahl, T.; Alfheim, I.; Rustad, S.; Olsen, T. *Chemosphere* 1982, 11 (6), 601-611.

Robinson, M.S., Chavez, J., Velazquez, S., Jayanty, R.K.M., 2004. Chemical speciation of PM_{2.5} collected during prescribed fires of the Coconino National Forest near Flagstaff, Arizona. *Journal of Air & Waste Management Association*, 54, 1112-1123.

Roden, C.A., Bond, T.C., Conway, S., Pinel, A.B.O., 2006. Emission factors and real-time optical properties of particles emitted from traditional wood burning cookstoves. *Environmental Science & Technology*, 40, 6750–6757.

Romieu, I., Meneses, F., Ruiz, S., Sienra, J., Huerta, J., White, M., Etzel, R., 1996. Effects of air pollution on the respiratory health of asthmatic children living in Mexico City. *Am. J. Respir. Crit. Care Med.*, 154, 300-307.

Ryan, J.V., Characterization of emissions from the simulated open burning of scrap tires; October 1989. EPA-600/2-89-054, NTIS PB90-126004.

Sahai, S., Sharma, C., Singh, D.P., Dixit, C.K., Singh, N., Sharma, P., Singh, K., Bhatt, S., Ghude, S., Gupta, V., Gupta, R.K., Tiwari, M.K., Garg, S.C., Mitra, A.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.

Samara, J.S., Singh, B. and Kumar, K., 2003. Managing crop residue in the rice-wheat system of the Indo-Gangetic Plain. *Improving the Productivity and Sustainability of Rice-Wheat Systems: Issues and Impacts*, Special Publication 65, Wisconsin, USA.

Schultz, M.G., 2002. On the Use of ASTR fire Count Data to Estimate the Seasonal and Interannual Variability of Vegetation fire Emissions. *Atmospheric Chemistry and Physics Discussions*, 2, 1159-1179.

Sheesley, R.J., Schauer, J.J., Clowdhury, Z., Cass, G. R., Simoneit, B.R.T., 2003. Characterization of organic aerosols emitted from the combustion of biomass indigenous to South Asia. *J. Geophys. Res.*, 108, D9, 4285.

Simoneit, B.R.T., 2002. Biomass burning- a review of organic tracers for smoke from incomplete combustion. *Applied Geochemistry*, 17, 129-162.

Sloss, L.L., Smith, I.M., 2000. PM₁₀ and PM_{2.5}: an international perspective, *Fuel Processing Technology*, 65-66, 127-141

Snyder, J.W., Blackwood, T.R., Source assessment: mechanical harvesting of cotton State of the art. EPA/600/2-77-107d, US EPA, Research Triangle Park, NC (1977)

Spracklen, D.V., Logan, J.A., Mickley, L.J., Park, R.J., Yevich, R., Westerling, A.L., Jaffe, D., 2007. Fires drive interannual variability of organic carbon aerosol in the western U.S. in summer. *Geophys. Res. Lett.*, 34, L16816; doi:10.1029/2007GL030037.

Street, D.G., Yarber, K.F., Woo, J.H., Carmichael, G. R. Biomass burning in Asia: annual and seasonal estimates and atmospheric emissions. *Global Biogeochem. Cycles* 2003, 17 (4), 1099, doi: 10.1029/ 2003GB002040.

Streets, D.G., Bond, T.C., Carmichael, G.R., Fernandes, S.D., Fu, Q., He, D., Klimont, Z., Nelson, S.M., Tsai, N.Y., Wang, M.Q., Woo, J.H., Yarber, K.F., 2003. An Inventory of Gaseous and Primary Aerosol Emissions in Asia in the Year 2000. *Journal of Geophysical Research*, 108(D21), doi:10.1029/2002JD003093.

Streets, D.G., Gupta, S., Waldhoff, S.T., Wang, M.Q., Bond, T.C., Bo, Y., 2001. Black carbon emissions in China. *Atmospheric Environment*, 35, 4281-4296.

Sutherland, E.R., 2004. Outpatient treatment of chronic obstructive pulmonary disease, comparisons with asthmatics. *J. Allergy Clin. Immunol.*, 114, 715-724.

Sutherland, E.R., Martin, R.J., 2003. Airway inflammation in chronic obstructive pulmonary disease, comparisons with asthma. *J. Allergy Clin. Immunol.*, 112, 819-827.

Teinila, K., Hillamo, R., Kerminen, V.M., Beine, H.J., 2004. Chemistry and modal parameters of major ionic aerosol components during the NICE campaigns at two altitudes. *Atmospheric Environment*, 38, 1481-1490.

The Global Fire Monitoring Center, GFMC (<http://www.uni-freiburg.de/fireglobe/>).

Tucker, W.G., 2000. An overview of PM_{2.5} sources and control strategies, *Fuel Processing Technology* (65-66) 379-392

Turn, S.Q., Jenkins, B.M., Chow, J.C., Pritchett, L.C., Campbell, D., Cahill, T., Whalen, S.A., 1997. Elemental characterization of particulate matter emitted from biomass burning: wind tunnel derived source profiles for herbaceous and wood fuels. *Journal of Geophysical Research*, 102 (D3), 3683-3699.

U.S.EPA, Public review draft: exposure and health reassessment of 2,3,7,8-tetrachloro dibenzo-p-dioxin (TCDD) and related compounds. National Center for Environmental Assessment, Washington, DC; September 2000. EPA-600/P-00-001Bb.

U.S.EPA. Part II, 40 CFR Part 51, Regional Haze Regulations; Final Rule. *Fed. Regist.* 1999, (64) 126; available at www.epa.gov/ttncaaa/t1/fr_notices/rhfredreg.pdf.

U.S.EPA. Stationary point and area sources, vol. 1. 5th ed. AP- 42; 1996.

U.S.EPA; 2001, EIIP main web address: <http://www.epa.gov/ttn/chief/eiip/techreport/index.html>

Uno, I., Carmichael, G.R., Streets, D., Satake, S., Takemura, T., Woo, J.H., Uematsu, M., Ohta, S., 2003. Analysis of Surface Black Carbon Distributions During ACE-Asia Using a Regional-Scale Aerosol Model. *Journal of Geophysical Research*, 108(D23), DOI:10.1029/2002JD003252.

Ward, T.J., Hamilton, R.F., Smith, G.C., 2004. The Missoula, Montana PM_{2.5} speciation study seasonal average concentrations. *Atmospheric Environment*, 38, 6371-6379.

Westerling, A.L., Cayan, D.R., Brown, T.J., Hall, B.L., Riddle, L.G., 2004. Climate, Santa Ana winds and autumn wildfires in Southern California. *Eos, Trans., Am. Geophys. Union*, 85 (31), 289-300; doi:10.1029/2004EO310001.

Westerling, A.L., Hidalgo, H.G., Cayan, D.R., Swetnam, T.W., 2006. Warming and earlier spring increase Western U.S. forest fire activity. *Science*, 313, 940-943.

Winberry, W.T., Murphy, N.T., Riggan, R.M., Compendium method TO-14. The determination of volatile organic compounds in ambient air using SUMMAw passivated canister sampling and gas chromatographic analysis. In: *Compendium of methods for the determination of toxic organic compounds in ambient air*, Quality Assurance Division, Environmental Monitoring Systems Laboratory, US EPA; 1988. EPA-600/4-89-017, NTIS PB90-127374

Wotawa, G., Trainer, M., 2000. The influence of Canadian forest fires on pollutant concentrations in the United States. *Science*, 288, 324-328.

Xiu, G.L., Zhang, D.N., Chen, J.Z., Huang, X.J., Chen, Z.X., Guo, H.L., Pan, J.F., 2004. Characterization of major water-soluble inorganic ions in size-fractionated particulate matters in Shanghai campus ambient air. *Atmospheric Environment*, 38, 227-236.

- Yamasoe, M.A., Artaxo, P., Miguel, A.H., Allen, A.G., 2000. Chemical composition of aerosol particles from direct emissions of vegetation fires in the Amazon Basin: water-soluble species and trace elements. *Atmospheric Environment*, 34, 1641-1653.
- Yan, X., Ohara, T., Akimoto, H., 2006. Bottom-up estimate of biomass burning in mainland China. *Atmospheric Environment*, 40, 5262-5273.
- Yang, S., He, H., Lu, S., Chen, D., and Zhu, J., 2008. Quantification of crop residue burning in the field and its influence on ambient air quality in Suqian, China. *Atmospheric Environment*, 42 (9) 1961-1969.
- Yin, J., Allen, A.G., Harrison, R.M., Jennings, S.G., Wright, E., Fitzpatrick, M., Healy, T., Barry, E., Ceburnis, D., McCusker, D., 2005. Urban PM₁₀ and PM_{2.5} measurements in Ireland. *Atmos. Res.*
- Yongtaohu, D., Wang Y., Boylan J.W., Meizheng and Russell, A.G., 2009. Assessment of Biomass Burning Emissions and Their Impacts on Urban and Regional PM_{2.5}: A Georgia Case Study, *Environmental Science & Technology*, 43, 299-305.
- Zarate, I.O., Ezcurra, A., Lacaux, J.P., Dinh, P.V., 2000. Emission factor estimates of cereal waste burning in Spain. *Atmospheric Environment*, 34, 3183-3193.
- Zhang, H., Ye, X., Cheng, T., , Chen, J., Yang, X., Wang, L., and Zhang R., 2008. A laboratory study of agricultural crop residue combustion in China: Emission factors and emission inventory, *Atmospheric Environment*, 42 (36) 8432-8441
- Zhang, J., Chen, Z.L., Wang, W., 1998. Source apportionment on fine particulate in Beijing. *Acta Scientiae Circumstantiae* 18 (1), 62–67 (in Chinese with abstract in English.
- Zhang, Q., Streets, D.G., He, K., Klimont, Z., 2007. Major components of China's anthropogenic primary particulate emissions. *Environmental Research Letters*, 2, 045027.

CHAPTER 3
MATERIALS AND METHODS

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3.1 Study design

Air pollution monitoring studies need to be designed to accomplish specific objectives like; to facilitate background concentrations measurements, monitor current air pollution levels as a baseline for assessment, check the air quality relative to standards or limit values, health effects of air pollutants, detect the importance of individual sources, to develop abatement strategies, facilitate source apportionment and identification, develop and test analytical instruments, support legislation in relation to air quality limit values and guidelines, etc. According to the objectives, they need study design, field sampling, laboratory analysis, data management and data analysis. In the present study, field measurements were conducted to characterize the emissions of particulate and trace gases mainly from open burning practices of typical agricultural residues (rice and wheat crops) in and around Patiala city in India.

Patiala was chosen for research because there is no industry in the vicinity of the city and hence there is no point source of air pollution in the city. But, from the field survey it was estimated that there is a major problem of open burning of crop stubble in and around the city during April-May and October-November every year after wheat and rice crop harvesting, respectively. We examined the influence of stubble burning on the air quality of the city with respect to some selected parameters like suspended particulate matter, SO₂ and NO₂ in addition to the effect of wind speed and wind direction on the pollutant concentration. The amounts and types of emissions are likely to change every year due to changes in the nation's economy, technology improvements, industrial activity, traffic and some other factors. Air pollution regulations and emission controls also have an effect on the quality of ambient air. This study summarizes annual trends in emissions of air pollutants and gives an in-depth analysis of emissions during the years 2006 to 2010.

3.2 Study area and characteristics of sampling sites

Patiala is an earstwhile princely city of the state of Punjab, India with no major industry in and around its vicinity. It has 15 state government head offices including that of Punjab Pollution Control Board (PPCB), and has a railway and a bus terminus. It is located (Figure 1) in the southeastern part of the Punjab state of India (latitude between 29°49' and 30°47' N, longitude between 75°58' and 76°54' E). The area around Patiala city is predominantly agricultural (rural) with wheat and rice (paddy) as the two major crops with a combined cropping area of more than 86% of the total cultivated land. Farmers usually burn crop residue after crop harvesting during April–May (wheat crop harvesting period) and October–November (rice crop harvesting period).



Figure 3.1 Location map of Patiala, India

The climate here is typical of the Punjab plain, i.e., very hot in summer (average maximum temperature $43\pm 2^{\circ}\text{C}$) and very cold in winter (average minimum temperature $2\pm 2^{\circ}\text{C}$). On an average there are 61 rainy days with an annual average rainfall of $650\pm 30\text{ mm}$. The

variation in rainfall is appreciable. May is the hottest month and January is the coldest month (TERI, 2003). Wind direction of Patiala is North-West (NW) for most of the time period (Mittal et al., 2009).

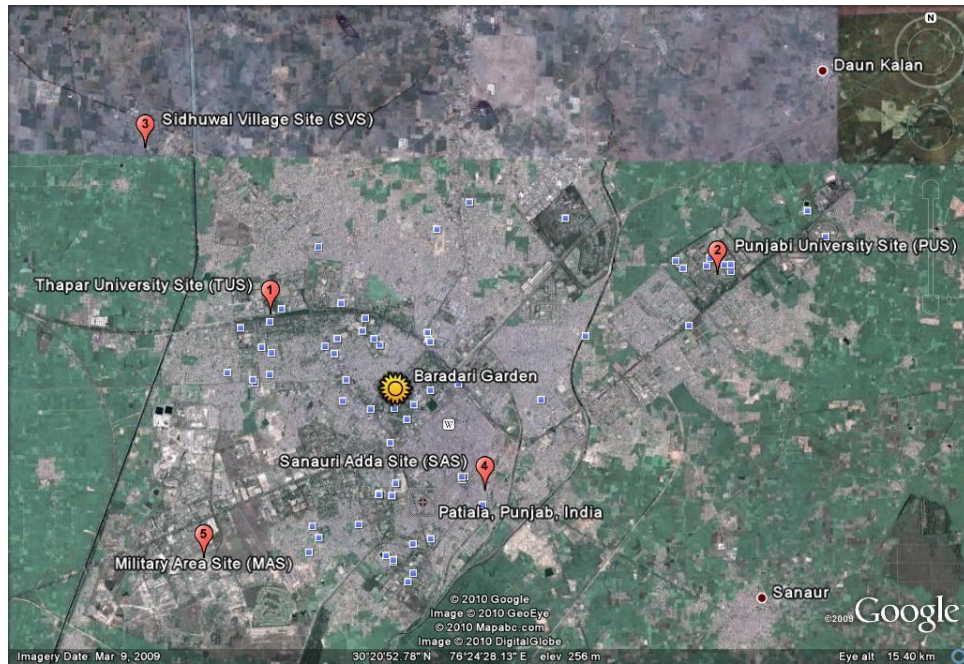


**Figure 3.2 Location map of different observation sites in and around Patiala
(Downloaded from Google Earth Software)**

Table 3.1 Summary of sampling locations

Site No.	Site Name (Ellipsis)	Landuse Pattern	Grid Reference	Direction and Distance from the centre of the city
1	Thapar University Site (TUS)	Urban site	Latitude - 30°21'05.42" N Longitude - 76°21'57.93" E	NW, 3 Km
2	Punjabi University Site (PUS)	Semi-urban site	Latitude - 30°21'28.10" N Longitude - 76°27'02.57" E	NE, 7 Km
3	Sidhuwal Village Site (SVS)	Rural site	Latitude - 30°22'42.14" N Longitude - 76°20'31.52" E	NW, 7 Km
4	Sanauri Adda Site (SAS)	Commercial site	Latitude - 30°19'23.14" N Longitude - 76°24'23.88" E	SE, 2 Km
5	Military Area Site (MAS)	Semi-urban site	Latitude - 30°18'41.31" N Longitude - 76°21'12.82" E	SW, 7 Km

Five locations (Figure 2) were selected in and around Patiala city for the monitoring of aerosol, SO₂ and NO₂ concentrations. These locations were selected carefully, taking natural wind direction and land use patterns into consideration. Accessibility of logistics like security of sampling instruments and electricity supply during air sampling was also taken into account. These five locations covered residential areas, urban areas, agricultural areas (rural areas), commercial and sensitive areas to observe the effect of crop residue burning on these areas. No industrial area was covered, as there is no major industry in the vicinity of Patiala city. All the sampling sites were located in downwind direction within a radius of 10 km. Baradari Garden was considered as the centre point of the city and distance of the various sampling sites was measured. A summary of the sampling sites is given in [Table 3.1](#).

3.2.1 Thapar University Site (TUS)

Thapar University has a campus of 250-acre (1.0 km²) in the historic city of Patiala (Punjab) having around 6,000 population. Use of powered vehicles by the boarding students (constituting about 60% of the population) is not allowed on the campus. However, day scholars are allowed bikes/scooters up to the University parking lot only. This site was considered as an urban area site. A sampling device (High Volume Sampler, HVS) was placed on the rooftop (at an appropriate height of the 12 meters from the ground level) of the PG Hostel building at Thapar University (Figure 3), about 25 meter away from the state highway (Patiala-Nabha) with a high proportion of three wheelers, bikes, cars and buses and about 5 km away from agricultural fields to the North-West (NW). The site had a broad open area with no side buildings.

3.2.2 Punjabi University Site (PUS)

Another HVS was placed on the rooftop of the Biotechnology Department building, Punjabi University, Patiala (Figure 4) at a height of 11 meters above ground level with no side buildings around and about 7 km away towards the North-East (NE) of the main city (Baradari Garden taken as centre of the city for reference point). It was located about 500 meters away from a very busy state highway (Patiala-Ambala) with high concentration of

heavy and light vehicles. Punjabi University Campus is very close to the agricultural fields (about 1 Km) on its northern side. Other land around the Punjabi University is covered with residential areas. The site is considered as a semi-urban area.

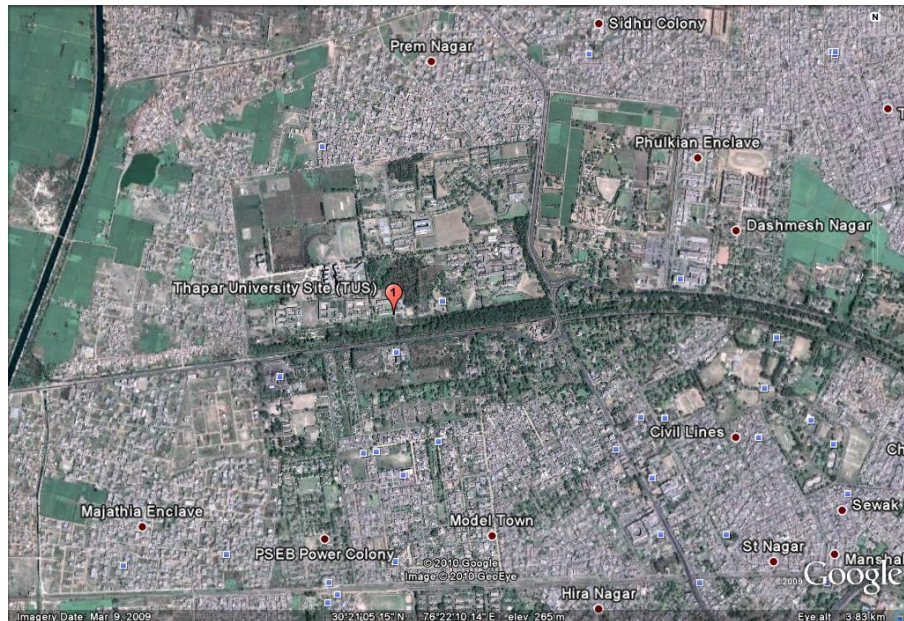


Figure 3.3 Land use pattern in and around Thapar University Site (TUS)



Figure 3.4 Land use pattern in and around Punjabi University Site (PUS)

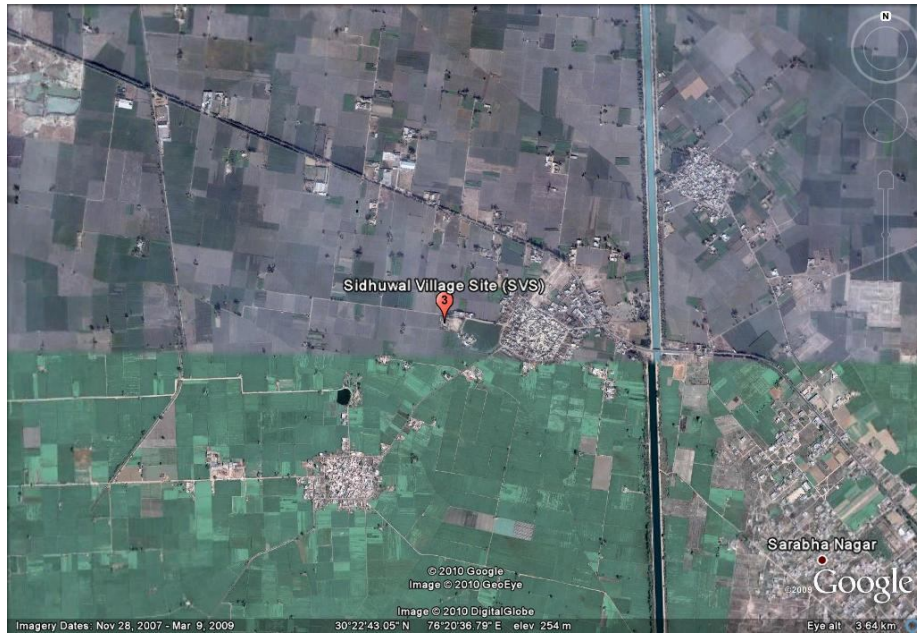


Figure 3.5 Land use pattern in and around Sidhuwal Village Site (SVS)

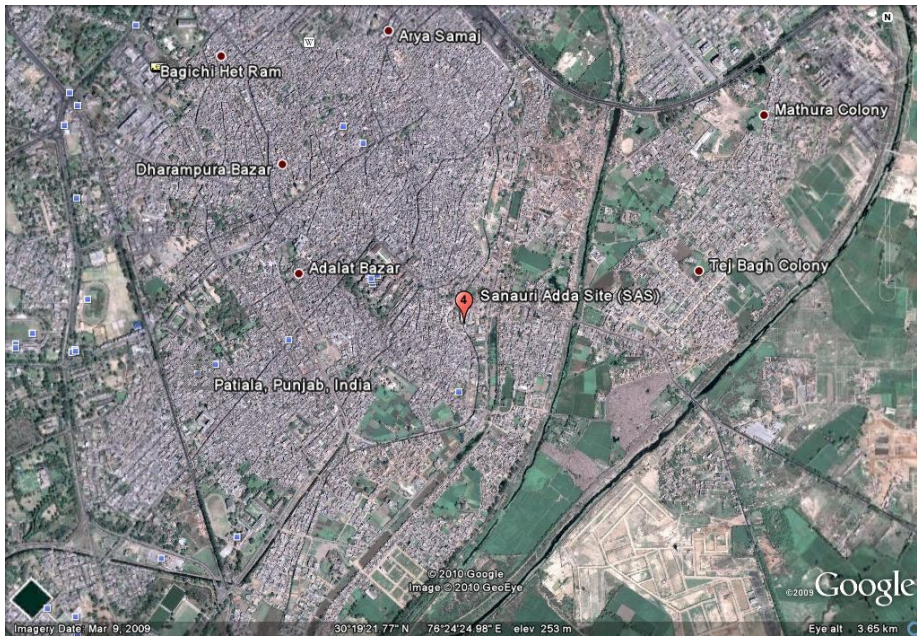


Figure 3.6 Land use pattern in and around Sanauri Adda Site (SAS)

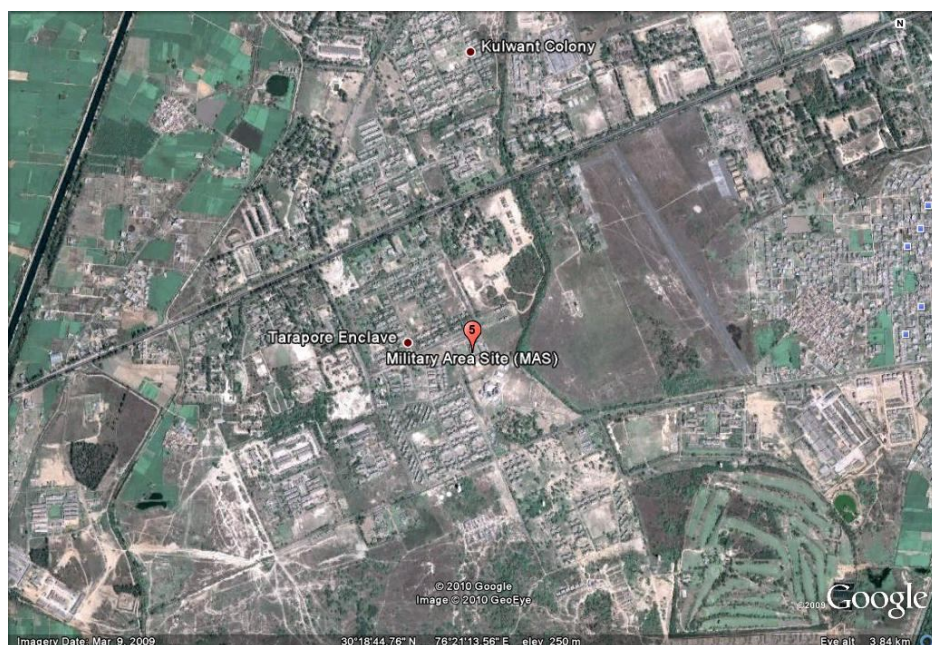


Figure 3.7 Land use pattern in and around Military Area Site (MAS)

3.2.3 Sidhuwal Village Site (SVS)

Sidhuwal village having a population of almost 2000 residents and about 7 km towards North-West (NW) of the Patiala city is a completely rural area around which a lot of agricultural fields are present. There is no activity in its vicinity other than agriculture. Also there is no industry in and around this village. The sampling device was placed on the first floor at the height of about 4.5 meter from the ground level. This site is located at the Govt Elementary School of Sidhuwal village. There is a pond in one side of the school and other sides are covered with agricultural fields.

3.2.4 Sanauri Adda Site (SAS)

Sanauri Adda region located in SE direction of the Patiala city is a very old area of the city having dense population and high vehicular activities. It is a commercial area with 3-4 small units of cotton seed oil mills. There is also a solid waste dumping place in this area spread over 5-7 acres of land. It releases foul smell and the intoxicants mix with groundwater and ambient air. This site is surrounded by urban area where there is no other source of air pollutants except for emissions from automobile movements and some diesel

driven power generation sets (installed in cotton seed extraction units) working for 4-5 hours daily. An HVS was placed on the second floor of a Secondary School (Prem Dham Sarvhitkari Vidya Mandir) about 8 meters above the ground level at the Sanauri adda market. Sanauri adda market located on the South-East (SE) of Patiala city is densely populated with a number of shops. This site was considered as a commercial site.

3.2.5 Military Area Site (MAS)

Military area in Patiala city is very less populated area as only military personnel are allowed to reside here within its vicinity. It is near about 7 kilometers away from the city. The fifth high volume sampler was installed on a rooftop of a central government school building (Kendriya Vidyalaya-3) in the military area. This sampling site is surrounded by some agricultural fields as most of the land is kept vacant and is used for the training of military persons. There is no industry in and around its vicinity of 5-10 Kms.

3.3 Monitoring and collection of SPM samples

To get entire coverage of air for SPM emanating from CRB and other activities, five High Volume Samplers (HVS, APM-430, Envirotech Instruments Pvt. Ltd, India) without size selective inlet were installed at five different sites and operated actively during the period 2006-2010 under natural atmospheric conditions at all the selected sites in Patiala (Pulikesi et al., 2006). SPM samples (particles of less than 100 μm size) were collected for 24 hours on pre-weighed Glass Micro Fiber Filter Sheets (GMF/A, 20 $\times$ 25 cm^2 size, Whatmann) at an average air flow rate of 1.5 $\text{m}^3 \text{min}^{-1}$ (Marrero et al 2005). Weight of SPM was estimated gravimetrically (IS: 5182 (Part XV), 1974) for the determination of concentration of aerosols in the ambient air. All the high volume samplers were calibrated and standardized once in every 6 months. Before and after the sampling, each blank unexposed filter sheet and exposed sampled filter sheet was conditioned for 24 h and then weighed at room temperature (25° C) and humidity (40%). This was to reduce the weighing errors produced by differences in temperature and humidity between weighings. After 24 hours continuous sampling, each filter sheet was removed from the sampler, folded with the particulate matter inside, placed in a clean polythene bag and carried into the laboratory for

conditioning and weighing. Silica gel (Loba Chemie) was used as a conditioning agent in desiccator and electronic balance (Sartorius, BT224S, Germany) was used for pre- and post- weighings (IS: 5182 (Part XIV), 1974). Electronic balance was calibrated with the automatic calibration system inbuilt in the balance after every 10 weighing. Samples were preserved in refrigerator (Samsung) maintained at 4° C after gravimetric estimation of SPM for further analysis.



Figure 3.8 Standardization of high volume samplers (HVS)

Weekly sampling was carried out during non-stubble burning months (pre- and post-burning months) and almost alternate day sampling was done consecutively during the stubble burning period from April 15 to May 15 (wheat harvesting period) and from October 15 to November 15 (rice harvesting period) each year. Sampling was carried out

two times in a week from October 1 to October 15 and from November 15 to November 30, at all the selected sampling locations. Thus, around 1000 aerosol samples were collected during the study campaign covering three wheat crop stubble burning periods and four rice crop stubble burning periods.

3.4 Sampling and measurement of NO₂ and SO₂ in ambient air of Patiala

Samples of NO₂ and SO₂ were collected from the ambient air simultaneously with the sampling of aerosols from five sites in and around Patiala city using Thermoelectric Gaseous Attachments VTG1 (APM411) used with HVS (APM410). Ambient air was incessantly drawn into 25 mL of NaOH solution in borosilicate glass impingers for 24 hour for the sampling of NO₂ and concentration was estimated by Jacob and Hochheiser (Modified Na-Arsenite) method (IS: 5182 (Part VI), 1974). For the sampling of SO₂, 25 mL of 0.04 M potassium tetrachloro-mercurate (TCM) solution was used as an absorber in the borosilicate glass impingers and concentration of SO₂ was determined by West-Gaeke method (West and Gaeke, 1956). Specified absorbing solution (TCM for SO₂ and NaOH for NO₂) was kept inside a Thermoelectric Gaseous Attachment and airflow rate was adjusted in individual impingers with the help of the manifold provided. Impingers had been placed in an ice tray to improve the absorption efficiency of the system and prevent loss of absorbing solutions by evaporation. Gas samplers were also standardized and calibrated once in 6 months by running all the instruments simultaneously at one location and correcting the difference in gas flow meters, if any. Samples were brought to the laboratory and stored in a refrigerator in 60 mL size plastic bottles at 4° C.

3.5 Measurement of meteorological parameters

Concentration of air pollutants is not a steady value and depends on a number of factors including the sources and the ambient climate. A high wind velocity and the frequency of the wind direction can play an essential role in spatial and seasonal variations of air pollutants. Humidity and temperature can also play a crucial role in seasonal and temporal variations in the concentration of air pollutants. Meteorological parameters like wind direction, wind speed, temperature, relative humidity, atmospheric pressure and rainfall

were monitored during the sampling periods (Gupta and Cheong, 2006). The data were obtained from the global weather monitoring website (www.wunderground.com).

3.6 Characterization of aerosol samples

Collected ambient air SPM samples were analyzed for the determination of organic tarry matter content (OTM), and ignitable matter in terms of loss on ignition (LOI). Following methods were adopted for the analysis of samples:

3.6.1 Determination of organic tarry matter (OTM)

Soxhlet extraction technique has been widely used for extracting a variety of organic compounds from solid matrices. Organic solvents like benzene, cyclohexane, dichloromethane, methanol-chloroform, etc. are commonly used for extraction (Bowyer and Pleil, 1997; Appel et al., 1976, 1979). In the present study, soxhlet extraction was applied to determine organic tarry matter concentration. A fraction soluble in organic solvents represents the organic tarry matter (OTM) present in samples. Samples were extracted with dichloromethane (DCM) using a customized procedure based on various used practices (Shannigrahi et al., 2005; Stephanou and Stratigakis, 1993; Gogou et al., 1998; Alves et al., 1999, Oros and Simoneit, 2001).

A quadrant of each aerosol sample was extracted with 150 mL DCM (Merck, India) for a period of 8 hours using a soxhlet extractor. Solvent was reduced to 5 mL at steam bath temperature (steam bath treatment of organic extracts is not expected to produce significant loss of organic aerosol constituents). The extracts were then filtered through Whatman filter thimbles and transferred to pre-weighed chromatographic amber vials. The filtrates were dried at room temperature and the weight of the extracts was determined with a microbalance (Sartorius, BT224S, Germany).

3.6.2 Determination of loss on ignition (LOI)

Loss on ignition (LOI) test has been widely used as a screening tool to estimate the organic and carbonate contents of sediments as an indicator of non-volatile organic matter in the

sample. (Dean et al., 1974; Bengtsson and Enell, 1986; Heiri et al., 2001; Boyle, 2004; Folliard et al., 2006). Despite the importance and relevance of the LOI test, the LOI test results are sensitive to practical variations that are within the requirements of the ASTM C 311 test standard. When thermal treatment is applied to any particulate sample, in the first reaction organic matter is oxidized at 500-550° C to carbon dioxide (CO₂) and ash. In the second reaction, CO₂ is evolved from carbonate leaving oxide.

LOI tests on ambient aerosol samples were performed considering cooling time, sample size, ignition duration, and ignition temperature. An electrically heated temperature controlled Muffle Furnace (Sciential, India) capable of maintaining a high temperature of 800°±10° C was used for the determination of loss on ignition in aerosol samples. A quadrant of each exposed filter was placed in a pre-weighed silica crucible and ignited at 600±10° C in a muffle furnace for 3 hours. The crucibles were removed from the furnace (at 50° C), placed in the desiccator for cooling and weighed to a constant weight using a microbalance. A blank glass micro fiber filter was also ignited under the same conditions and the weight of the residue was subtracted from the observed weights (Marr et al., 1999; Rukmangad et al. 1991).

3.7 Quantification of heavy metals in ambient air

Preserved SPM samples were analyzed for the determination of potassium (K), copper (Cu), nickel (Ni) and zinc (Zn) concentration in the ambient air of Patiala. The collected SPM samples were prepared by digesting ¼ portion of each filter sheet in a mixture of concentrated nitric acid (HNO₃) (AR grade, Sdfine Chem, India) and concentrated hydrochloric acid (HCl) (35-40%, GR, Lobachemie, India) (3:1 ratio) at 70° C temperature for one and half hour using hot plate digestion system placed in a fuming hood fitted with a system to exhaust the fumes and gases (Method IO-3.2, 1999; NIOSH Method-7300, 1984, US EPA, 1999b). The extract was filtered through Whatman filter and final volume was made up to 100 mL in a volumetric flask by adding deionized water. Metals concentration was determined in the flask. Potassium concentration was determined by Flame Photometer at an airflow rate of 15 lpm (Zhuang et al., 1992, 2001; Park et al., 2001, 2005; Sun et al., 2004) while Cu, Ni and Zn concentrations were determined by the Atomic Absorption

Spectrophotometer (AAS) (Elementas, AAS4129, ECIL, India) with the analytical conditions as shown in Table 3.2. Metals concentrations were also measured in solutions of blank filters and were treated in a similar way as the filters loaded with SPM to establish a baseline and the concentration was subtracted from the concentration of true samples (Marrero et al., 2005). Analytical standards were purchased from Merck, India and used for the calibration of Atomic Absorption Spectrophotometer.

Table 3.2 Analytical conditions of Atomic Absorption Spectrophotometer for the analysis of different metals

Metal	Analytical conditions
Copper (Cu)	Lamp current 3.5mA, Air flow 12 lpm, Acetylene 1.8 lpm, Wavelength 324.8 nm, Slit 0.5 nm.
Nickel (Ni)	Lamp current 3.5mA, Air flow 12 lpm, Acetylene 1.8 lpm, Wavelength 232.0 nm, Slit 0.2 nm.
Zinc (Zn)	Lamp current 5mA, Air flow 12 lpm, Acetylene 1.8 lpm, Wavelength 213.9 nm, Slit 1.0 nm.

3.8 Quantification of polycyclic aromatic hydrocarbons (PAHs) in ambient air

SPM samples were analyzed by Gas Chromatography (USEPA, Compendium method TO-13A, 1999; TO-13A, 1999) to determine the levels of PAHs during WCRB, RCRB and NCRB months. SPM samples collected during 2006-2007 were prepared for the analysis. Glasswares were properly cleaned and dried before use to avoid any contamination in samples. Organic Tarry Matter (OTM) extracts were further analyzed for PAHs by using a gas chromatograph (NUCON5765). Each extracted samples was prepared in 1 mL acetonitrile (HPLC grade, Merck, India) for the analysis. A volume of 1 μ L of each prepared sample was injected into the Gas Chromatograph (NUCON5765) fitted with FID and the corresponding peaks were obtained.

3.8.1 Optimization of GC-FID parameters

GC-FID parameters were optimized prior to the analysis of samples. A standard mixture of 16-PAHs was used (standard solution from Sigma-Aldrich, 1 ml of which contains 10 μ g of each of 16 PAHs) for standardization as well as optimization of GC-FID conditions. 1 μ L of

standard PAH solution was injected frequently for determining the retention time of different PAHs for studying the reproducibility of the detector. All the 16 PAHs were well resolved. The optimum conditions of GC were obtained after a series of experiments so that the targets PAHs species were well resolved (Table 3.3). These conditions were used for determination of 16 PAHs in ambient air SPM samples.

Table 3.3 Conditions for Gas Chromatograph with FID (GC-FID)

Parameters	Specification/ operating conditions
GC column	Supelco 28089-U, Equity-5, 30 m, 0.25mm i.d., 0.25 μ m film thickness
Liner	Liner Splitless glass liner
Carrier gas	Ultra purified Nitrogen gas, 99.99% pure, (35 ml min ⁻¹)
Injection type	Split (1:9)
Injection port temperature	280°C
Detector (temperature)	FID (325°C)
Oven temperature	50°C (hold 5 min) to 275°C @4°C min ⁻¹ to 320 @5°C min ⁻¹
Injection volume	1 μ L
Fuel gas and flow rate	Hydrogen gas (30 ml min ⁻¹)
Oxidant gas and flow rate	Air (300 ml min ⁻¹)

Table 3.4 Retention Times (R_t) of 16 PAHs for standard solution (Sigma-Aldrich)

S. No.	PAH	Ellipsis	Retention Time (R _t) (Minutes)
1	Naphtahlene	Nap	7.5
2	Acenaphthene	Acp	13.04
3	Acenaphthylene	AcPy	13.4
4	Fluorene	Flu	15.22
5	Phenanthrene	PA	18.26
6	Anthracene	Ant	18.34
7	Fluoranthene	FL	19.15
8	Pyrene	Pyr	21.59
9	Benzo[a]anthracene	B(a)A	22.37
10	Chrysene	CHR	23.4
11	Benzo[b]fluoranthene	B(b)F	26.11
12	Benzo[k]fluoranthene	B(k)F	26.24
13	Benzo[a]pyrene	B(a)P	27.15
14	Indeno(1,2,3-c,d)pyrene	IND	30.38
15	Dibenzo(a,h)anthracene	DBA	30.44
16	Benzo(g,h,i)perylene	B(ghi)P	32.19

3.8.2 Identification and quantification of PAHs

The identification and quantification of PAHs was accomplished by using a gas chromatograph (NUCON5765) with an Equity-5 (Supelco) capillary column with FID. The GC-FID operating conditions and the retention times of 16 PAHs (Sigma Aldrich) are given in Tables 3.3 and 3.4 respectively. The retention time of each PAH component in sample was compared with the retention times of standard PAHs and were quantified by considering area under the respective peak (in terms of mV-sec) as a quantitative parameter.

References

Alves, C.P., Duarte, A., 1999. The organic composition of air particulate matter from rural and urban portuguese areas. *C Physics and Chemistry of the Earth, Part B: Hydrology, Oceans and Atmosphere* 24 (6), 705-709.

Appel, B.R., Colodny, P., Wesolowski, J.J., 1976. Analysis of carbonaceous materials in southern California atmospheric SPM. *Environmental Science & Technology* 10 (4), 359-363.

Appel, B.R., Hoffer, E.M., Kothny, E.L., Wall, S.M., Haik, M., 1979. Analysis of Carbonaceous Material in Southern California Atmospheric SPM. *Environmental Science & Technology* 13 (1), 98-104.

Bengtsson, L., Enell, M., 1986. Chemical analysis, In Berglund B.E. (ed.), *Handbook of Holocene Palaeoecology and Palaeohydrology*. John Wiley & Sons Ltd., Chichester, 423-451.

Bowyer, J.R., Pleil, J.D., 1997. Comparison of supercritical fluid extraction and Soxhlet extraction of organic compounds from carpet samples. *Journal of Chromatography A* 787 (1-2), 171-179.

Boyle, J.F., 2004. A comparison of two methods for estimating the organic matter content of sediments: comment. *Journal of Paleolimnology* 31 (1) 125-127.

Dean, W.E., 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. *Journal of Sedimentary Research* 44, 242-248.

Folliard, K.J., Harris, N.J., Hover, K.C., Ley, T., 2006. Variables Affecting the ASTM Standard C 311 Loss on Ignition Test for Fly Ash. *Journal of ASTM International* 3 (8), 1-12.

Gogou, A., Apostolaki, M., Stefanou, E.G., 1998. Determination of organic molecular markers in marine SPM and sediments: One-step flash chromatography compound class fractionation and capillary gas chromatography analysis. *Journal of Chromatography* 799, 215-231.

IS: 5182 (Part VI), 1974. Nitrogen oxides, Indian standard methods for measurement of air pollution.

IS: 5182 (Part XIV), 1974. Guidelines for planning the sampling of atmosphere, Indian standard methods for measurement of air pollution.

IS: 5182 (Part XIV): Guidelines for planning the sampling of atmosphere, Indian standard methods for measurement of air pollution (1974)

IS: 5182 (Part XV), 1974. Mass concentration of particulate matter in the atmosphere, Indian standard methods for measurement of air pollution.

Katz, M.: *Methods for Air Sampling and Analysis*, 2nd ed., APHA Press, INC, Springfield, VA (1977)

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.

Marrero, J., Rebagliati, R.J., Gomez, D., 2005. Smichowski, P.: A study of uniformity of elements deposition on glass fiber filters after collection of airborne particulate matter (PM-10), using a high-volume sampler. *Talanta* 68, 442-447.

Method IO-2.1: Sampling of ambient air for total suspended particulate matter (SPM) and PM10 using high volume sampler. In *Compendium of methods for the determination of inorganic compounds in ambient air*, EPA/625/R-96/010a, US Environmental protection agency, Cincinnati, OH (1999)

Method IO-3.2: Determination of metals in ambient particulate matter using Atomic Absorption (AA) spectroscopy. In *Compendium of methods for the determination of inorganic compounds in ambient air*, EPA/ 625/R-96/010a, US Environmental protection agency, Cincinnati, OH (1999)

Mittal, S.K., Goyal, S., 2004. SPM levels of an urban area (Patiala City) and its relation to automobile exhaust. *Clean Technology Environment Policy* 6, 263-267.

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

NIOSH Method-7300: NIOSH manual of analytical methods. Cincinnati: National Institute of Occupational Safety and Health (1984)

Oros, D.R., Simoneit, B.R.T., 2001. Identification and emission factors of molecular tracers in organic SPM from biomass burning Part 1: Temperate climate conifers. *Applied Geochemistry* 16 (13), 1513-1544.

Park, S.S., Bae, M.S., Kim, Y.J., 2001. Chemical composition and source apportionment of PM_{2.5} particles in the Sihwa area, Korea. *Journal of Air & Waste Management Association* 51, 393-405.

Park, S.S., Kim, Y.J., 2005. Source contribution to fine particulate matter in an urban atmosphere. *Chemosphere* 59, 217-226.

Pulikesi, M., Baskaralingam, P., Elango, D., Rayudu, V.N., Ramamurthi, V., Sivanesan, S., 2006. Air quality monitoring in Chennai, India, in the summer of 2005. *Journal of Hazardous Materials* 136 (3), 589-596.

Rukmangad, P.P., 1991. Particle size distribution and its elemental composition in the ambient air of Nagpur City. *Indian Journal of Environmental Protection* 11 (6) 409-412.

Sun, Y., Zhuang, G., Wang, Y., Han, L., Guo, J., Mo Dan, Wenjie, Wang, Z., Hao Z., 2004. The air borne particulate pollution in Beijing-concentration, composition, distribution and sources, *Atmospheric Environment* 38, 5991-6004.

TERI: Report No. 2003SF62, ch. 15, Patiala, DBAS (Patiala), Punjab, pp. 317-338 (2003).

TO-13A: Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatographic/Mass Spectrometry (GC/MS), January 1999

USEPA, Compendium method TO-13A, 1999, Determination of polycyclic aromatic hydrocarbons (PAHs) in ambient air using gas chromatography-mass spectrometry (GC-MS),.

West, P.W., Gaeke, G.C., 1956. Fixation of sulfur dioxide as Disulfitomercurate (II) and Subsequent Colorimetric Estimation. *Analytical Chemistry* 28 (12), 1816-1819.

Zhuang, G., Guo, J., Yuan, H., Zhao, C., 2001. The compositions, sources, and size distribution of the dust storm from China in spring of 2000 and its impact on the global environment. *Chinese Science Bulletin* 46, 895-901.

Zhuang, G., Yi, Z., Duce, R.A., Brown, P.R., 1992. Link between iron and sulfur suggested by the detection of Fe (II) in remote marine SPMs. *Nature* 355, 537-539.

CHAPTER 4

EFFECT OF WHEAT AND RICE CROP RESIDUE BURNING EPISODES ON THE AMBIENT AIR LEVELS OF SPM, SO₂ AND NO₂

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4.1 Rice and Wheat cultivation around the world and in India

Rice or paddy (*Oryza sativa*) is the most important staple food for a large part of the world's human population, especially in East, South, Southeast Asia, the Middle East, Latin America and the West Indies. It is the grain with the second highest worldwide production after maize (corn). Rice cultivation is the principal activity and source of income for millions of households around the globe. Several countries of Asia and Africa are highly dependent on rice as a source of foreign exchange earnings and government revenue. Rice can be grown practically anywhere, even on a steep hill or mountain. Although its parent species are native to South Asia and certain parts of Africa, centuries of trade and exportation have made it commonplace in many cultures worldwide. Wheat (*Triticum aestivum*) is also a staple food and cultivated worldwide. In 2008-2009, the world production of wheat was 682-683 million tons respectively, making it the third most-produced cereal after maize and rice.

4.2 Episodes of rice and wheat crop residue burning

Burning of crop residue is a global problem and the period of burning depends upon the harvesting time, which further varies from region to region. Every country or even different regions within a country have their own way of harvesting and processing of different crops. Rice and wheat are the two major crops in Punjab. Rice crop is harvested during October and wheat crop is harvested in April every year. Farmers perform burning of crop residue after harvesting of these crops. Rice crop residue burning (RCRB) starts by the mid of October and continues up to the middle of November while that of Wheat crop residue burning (WCRB) (Figure 4.1) starts from the middle of April and continues up to the mid of May every year in different regions of India, especially Punjab, Haryana and western Uttar Pradesh. After harvesting of these crops, a large amount of residue is left in the fields.

Farmers burn this residue to clear the fields for the next crop. This releases a lot of particulate and gaseous pollution into the atmosphere.

4.3 Biomass burning as a source of SPM and gaseous pollution

Biomass burning is an important source of suspended particulate matter (SPM) and gaseous pollution in the atmosphere, having potential impact on global air quality and climate chemistry (Andreae, 1991; Levine et al., 1995; Duan et al., 2004; Lemieux et al., 2004; Andreae and Merlet, 2001; Yang et al., 2008). Pollutants emanated from biomass burning can also affect properties, materials and moreover human health when they are inhaled, causing respiratory problems (Schwartz, 1993; Godish, 1997; Mohanraj and Azeez, 2004; Thaller et al., 2004; WHO, 2004; Pandey et al., 2005). Limited studies on emissions from open burning of agricultural residues have been conducted. An experiment (in situ) for wheat straw burning was undertaken in India for developing specific emission factors (EFs). Although these EFs were generated from a single field experiment, yet they addressed an important information gap on field burning of crop residue in the region (Sahai et al., 2007). Jenkins and Turn urbanized a wind channel to simulate agricultural burning and measured its particulate and gaseous emissions (Turn et al., 1997; CARB, 1996). Oppenheimer et al., (2004) reported NO₂ emissions from sugar cane field burning in Sao Paulo, Brazil. Hays et al. (2005) simulated agricultural fire in an enclosure and presented the physical and chemical characterization of SPM emissions. Nguyen et al., 1994 conducted ground experiments and measured CO₂, CO, and CH₄ outcomes from rice straw burning in Vietnam. Li et al. (2007) reported particulate and trace gas emissions from open burning of wheat straw and corn stover in China. Dhammapala et al. (2006) performed wheat and bluegrass residue burn experiments at the USEPA open burning test chamber and measured PM_{2.5}, CO₂, CO, and total hydrocarbon emissions. In contrast to the wealth of data generated in industrialized countries, there have been few studies on air pollution in developing areas of the world. Moreover, data on crop residue burning effects on ambient air are inadequate. The emission factors in the database for agricultural residues are mainly based on extrapolation, which may cause high uncertainty in emission estimates. In addition, air quality is significantly affected because of agricultural field burning during

the harvest period. To determine its contribution to ambient air quality, SPM and gaseous pollutants source profiles from agricultural fire are needed.



Figure 4.1 Residue burning in Sidhuwal Village (Patiala) during wheat harvesting month (May) in 2007

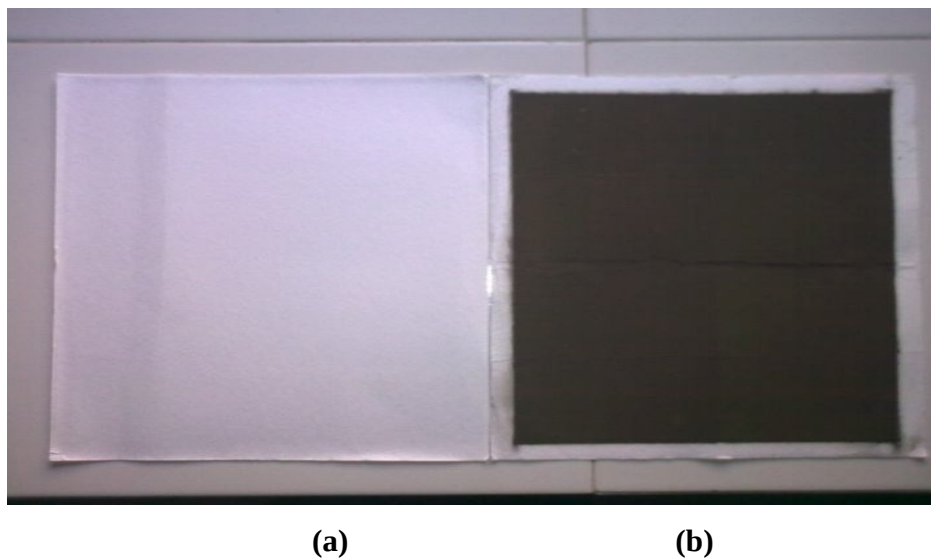


Figure 4.2 Physical appearances of GMF/A filters before sampling (a) and after SPM loading (b). Filters become black after 24 hour SPM sampling.

Results of analyzed IRS-P6 Advanced Wide Field sensor (AWiFS) satellite data of Punjab state of India for two different crop harvesting seasons have shown that nearly 5504 Km² [75]

area was under WCRB and 12,685 Km² under RCRB in 2005 (Badrinath et al., 2006). In another study an attempt was made to identify biomass burning areas of agriculture residue for Punjab during May 2005 (WCRB month) using satellite remote sensing data (AWiFS) obtained from a knowledge-based classification approach using See5 algorithm which showed a district- wise burned area distribution. The estimated total burnt area was found to be around 4315 Km² during the wheat harvesting season (Punia et al., 2008). Emissions estimated from the rice field burning were 261 Gg of CO, 19.8 Gg of NO_x, 3 Gg of CH₄, 30 Gg of PM₁₀ and 28.3 Gg of PM_{2.5} during October 2005 (Badrinath et al., 2006). In Punjab, more than 90% of the rice and 80% of the wheat is harvested using combine harvesters, leaving loads of up to 9 tonnes per hectare of rice residue in the fields, and 80% of farmers burn the residue. More than 15 million tonnes of rice residue and around 5 million tonnes of wheat residue are burned each year in Punjab (Patel, 2008).

4.4 Results and Discussion

SPM, SO₂ and NO₂ levels were monitored during September 2006 to February 2010 at five different locations in Patiala, India covering three rice and four wheat harvesting seasons to estimate the contribution of crop residue burnings in the increase in levels of these parameters. The frequency of sampling was kept low at once in a week at each site during non-crop residue burning (NCRB) periods, as there was not much variation during these months, but during crop residue burning (CRB) periods, alternate day sampling was carried out throughout the study period. This was done to average out the monthly variation in SPM, SO₂ and NO₂ levels. Glass Micro Fibre filter sheets become black after loadings of SPM (Figure 4.2) from 24 hour sampling.

4.5 SPM variations during NCRB and CRB months

As described earlier, SPM sampling was carried out at five monitoring sites having different land use patterns. Depending upon the nature of the site, various trends were observed and monthly averaged data are discussed. Levels were compared with the National Ambient Air Quality Standards (NAAQS) (100 µgm⁻³ for sensitive area, 200 µgm⁻³ for residential area and 500 µgm⁻³ for industrial area) set by the Central Pollution Control

Board (CPCB) and many times the observed values were found to exceed the NAAQS standards. Overall SPM concentration (monthly average of all the sampling sites) ranged between $126 \mu\text{gm}^{-3}$ - $458 \mu\text{gm}^{-3}$ during 2006-2010. The monthly average SPM mass concentrations with standard deviation at different monitoring sites are given in Table 4.1 and the overall trend is shown in Figures 4.3 and 4.4. The monthly average SPM concentration ranged from a minimum $70 \mu\text{gm}^{-3}$ to a maximum of $560 \mu\text{gm}^{-3}$ during September 2006 to February 2010. The monthly average data of SPM mass concentration with standard deviation at different monitoring sites is presented in Table 4.1.

4.5.1 SPM concentration during NCRB months

Average SPM concentration levels at different monitoring sites varied between $189 \mu\text{gm}^{-3}$ and $247 \mu\text{gm}^{-3}$ during NCRB months with highest concentration at SAS and lowest at TUS (Figure 4.3). The succession of different sites in the increasing order of SPM concentration levels was $\text{TUS} < \text{PUS} < \text{MAS} < \text{SVS} < \text{SAS}$. The reason for higher concentration levels of SPM at SAS is that it is a mixed use area site covering commercial and residential area with 3-4 cottonseed oil mills and a lot of vehicular movement. Moreover, the site is situated in South-East (SE) of the city and collects all the particulate matter coming from the North-West (NW) of the city since wind direction of the city was NW for most of the monitoring period as is seen from wind rose diagrams (4.13 a-e).

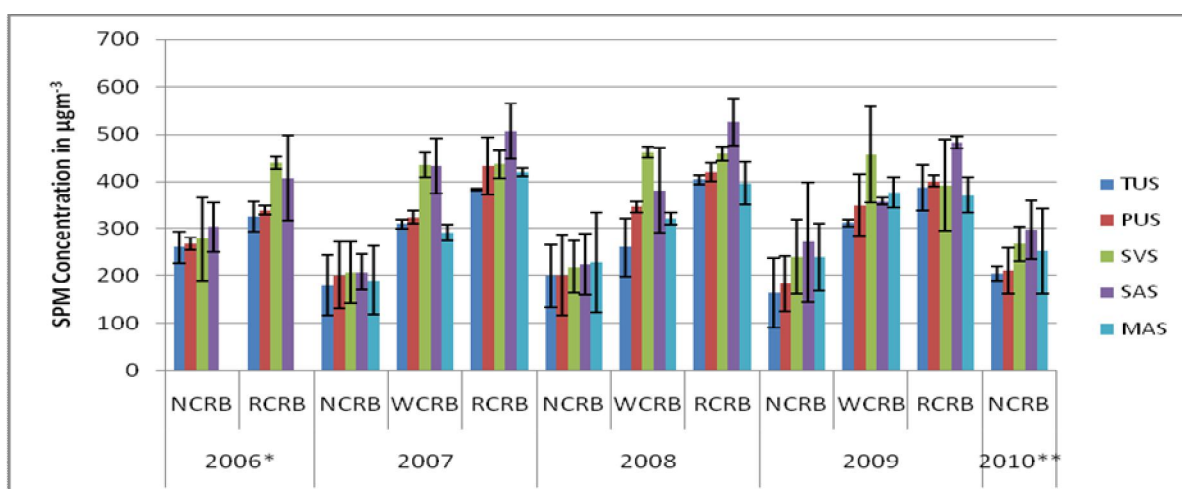


Figure 4.3 Sporadic variation in SPM levels at different monitoring sites; *an average of 4 months observations (September to December); and **an average of 2 months observations (January-February).

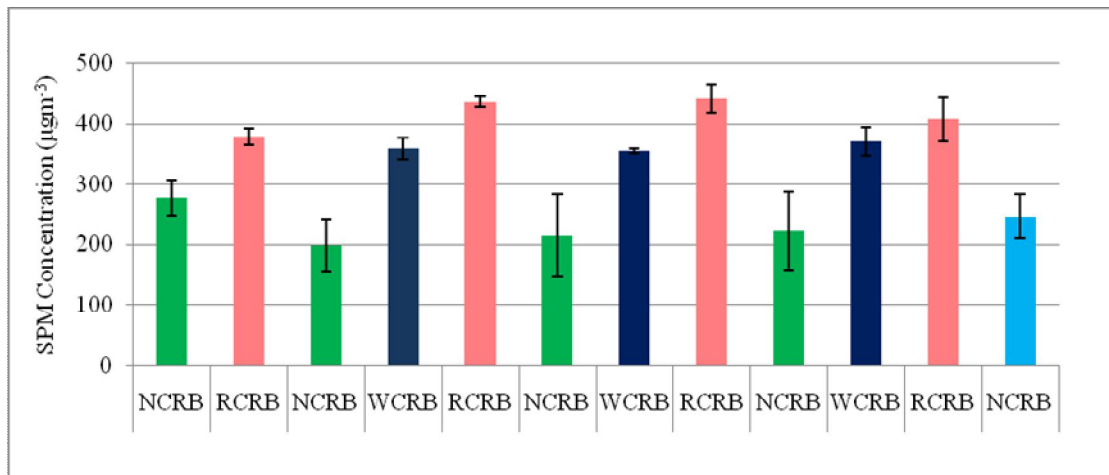


Figure 4.4 Variation in SPM levels during different sampling episodes

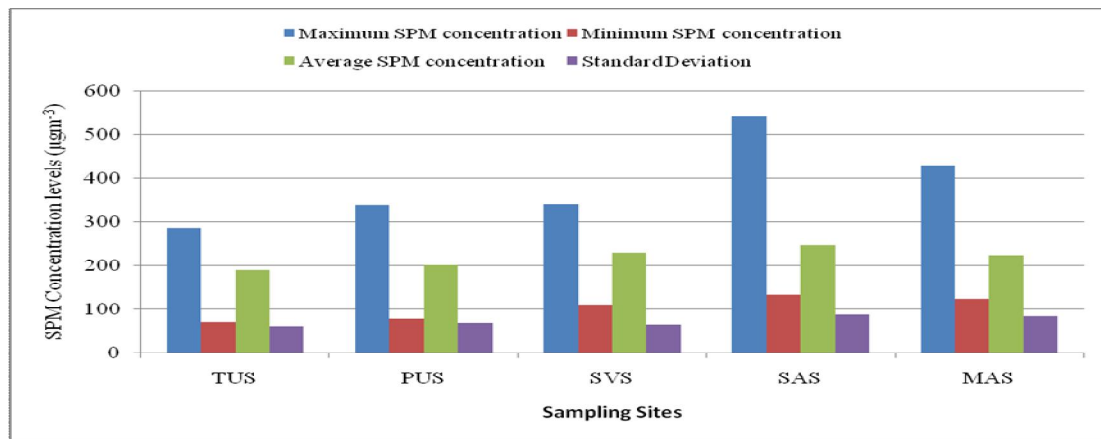


Figure 4.5 (a) SPM levels at different monitoring sites

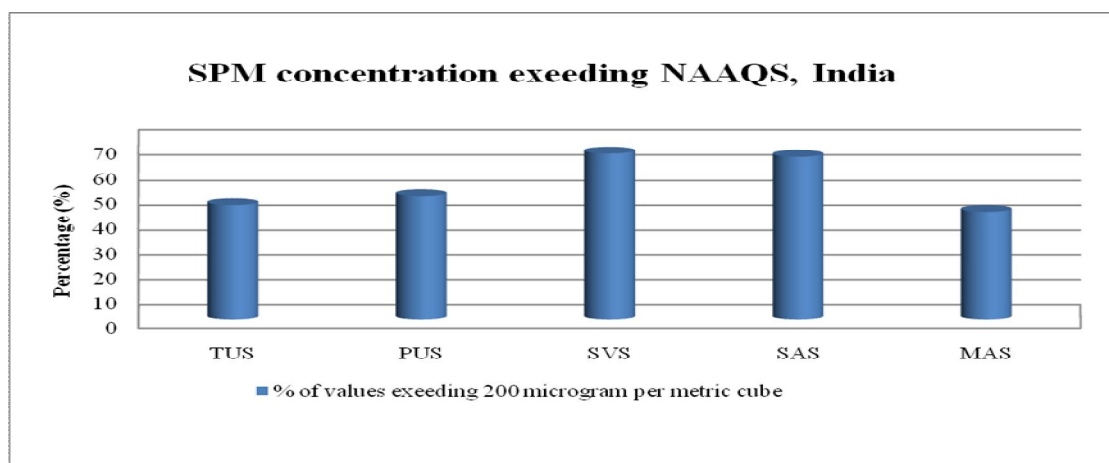


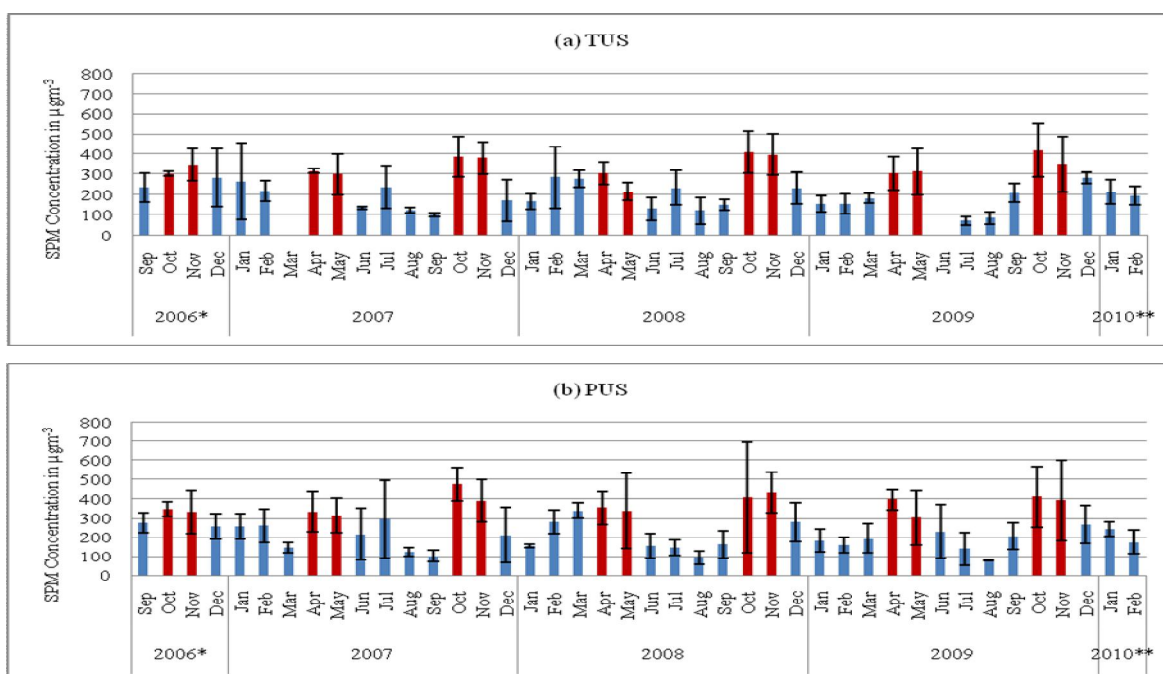
Figure 4.5 (b) SPM concentration levels exceeding the permissible limit of 200 µgm⁻³ at different monitoring sites

Table 4.1 Monthly average concentrations of SPM at different monitoring sites

Year	Periods	Month	SPM concentration ($\mu\text{gm}^{-3}\pm\text{SD}$)				
			Sampling Sites				
			TUS	PUS	SVS	SAS	MAS
2006*	NCRB	Sep	235 $\pm$ 72	276 $\pm$ 50	341 $\pm$ 60	340 $\pm$ 55	NA
	RCRB	Oct	302$\pm$13	345$\pm$37	429$\pm$98	470$\pm$101	NA
		Nov	347$\pm$81	332$\pm$112	449$\pm$132	343$\pm$176	NA
	NCRB	Dec	283 $\pm$ 144	257 $\pm$ 64	215 $\pm$ 40	265 $\pm$ 6	NA
2007	NCRB	Jan	266 $\pm$ 189	257 $\pm$ 67	257 $\pm$ 61	157 $\pm$ 12	NA
		Feb	218 $\pm$ 50	261 $\pm$ 87	282 $\pm$ 103	NA	144 $\pm$ 19
		Mar	NA	146 $\pm$ 29	NA	NA	180 $\pm$ 36
	WCRB	Apr	316$\pm$12	334$\pm$103	453$\pm$169	474$\pm$89	278$\pm$60
		May	301$\pm$101	313$\pm$89	416$\pm$98	392$\pm$99	303$\pm$70
	NCRB	Jun	135 $\pm$ 8	214 $\pm$ 136	179 $\pm$ 108	239 $\pm$ 120	302 $\pm$ 153
		Jul	238 $\pm$ 104	293 $\pm$ 203	266 $\pm$ 139	175 $\pm$ 112	NA
		Aug	121 $\pm$ 14	122 $\pm$ 22	111 $\pm$ 22	209 $\pm$ 56	137 $\pm$ 14
		Sep	100 $\pm$ 11	100 $\pm$ 30	145 $\pm$ 50	205 $\pm$ 80	126 $\pm$ 37
	RCRB	Oct	385$\pm$101	475$\pm$86	457$\pm$106	465$\pm$91	426$\pm$124
		Nov	381$\pm$80	390$\pm$110	416$\pm$171	547$\pm$152	413$\pm$138
	NCRB	Dec	172 $\pm$ 103	210 $\pm$ 144	200 $\pm$ 46	257 $\pm$ 119	250 $\pm$ 164
2008	NCRB	Jan	166 $\pm$ 38	154 $\pm$ 10	159 $\pm$ 23	198 $\pm$ 13	200 $\pm$ 10
		Feb	285 $\pm$ 153	281 $\pm$ 60	302 $\pm$ 88	274 $\pm$ 64	294 $\pm$ 50
		Mar	276 $\pm$ 42	337 $\pm$ 40	251 $\pm$ 76	354 $\pm$ 63	301 $\pm$ 41
	WCRB	Apr	303$\pm$55	354$\pm$85	470$\pm$164	317$\pm$98	311$\pm$91
		May	216$\pm$47	337$\pm$197	452$\pm$218	445$\pm$162	330$\pm$148
	NCRB	Jun	131 $\pm$ 57	154 $\pm$ 65	204 $\pm$ 109	191 $\pm$ 64	133 $\pm$ 69
		Jul	233 $\pm$ 83	145 $\pm$ 41	241 $\pm$ 43	221 $\pm$ 17	165 $\pm$ 82
		Aug	121 $\pm$ 65	93 $\pm$ 33	132 $\pm$ 88	155 $\pm$ 26	124 $\pm$ 72
		Sep	148 $\pm$ 27	162 $\pm$ 73	195 $\pm$ 118	162 $\pm$ 91	175 $\pm$ 52
	CRB-R	Oct	410$\pm$105	405$\pm$288	447$\pm$201	490$\pm$144	363$\pm$182
		Nov	397$\pm$103	433$\pm$106	469$\pm$186	560$\pm$128	428$\pm$170
	NCRB	Dec	232 $\pm$ 76	279 $\pm$ 100	257 $\pm$ 95	233$\pm$49	428 $\pm$ 170
2009	NCRB	Jan	154 $\pm$ 41	183 $\pm$ 60	213 $\pm$ 71	212 $\pm$ 34	150 $\pm$ 28
		Feb	154 $\pm$ 51	160 $\pm$ 42	159 $\pm$ 34	196 $\pm$ 30	177 $\pm$ 61
		Mar	183 $\pm$ 26	194 $\pm$ 75	171 $\pm$ 35	283 $\pm$ 171	194 $\pm$ 74
	CRB-W	Apr	306$\pm$83	395$\pm$54	528$\pm$176	353$\pm$87	353$\pm$61
		May	316$\pm$114	303$\pm$141	384$\pm$174	363$\pm$110	399$\pm$221
	NCRB	Jun	NA	230$\pm$139	338$\pm$118	330$\pm$128	231$\pm$7
		Jul	70 $\pm$ 20	139 $\pm$ 85	203 $\pm$ 127	183 $\pm$ 100	274 $\pm$ 112
		Aug	84 $\pm$ 29	78 $\pm$ 3	334 $\pm$ 57	134 $\pm$ 10	288 $\pm$ 106
		Sep	209 $\pm$ 46	207 $\pm$ 70	174 $\pm$ 33	290 $\pm$ 35	NA
	CRB-R	Oct	421$\pm$133	410$\pm$155	459$\pm$88	474$\pm$80	398$\pm$103
		Nov	352$\pm$137	392$\pm$208	323$\pm$82	491$\pm$243	344$\pm$123
	NCRB	Dec	283 $\pm$ 26	265 $\pm$ 98	321 $\pm$ 68	541 $\pm$ 56	355 $\pm$ 73
2010**	NCRB	Jan	214 $\pm$ 58	244 $\pm$ 39	241 $\pm$ 17	341 $\pm$ 62	315 $\pm$ 46
		Feb	194 $\pm$ 46	176 $\pm$ 62	292 $\pm$ 47	253 $\pm$ 84	187 $\pm$ 52

NA: Data not available due to some technical reasons; *: Study conducted only for four months; **: Study conducted only for two months

During the study period, the annual average SPM concentrations (24 hour sampling) at TUS were $179 \pm 63 \mu\text{gm}^{-3}$, $200 \pm 65 \mu\text{gm}^{-3}$ and $163 \pm 73 \mu\text{gm}^{-3}$ in 2007, 2008 and 2009, respectively. The average SPM concentration ranged from $71 \pm 20 \mu\text{gm}^{-3}$ (minimum, July 2009) to $285 \pm 153 \mu\text{gm}^{-3}$ (maximum, February 2008) at TUS. At PUS, annual average SPM concentrations were $201 \pm 71 \mu\text{gm}^{-3}$, $201 \pm 76 \mu\text{gm}^{-3}$ and $183 \pm 58 \mu\text{gm}^{-3}$ in 2007, 2008 and 2009, respectively. Similarly, SPM concentration varied between $79 \pm 3 \mu\text{gm}^{-3}$ (minimum, August 2009) and $338 \pm 40 \mu\text{gm}^{-3}$ (maximum, March 2008) at this site. In the month of January during 2007, 2008 and 2010, PUS and SVS showed almost similar concentration levels ($257 \mu\text{gm}^{-3}$ and $257 \mu\text{gm}^{-3}$; $154 \mu\text{gm}^{-3}$ and $159 \mu\text{gm}^{-3}$; $244 \mu\text{gm}^{-3}$ and $241 \mu\text{gm}^{-3}$) except in January 2009 ($183 \mu\text{gm}^{-3}$ and $213 \mu\text{gm}^{-3}$) due to the location of these two sites in the downwind direction of agricultural fields. Concentration levels at these two sites were higher in March as compared to the levels in January and February, throughout the study period. Lowest concentration was obtained ($70 \mu\text{gm}^{-3}$) at TUS while the highest level was obtained at SAS ($541 \mu\text{gm}^{-3}$). During July-September, monthly average SPM levels at Patiala city remained almost in the range of $100 \mu\text{gm}^{-3}$ to $200 \mu\text{gm}^{-3}$ within the permissible level ($200 \mu\text{gm}^{-3}$; NAAQS India). Low SPM concentration levels obtained in the months of September were also due to rain fall.



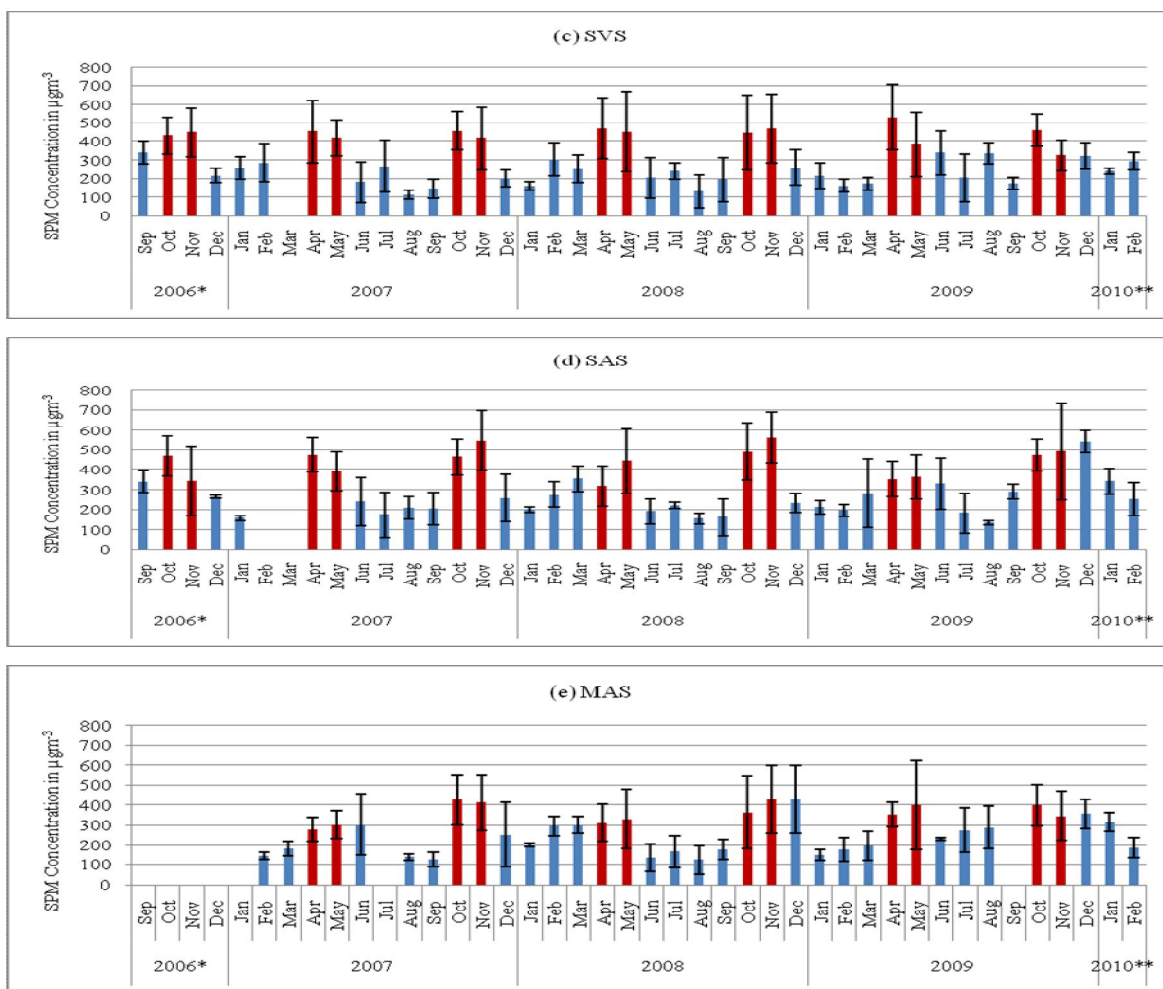


Figure 4.6 Trends of variation in monthly average levels of SPM at TUS (a), PUS (b), SVS (c), SAS (d) and MAS (e).

During the study period, annual average SPM concentrations at rural (agricultural) area site (SVS) showed an increasing trend from 2007 to 2009 ($206 \pm 65 \mu\text{gm}^{-3}$, $218 \pm 55 \mu\text{gm}^{-3}$ and $240 \pm 78 \mu\text{gm}^{-3}$, respectively) with highest annual concentration in 2009. At this site, the average monthly SPM levels ranged from $111 \pm 22 \mu\text{gm}^{-3}$ to $341 \pm 60 \mu\text{gm}^{-3}$ with minimum in August 2007. At SAS, the annual average SPM concentrations in 2007, 2008 and 2009 were observed at $207 \pm 37 \mu\text{gm}^{-3}$, $224 \pm 65 \mu\text{gm}^{-3}$ and $272 \pm 127 \mu\text{gm}^{-3}$, respectively and the highest concentration level was obtained in 2009. The highest SPM concentration ($541 \pm 56 \mu\text{gm}^{-3}$) was obtained at SAS indicating it as the most polluted area among all the sampling sites. Annual SPM concentrations at MAS were $190 \pm 71 \mu\text{gm}^{-3}$, $214 \pm 68 \mu\text{gm}^{-3}$ and $222 \pm 65 \mu\text{gm}^{-3}$ in 2007, 2008 and 2009, respectively. At this site, the monthly minimum

concentration was $125 \pm 72 \mu\text{gm}^{-3}$ (August, 2008) while the maximum concentration was $429 \pm 170 \mu\text{gm}^{-3}$ (December, 2008).

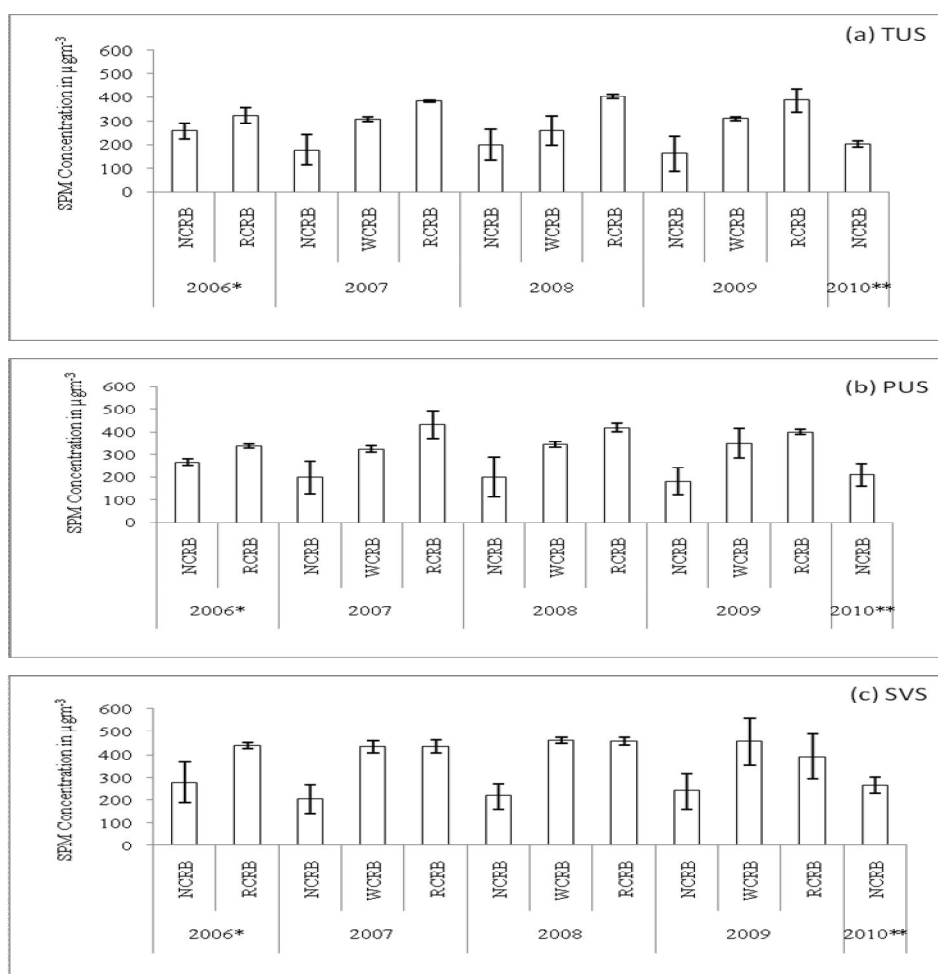
Results show that the SPM levels during NCRB months were higher than the Indian NAAQS at SVS, SAS and MAS. Overall, SPM levels during NCRB periods of the study remained at $189 \pm 62 \mu\text{gm}^{-3}$, $201 \pm 68 \mu\text{gm}^{-3}$, $230 \pm 65 \mu\text{gm}^{-3}$, $247 \mu\text{gm}^{-3}$, and $224 \mu\text{gm}^{-3}$ at TUS, PUS, SVS, SAS and MAS, respectively. At these sites, the monthly average SPM values were higher by 46%, 50%, 67%, 65% and 43% than the standard limit of $200 \mu\text{gm}^{-3}$ (Table 4.1, Figure 4.5) for 2006-2010, respectively.

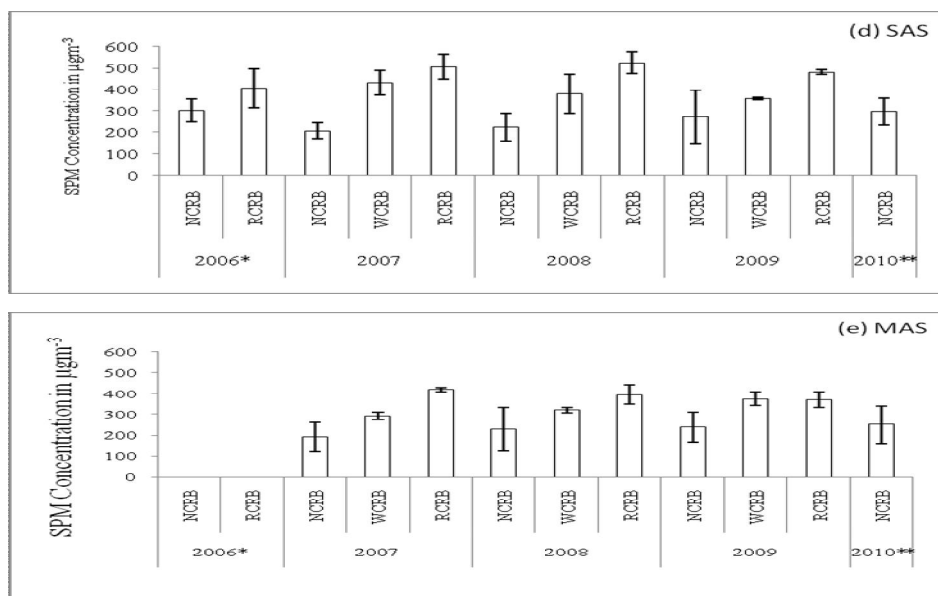
During NCRB months, the SPM concentration levels lie in the range as low as $71 \mu\text{gm}^{-3}$ to $350 \mu\text{gm}^{-3}$ (without temperature sounding), which is not very high comparing the situation in other cities of population in the range of half a million. The reason lies in the land use pattern of Patiala and its surroundings. There are practically no industrial unit in the vicinity of around 20 kms from the city. The Patiala city is known as a good education hub for the state of Punjab where there are three Universities, three medical colleges and about a dozen more educational institutions. Moreover, there are 15 state Government head offices operating from Patiala. The city is surrounded by agricultural fields all around. The rise and fall of SPM levels throughout the year is due to the climatic reasons like temperature inversion, very high ambient temperature during summer (about 45°C) and very cold weather in the winter (2°C), hot and humid environment and a good rainy season (average rainfall 600 mm). In addition to these, there is no National Highway (NH) crossing across the city (the nearest NH is about 30 Kms NW of the city)

4.5.2 SPM concentration during WCRB months

The SPM load on the ambient environment of the city is very high during the wheat stubble burning months (April and May) was very high. The levels were around two times higher in April and May as compared to the levels in March. At TUS, PUS and MAS, the SPM concentration levels ranged between $216 \pm 43 \mu\text{gm}^{-3}$ to $316 \pm 114 \mu\text{gm}^{-3}$, $303 \pm 141 \mu\text{gm}^{-3}$ to $396 \pm 54 \mu\text{gm}^{-3}$ and $278 \mu\text{gm}^{-3}$ to $399 \mu\text{gm}^{-3}$ with lowest SPM concentration observed at PUS and highest levels at MAS. SPM concentration levels during the study period were higher in April as compared to those obtained in May at all the sites except for SAS during

2008-09. Levels were distinctly higher at SVS ($384 \mu\text{gm}^{-3}$ - $528 \mu\text{gm}^{-3}$) as compared to those at other four locations indicating an enormous increase of (%) due to the effect of WCRB at this village (rural-agricultural area) site. SAS showed higher levels compared to the TUS, PUS and MAS, because of its different land use pattern. The SAS is a highly populated area with a lot of commercial and vehicular activities in its vicinity. Overall average SPM concentrations at SAS remained around $391 \pm 59 \mu\text{gm}^{-3}$ during WCRB months, much above the standard limit of $200 \mu\text{gm}^{-3}$. The levels of SAS were still higher than SVS, a purely rural site, because of the combined effects of CRB events, automobile exhaust contribution and its strategic location in SE of the city, amenable to downwind direction. Further analysis of samples is discussed in the following chapter which clearly indicates the contribution of WCRB practices in raising the levels of SPM in the ambient air of Patiala city.





*Average of four months (Sep, Oct, Nov and Dec) only, ** Two months (Jan-Feb) only.

Figure 4.7 Episodic levels of SPM at TUS (a), PUS (b), SVS (c), SAS (d) and MAS (e).

4.5.3 SPM concentration during RCRB months

During the rice harvesting period, i.e., in October and November, the monthly average SPM concentration was higher at all the monitoring sites [Figure 4.7(a-e)]. These levels were significantly higher as compared to the levels just before and after the harvesting season i.e., in September and December throughout the study period. During crop residue burning episodes of 2006 and 2009, an increase of about $100 \mu\text{gm}^{-3}$ was observed from September to October at all the sites, whereas an increase of about $(250 \pm 50 \mu\text{gm}^{-3})$ was observed during 2007-2008. In December, levels fall by about 50% of the value in November of the corresponding year. The reason for higher levels in November is the burning of residue after harvesting of the rice crop in October. The results show that the trend of variation in SPM concentration was the same in each year, i.e., concentration was higher during CRB periods and lower during NCRB periods. The levels of SPM were more during the rice stubble burning months (October-November) because the volume of left stubble after harvesting of rice crop is more than that of wheat crop residue which is cut to a lower height. The stubble after rice crop harvesting is larger than that after wheat crop harvesting, because the wheat crop stubble is also used as animal fodder and as binder in building material and is removed as much as possible.

The rice stubble is bulky and contains silica which makes it unfit for consumption by animals, hence, not used for animal feed. This may be the reason for higher SPM concentration during the rice crop stubble burning period (Badrinath et al., 2006). From the above data it can be concluded that crop residue burning contributes to raising the level of SPM pollution in the ambient air, as there is no other point source such as industry or power plants in the vicinity of the city, neither the meteorological parameters like wind direction favors any increase in SPM levels.

During the period of study from 2007 till 2010, there has not been much change in the cultivation area of land for wheat and rice crops. Moreover, there has not been any change in technology used by farmers for harvesting the crops as is indicated from the following data collected from state government sources. Hence, any change in SPM, levels either during WCRB or RCRB can be assigned mainly to the CRB practices being followed by the farmers.

A close look at variations in SPM levels during NCRB, WCRB and RCRB, at the sites TUS, PUS, SAS and MAS, indicates a clear increase in levels in the given sequence. However, variations at SVS (a purely rural site closely surrounded by fields all around) are little peculiar in nature, where the monthly average levels for WCRB and RCRB are almost same in contrast to the observations as indicated above. The reason for this peculiar observation might be due to the excessive SPM loading thereby changing the flow rate during WCRB and RCRB and hence did not indicate true SPM levels (which must have been higher than the observed one).

4.6. Gaseous levels during CRB and NCRB months

The months, April-May and October-November are considered as the CRB months while rest of the months in a year were regarded as NCRB months. During April and May, wheat crop stubble is burnt after harvesting where as RCRB is performed during October and November. During the study period, the monthly average levels of SO₂ and NO₂ during

NCRB months varied between $1 \mu\text{gm}^{-3}$ to $43 \mu\text{gm}^{-3}$ and $1 \mu\text{gm}^{-3}$ to $68 \mu\text{gm}^{-3}$, respectively. SO_2 concentration was higher in August during 2009 ($17 \mu\text{gm}^{-3}$, SAS) as compared to the other NCRB months while NO_2 concentration remained distinctly higher in December 2009 ($68 \mu\text{gm}^{-3}$, SAS) and in February 2010 ($68 \mu\text{gm}^{-3}$, PUS).

During CRB months, the NO_2 concentration ranged from a minimum of $2 \mu\text{gm}^{-3}$ to a maximum of $102 \mu\text{gm}^{-3}$, whereas, SO_2 concentration varied from $2 \mu\text{gm}^{-3}$ to $55 \mu\text{gm}^{-3}$. Although levels of NO_2 and SO_2 were higher during both the rice and wheat crop residue burning months but NO_2 concentration levels were higher during rice residue burning episodes (October-November) whereas, higher levels of SO_2 concentration were observed during WCRB episodes i.e., April-May. It was observed that there was a quantum jump in the SO_2 and NO_2 levels during burning months in 2007 (Figure 4.9 and 4.11).

The overall SO_2 concentration remained much lower than the standard limit of $80 \mu\text{gm}^{-3}$ at all the sites. Variations in the levels of these primary pollutant gases are discussed in the following paragraphs.

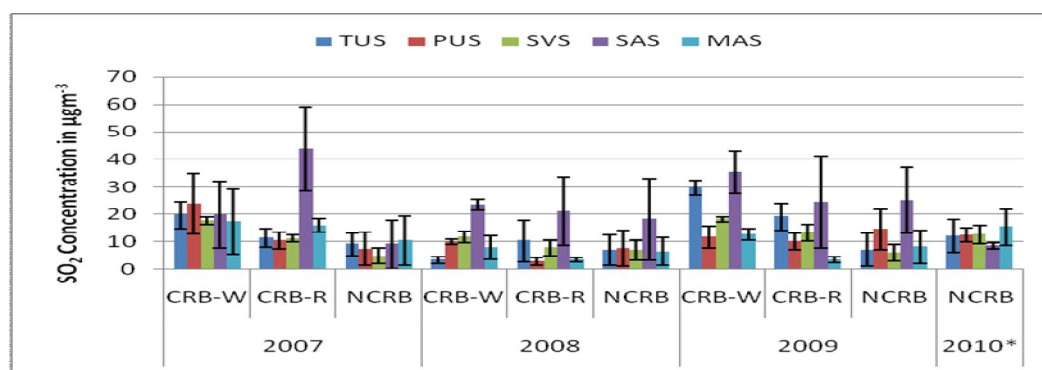


Figure 4.8 Monthly variations in SO_2 concentration during CRB and NCRB months of the study period at different sites in Patiala; 2010*: Data collected for January and February months only

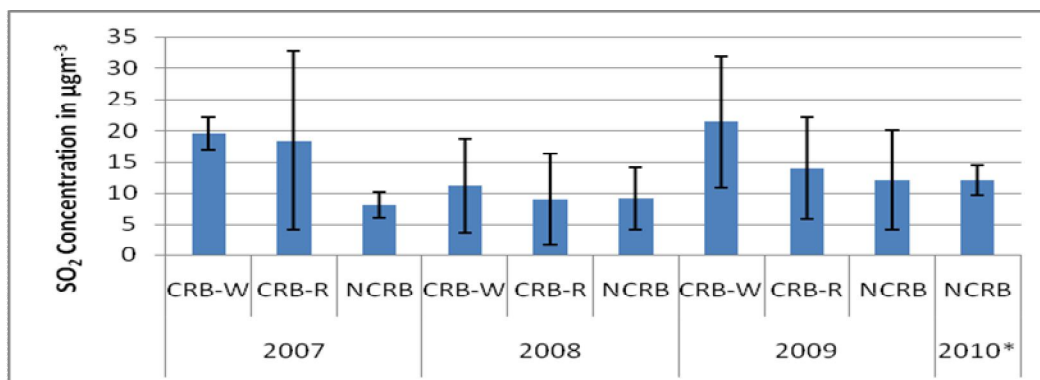


Figure 4.9 Episodic variations in SO₂ concentration levels during CRB and NCRB months of the study period; 2010*: Data collected for January and February months only

4.6.1. SO₂ levels during NCRB months

The annual average of SO₂ concentrations during NCRB months of 2007, 2008 and 2009 ranged between a minimum level of $6 \pm 5 \mu\text{gm}^{-3}$ (MAS, 2008) to a maximum level of $25 \pm 12 \mu\text{gm}^{-3}$ (SAS, 2009). Generally, levels ranged between $6 \mu\text{gm}^{-3}$ to $10 \mu\text{gm}^{-3}$ at TUS, PUS, SVS and MAS except the levels obtained in 2009 at PUS. The annual average levels were distinctly higher at SAS ranging between $9 \mu\text{gm}^{-3}$ to $25 \mu\text{gm}^{-3}$. The 24-hour average monthly SO₂ concentration at different monitoring sites ranged from 1 ± 1 (Min.) to 43 ± 22 (Max.) with the maximum concentration at SAS in 2009. The base line 24-hour monthly average concentration of SO₂ was $1 \mu\text{gm}^{-3}$ at all the sites except MAS ($2 \mu\text{gm}^{-3}$). The maximum levels at different sites ranged between $15 \mu\text{gm}^{-3}$ to $26 \mu\text{gm}^{-3}$ at all the sites except a peak concentration of $43 \mu\text{gm}^{-3}$ at SAS indicating highest polluted site among all the selected sampling sites. This site has observed the high levels of SO₂ more frequently as compared to the other sites. During the study campaign, the average SO₂ level was obtained as the highest at SAS ($18 \mu\text{gm}^{-3}$) while, there was not much variation in the average levels of SO₂ (SD=1.56) at other sites.

At all the sampling sites, SO₂ concentrations during NCRB months lie much lower than the permissible limit of $80 \mu\text{gm}^{-3}$. The trend indicates a slight increase in the overall average concentration levels from 2007 to 2008 at each respective sampling site. However, the concentration of SO₂ in the ambient air of Patiala city remarkably increased in 2009. This

was true for all the sampling sites. However, the magnitude of change was more at SAS and PUS sites indicating that the reason for this increase is due to increased emissions from automobile vehicles. As no other contributor is insight.

Table 4.2 Concentration levels of SO₂ at different monitoring sites

Year	Period	Month	SO ₂ Concentration (µgm ⁻³ ±SD)				
			Sampling Sites				
			TUS	PUS	SVS	SAS	MAS
2007	WCRB	Apr	23±2	16±5	16±7	28±5	26±15
		May	16±5	32±5	18±2	11±3	9±8
	NCRB	Jun	6±5	4±1	1±1	4±3	3±2
		Jul	12±3	6±1	5±1	1±1	--
		Aug	5±1	3±1	3±2	6±1	3±1
		Sep	15±4	5±4	6±3	10±3	9±1
	RCRB	Oct	9±7	13±8	12±10	33±24	14±4
		Nov	14±10	8±7	10±3	55±34	17±5
	NCRB	Dec	7±2	18±5	8±4	24±16	26±4
2008	NCRB	Jan	18±1	22±9	11±2	25±22	22±1
		Feb	2±1	8±3	8±5	40±7	4±3
		Mar	10±5	7±4	9±4	39±21	11±8
	WCRB	Apr	2±1	11±3	13±3	22±12	5±4
		May	4±1	9±3	10±2	25±11	11±8
	NCRB	June	7±3	8±5	6±4	8±3	5±2
		July	3±2	2±2	2±1	8±6	2±1
		Aug	3±1	1±1	2±1	3±3	2±1
		Sep	9±2	4±1	7±4	13±10	4±1
	RCRB	Oct	16±10	4±1	6±2	12±5	3±2
		Nov	5±2	2±1	10±8	30±14	4±3
	NCRB	Dec	2±1	6±4	10±9	8±2	2±2
2009	NCRB	Jan	2±1	7±6	3±1	11±6	3±2
		Feb	1±1	6±5	4±2	12±3	2±2
		Mar	8±1	12±3	8±3	42±8	5±2
	WCRB	Apr	28±3	9±3	17±2	41±7	11±2
		May	32±9	14±8	15±2	30±7	14±3
	NCRB	Jun	--	21±7	10±8	23±15	15±10
		Jul	11±1	23±8	9±8	30±4	17±5
		Aug	12±2	18±3	2±1	43±13	11±10
		Sep	8±5	22±2	5±1	22±8	--
	RCRB	Oct	22±6	12±2	11±8	36±12	3±2
		Nov	15±6	8±4	15±7	13±5	4±3
	NCRB	Dec	3±2	7±5	5±2	19±8	2±1
2010*	NCRB	Jan	16±3	11±2	15±6	9±1	11±10
		Feb	8±1	14±5	10±1	8±2	20±2

2010*: Data collected for January and February months only

4.6.2 SO₂ levels during RCRB months

During RCRB months of 2007, 2008 and 2009, the annual average SO₂ concentrations varied between a minimum level of 3 µgm⁻³ (PUS-2008; MAS-2008, 2009) to a maximum 44 µgm⁻³ (MAS, 2007). The annual levels were distinctly higher at SAS during RCRB months as compared to the other sampling sites. At TUS and SVS, the annual average concentrations were higher in 2009 while at SAS and MAS; the highest SO₂ concentration was obtained in 2007. The 24-hour average monthly concentration varied between 2 µgm⁻³ to 55 µgm⁻³ with peak concentration at SAS and the minimal concentration at PUS during RCRB. During RCRB, the highest baseline concentration (12 µgm⁻³) was also observed at SAS. Thus SAS was identified as the most SO₂ polluted site.

A clear increase in the SO₂ levels was observed during RCRB months when compared with the levels in NCRB months (Figure 4.9). At PUS and SVS, a three times increase was observed in SO₂ levels from NCRB months to WCRB months (7 µgm⁻³ to 24 µgm⁻³, 5 µgm⁻³ to 17 µgm⁻³) while other monitoring sites showed two times increase in the levels. Thus, a clear impact of land use patterns as well as episodic effect of RCRB was observed at all the sites. The levels were fluctuating during the episodic burnings depending upon the area under burning and the effect of meteorological factors like temperature, humidity, wind speed and wind direction. But an overall increase was observed during RCRB months as compared to the NCRB months. The apparent increase in SO₂ levels during RCRB months cannot be due to CRB practices, as there is hardly any source of sulphur in the residue from harvesting of crops. Hence, the only probable reason for the increase is the exhaust gases released by diesel driven harvesting machines. Since, practically whole of the harvesting is done by machines, rather than by manual operations, the levels of SO₂ in the ambient air rises.

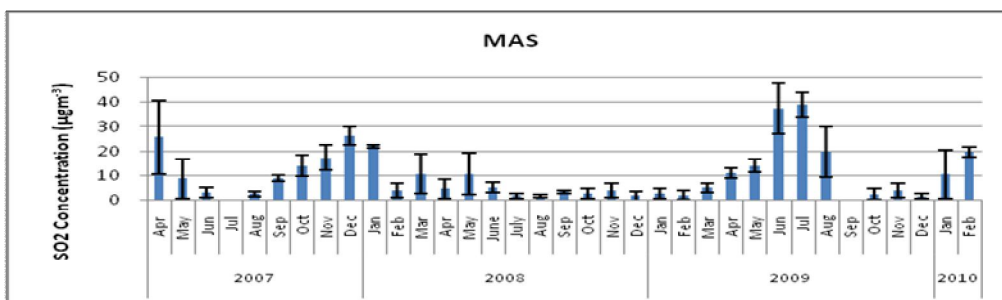
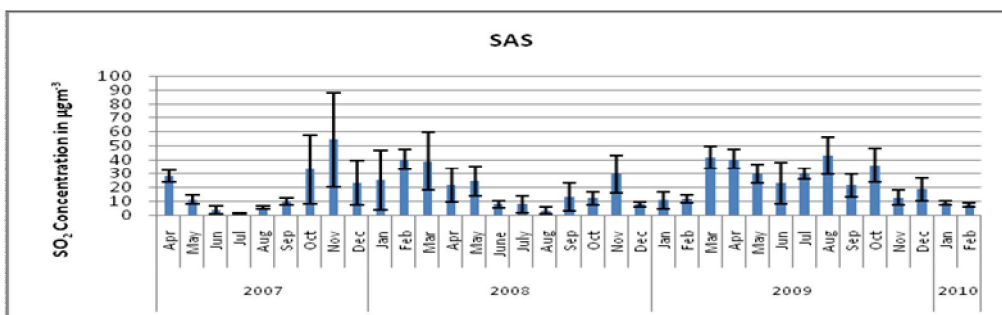
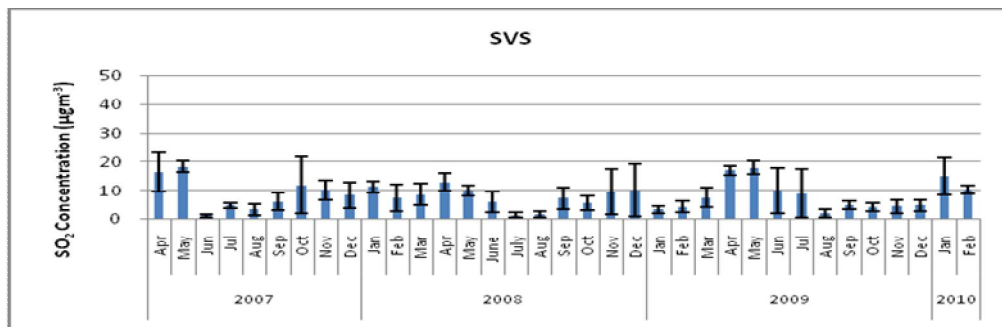
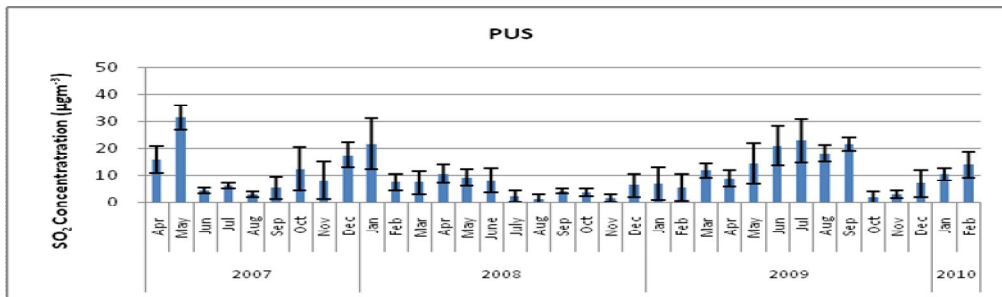
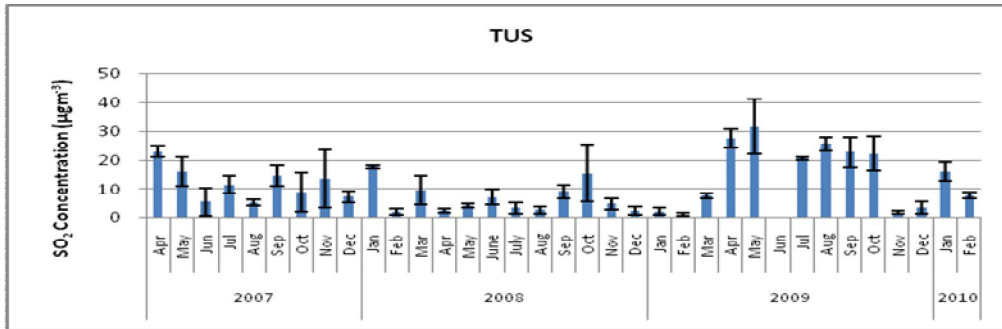


Figure 4.10 Trends of variation in monthly levels of SO₂ concentration at TUS, PUS, SVS, SAS, and MAS

4.6.3 SO₂ levels during WCRB months

During WCRB months of the study period (2007-09), the annual average levels of SO₂ concentrations varied between a minimum level of 3 μgm^{-3} (TUS, 2008) to a maximum of 35 μgm^{-3} (SAS, 2009) at different sampling sites. During RCRB months of 2007, the SO₂ levels varied between a range of 17 μgm^{-3} to 20 μgm^{-3} at different monitoring sites indicating very less deviation to each other (SD=2.89) while great deviation was observed in 2008 and 2009 in the annual concentration levels of SO₂ at different monitoring sites (SD=7.39 and SD=10.35, respectively). Starting from 2007 to 2009, an increase was obtained in the levels at SAS while other sites did not show any systematic increase in SO₂ levels. Overall, high levels were obtained in 2007 and 2009.

In 2007, 2008 and 2009, the annual average levels of SO₂ at SVS during NCRB months were 5 μgm^{-3} , 7 μgm^{-3} and 6 μgm^{-3} respectively while during WCRB months the levels were 17 μgm^{-3} , 12 μgm^{-3} and 18 μgm^{-3} respectively indicating two to three times increase in the levels from NCRB to WCRB. During the sampling campaign, the 24 hourly concentrations of SO₂ at selected monitoring sites varied between 2 μgm^{-3} and 41 μgm^{-3} with a highest concentration at SAS. Overall, average SO₂ levels were much below than the permissible limit set by the CPCB for residential and commercial areas at all the monitoring site. The farmers use to supplement N, P and K based fertilizers to the growing crops and these elements remained in the stubble even after the harvesting of crops.

4.6.4 NO₂ levels during NCRB months

At all the sites, the annual concentration of NO₂ during 2007, 2008 and 2009 were ranged between a minimum of 9 μgm^{-3} and a maximum of 38 μgm^{-3} with the highest concentration at SAS. NO₂ concentration levels during 2009 ranged between 1 μgm^{-3} (min.) and 68 μgm^{-3} (max.) with the highest concentration at SVS in December. During 2009, the baseline concentration varied between 1 μgm^{-3} to 7 μgm^{-3} while the top line concentration ranged between 54 μgm^{-3} to 68 μgm^{-3} at different monitoring sites. High NO₂ levels were [91]

comparatively more associated with the winter months due to the impact of temperature inversion. At TUS, PUS and SAS, a small increasing pattern was observed in the levels of NO₂ concentration from 2007 to 2009. But no such pattern was observed at SVS and MAS. The levels of NO₂ remained almost constant at SVS during NCRB months.

Table 4.3 Concentration levels of NO₂ during 2007-2010 obtained at five monitoring sites in Patiala, India

Year	Period	Month	NO ₂ Concentration ($\mu\text{gm}^{-3} \pm \text{SD}$)				
			Sampling Sites				
			TUS	PUS	SVS	SAS	MAS
2007	WCRB	Apr	7 $\pm$ 4	17 $\pm$ 5	10 $\pm$ 4	14 $\pm$ 1	20 $\pm$ 16
		May	8 $\pm$ 3	13 $\pm$ 2	--	68 $\pm$ 2	23 $\pm$ 24
	NCRB	Jun	18 $\pm$ 8	15 $\pm$ 3	10 $\pm$ 5	14 $\pm$ 10	20 $\pm$ 13
		Jul	--	12 $\pm$ 1	8 $\pm$ 8	34 $\pm$ 4	--
		Aug	--	10 $\pm$ 2	14 $\pm$ 2	--	11 $\pm$ 5
		Sep	22 $\pm$ 10	9 $\pm$ 1	10 $\pm$ 3	15 $\pm$ 3	3 $\pm$ 2
	RCRB	Oct	24 $\pm$ 14	12 $\pm$ 4	22 $\pm$ 11	67 $\pm$ 39	22 $\pm$ 12
		Nov	19 $\pm$ 6	19 $\pm$ 6	27 $\pm$ 8	91 $\pm$ 39	44 $\pm$ 23
	NCRB	Dec	11 $\pm$ 1	14 $\pm$ 2	14 $\pm$ 9	62 $\pm$ 15	24 $\pm$ 3
2008	NCRB	Jan	21 $\pm$ 15	16 $\pm$ 5	13 $\pm$ 1	23 $\pm$ 7	22 $\pm$ 0
		Feb	11 $\pm$ 6	21 $\pm$ 5	16 $\pm$ 6	46 $\pm$ 5	19 $\pm$ 3
		Mar	8 $\pm$ 3	9 $\pm$ 5	5 $\pm$ 1	36 $\pm$ 29	13 $\pm$ 5
	WCRB	Apr	15 $\pm$ 10	14 $\pm$ 4	8 $\pm$ 6	31 $\pm$ 12	12 $\pm$ 6
		May	18 $\pm$ 18	22 $\pm$ 7	11 $\pm$ 8	49 $\pm$ 22	13 $\pm$ 11
	NCRB	Jun	12 $\pm$ 3	13 $\pm$ 5	5 $\pm$ 3	15 $\pm$ 10	7 $\pm$ 3
		Jul	4 $\pm$ 2	4 $\pm$ 2	1 $\pm$ 0	7 $\pm$ 0	2 $\pm$ 1
		Aug	27 $\pm$ 19	19 $\pm$ 6	6 $\pm$ 4	39 $\pm$ 11	6 $\pm$ 4
		Sep	15 $\pm$ 6	8 $\pm$ 4	8 $\pm$ 2	26 $\pm$ 11	9 $\pm$ 2
	RCRB	Oct	20 $\pm$ 6	31 $\pm$ 11	27 $\pm$ 12	78 $\pm$ 28	19 $\pm$ 9
		Nov	22 $\pm$ 9	47 $\pm$ 10	39 $\pm$ 31	98 $\pm$ 45	13 $\pm$ 7
	NCRB	Dec	35 $\pm$ 16	34 $\pm$ 15	20 $\pm$ 11	48 $\pm$ 10	56 $\pm$ 39
2009	NCRB	Jan	26 $\pm$ 4	34 $\pm$ 5	26 $\pm$ 7	60 $\pm$ 35	11 $\pm$ 6
		Feb	25 $\pm$ 14	40 $\pm$ 10	14 $\pm$ 10	40 $\pm$ 9	35 $\pm$ 34
		Mar	15 $\pm$ 14	19 $\pm$ 6	5 $\pm$ 1	37 $\pm$ 17	10 $\pm$ 2
	WCRB	Apr	21 $\pm$ 10	21 $\pm$ 11	7 $\pm$ 2	24 $\pm$ 10	10 $\pm$ 9
		May	25 $\pm$ 6	22 $\pm$ 9	6 $\pm$ 4	35 $\pm$ 10	32 $\pm$ 8
	NCRB	Jun	--	13 $\pm$ 8	5 $\pm$ 3	17 $\pm$ 12	9 $\pm$ 2
		Jul	23 $\pm$ 14	17 $\pm$ 12	8 $\pm$ 3	30 $\pm$ 5	8 $\pm$ 2
		Aug	18 $\pm$ 3	15 $\pm$ 3	1 $\pm$ 1	26 $\pm$ 13	5 $\pm$ 2
		Sep	17 $\pm$ 3	26 $\pm$ 1	2 $\pm$	29 $\pm$ 5	--
	RCRB	Oct	23 $\pm$ 7	35 $\pm$ 14	7 $\pm$ 2	82 $\pm$ 28	14 $\pm$ 7
		Nov	35 $\pm$ 7	48 $\pm$ 27	3 $\pm$ 0	98 $\pm$ 44	2 $\pm$ 1
	NCRB	Dec	33 $\pm$ 3	52 $\pm$ 11	3 $\pm$ 1	68 $\pm$ 34	2 $\pm$ 1

2010*	NCRB	Jan	55±0	15±13	54±15	12±7	15±8
		Feb	30±4	68±10	12±9	20±0	14±6

*Data available for two months only

It has also been observed that the annual concentration levels were the lowest at SVS during the NCRB months. The increasing number of vehicles on the road might be the reason for the increasing trend of concentration levels of NO₂ at TUS, PUS and SAS. Less vehicular activities at SVS (rural-agricultural site) as compared to the urban sites (commercial, residential and educational sites) might be the reason for less NO₂ concentration levels at SVS. Thus, it can be concluded that vehicular activities are the major source of NO₂ during NCRB months in the ambient air of Patiala. Overall, SAS was identified as the site with highest NO₂ levels and SVS was recognized with lowest NO₂ levels for NCRB months. It is clear that NO₂ levels at all the monitoring sites during the NCRB period were much below than the permissible limit of 80 µgm⁻³ (for residential areas) of the NAAQS protocol, CPCB India (1998) (Annexure-I).

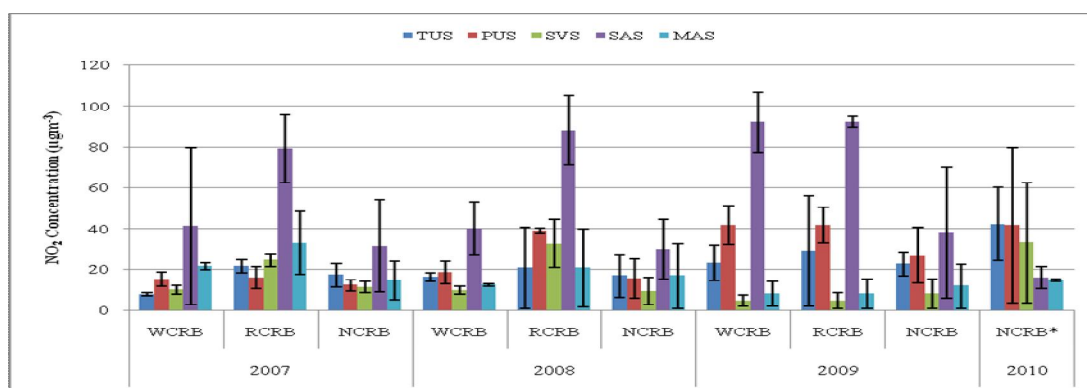


Figure 4.11 Periodic variations in NO₂ concentration at different monitoring sites

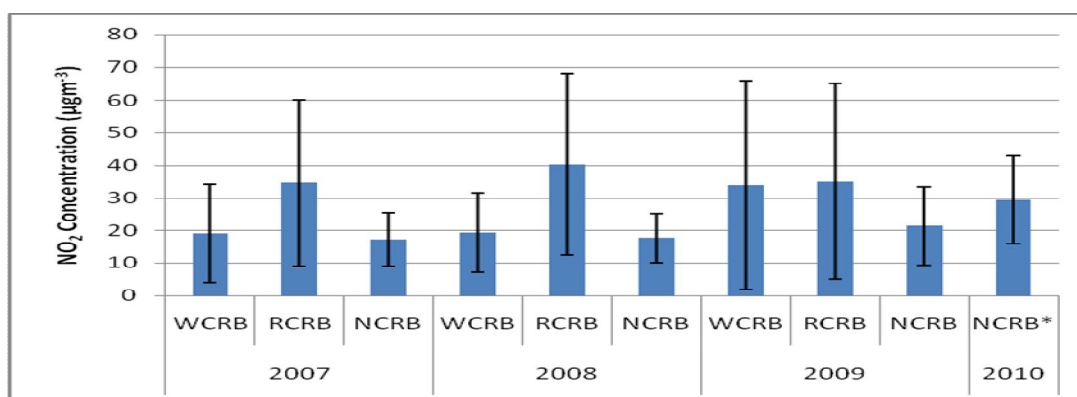


Figure 4.12 Average periodic variations in NO₂ concentration during the study campaign

4.6.5 NO₂ levels during RCRB months

The annual average NO₂ concentration ($40 \mu\text{gm}^{-3}$) at different monitoring sites during the RCRB periods was little higher ($5 \mu\text{gm}^{-3}$) as compared to the annual average levels in 2007 ($34 \mu\text{gm}^{-3}$) and 2009 ($35 \mu\text{gm}^{-3}$). Similar to that of SO₂ concentration levels, an increasing pattern was observed in the annual levels of NO₂ at TUS, PUS and SAS from 2007 to 2009. Since, NO₂ levels have been associated with the vehicular pollution, day by day increasing number of vehicles on the roads could be the reason for increasing annual concentration levels. SAS has observed the highest levels of annual NO₂ concentration throughout the study period ($79 \mu\text{gm}^{-3}$ in 2007, $88 \mu\text{gm}^{-3}$ in 2008 and $92 \mu\text{gm}^{-3}$ in 2009) as compared to the other monitoring sites. Lowest annual levels were obtained at TUS during 2007-2009 indicating low vehicular contribution at this site as well as its distant position from the agricultural areas. A clear increase (two to three times) was observed in NO₂ levels during the RCRB months as compared to the NCRB months at almost all the sites (Figures 4.11, 4.12). SVS, being a rural and agricultural area site, experienced low levels of NO₂ concentration compared to the other sampling sites, but the increased levels of NO₂ in RCRB in contrast with that in NCRB has shown a clear contribution of agricultural residue burning in the enhancement of NO₂ levels in ambient air at this site, when vehicular activities are very less at this rural site.

The 24-hourly average concentration varied between a minimum of $2 \mu\text{gm}^{-3}$ to a maximum of $102 \mu\text{gm}^{-3}$ with the highest concentration at SAS. In contrast to the levels during NCRB

months, the baseline of 24-hourly NO₂ concentration level shifted to 2 µgm⁻³ during RCRB months with an increase of 1 µgm⁻³ while the top line shifted to 102 µgm⁻³ with an increase of 34 µgm⁻³. Overall, the levels of NO₂ increased during RCRB months at all the selected sites. The levels exceeded the maximum permissible limit (80 µgm⁻³) at SAS during 2008 and 2009 (88 µgm⁻³ in 2008 and 92 µgm⁻³ in 2009, annual average concentration) while other sites indicated the levels within the limit.

The monthly average levels are found to be the highest at SAS, whereas the levels are very low at SVS. The only reason for this distinct concentration levels can be (i) contribution from automobile exhaust and, (ii) RCRB practices. The levels are clear indication of the influence of wind direction which is most of the time NW to SE. Hence both the above two factors have combined effect in raising the NO₂ concentration levels at SAS more than any other site due to its strategic location in SE of the study area. It can be seen clearly that there is a substantial increase in NO₂ levels during RCRB months as compared to the NCRB months at all the sites throughout the study period, which further consolidate the contribution of CRB practices in raising the NO₂ levels in ambient air of Patiala.

4.6.6 NO₂ levels during WCRB months

During the study period, the annual levels obtained in WCRB months at different monitoring sites varied between 5 µgm⁻³ to 92 µgm⁻³ with highest level at SAS in 2009. The annual concentration levels during WCRB in 2007 rose from 31 µgm⁻³ to 41 µgm⁻³ at SAS, 15 µgm⁻³ to 21 µgm⁻³ at MAS and 12 µgm⁻³ to 15 µgm⁻³ at PUS whereas, during 2009, levels increased from 22 µgm⁻³ to 23 µgm⁻³ at TUS, 27 µgm⁻³ to 42 µgm⁻³ at PUS and 38 µgm⁻³ to 92 µgm⁻³ at SAS indicating significant contribution of WCRB practices in increasing the ambient levels of NO₂.

The baseline concentration of 24-hourly NO₂ levels shifted to a higher level (4 µgm⁻³ to 10 µgm⁻³) during WCRB months, indicating incorporation of the NO₂ levels due to WCRBs to the ambient air. However, no direct increase was observed during WCRB months but overall increase was clearly seen. The reason for higher levels of NO₂ during WCRB could be the burning of N containing wheat crop residue after harvesting of the crop. Nitrogen

may combine with the atmospheric oxygen to form oxides of nitrogen. Increase in the levels was significant during WCRB but not as much as in the case of RCRB.

During April and May, wheat crop residue is burned after harvesting whereas RCRB is performed during October and November. During NCRB months, a distinctly higher concentration of SO_2 ($43 \mu\text{gm}^{-3}$ at SAS) was observed in the month of August 2009, as compared to other NCRB months while in the case of NO_2 concentration, a higher peak ($68 \mu\text{gm}^{-3}$) was obtained during December 2009, at the same site. It is indicated that the Sanauri Adda Site was the most polluted site in the year 2009, during this study. However, SO_2 and NO_2 levels were increased during both burning periods but the proportion of increment was different. Higher levels of SO_2 were observed during the WCRB episodes while NO_2 levels were greatly increased during RCRB. During the WCRB months, the overall NO_2 concentration was lower as compared to the levels in RCRB months, indicating higher production of NO_2 during RCRB. Differently, the overall SO_2 concentration was higher during WCRB periods as compared to the RCRB periods in that order indicating WCRB more responsible for the increased SO_2 levels as compared to the RCRB. The reason of higher production of NO_2 during October-November is the burning of N containing residue and some contribution from the exploding of crackers during the festive season of Diwali. Farmers supply N based fertilizers comparatively more during paddy crop than used in wheat crop cultivation. The source of S based gases in the ambient air cannot be associated directly with the crop residue burning. However, the increased levels of SO_2 during CRB episodes (more prominent during WCRB) is coming from the burning of diesel (containing S) as a fuel in the harvesting and threshing equipments to make fodder from wheat spikes. These observations become important in the absence of any other activity such as industrial or power generation in the near vicinity of about 20 km.

4.7 Wind speed and direction during the study period

Wind direction during the study period (2006-10) remained either NW or calm for most of the time. Wind rose plots made for the CRB and NCRB months of the year 2007 show the wind direction with wind frequency and wind speed of the study area (Patiala).

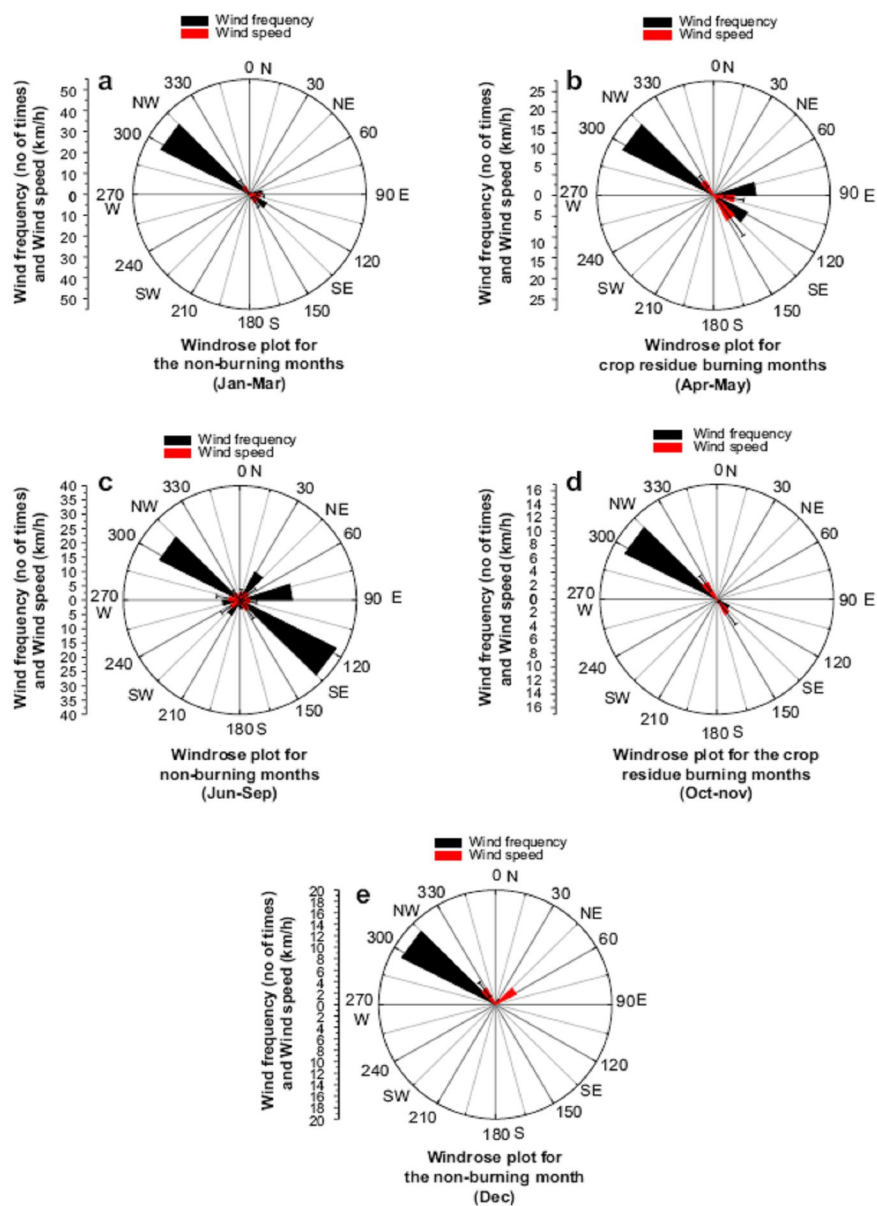


Figure 4.13 Windrose plots showing wind direction, wind speed and wind frequency in Patiala during burning and non-burning months (a-e)

The wind rose plot for the NCRB months (January-March) divided into eight sectors (Figure 4.13a) shows that the winds at Patiala during January-March remained NW for most of the time. However, sometimes SE and E wind directions were also observed, having wind speed between <1 and 8 Km per hour. The wind rose plot for January-March

also shows that the wind never blows from the North or NE. Almost the same information is obtained from the wind rose plot made for the WCRB period (April-May) (Figure 4.13b).

The plot indicates that frequency of the wind blowing from the NW was still high and the wind speed varied similarly from 1 to 8 Km per hour. During the non burning months of June-September, the wind was blowing from the NW and SE with almost equal frequency (37 and 31, respectively) (Figure 4.13c). On the contrary, winds were also blowing from NE, E and other directions during this period, but the frequency was negligibly small. Again it can be seen from Figure 4.13d and 4.13e that the wind was blowing from the NW for most of the time. Examining winds blowing from the NW (the longest spoke) it is found that approximately 90% of the time wind was blowing from the NW towards SE in Patiala at a speed between 1 and 8 Km per hour.

4.8 Conclusions

The crop residue burning after harvesting of wheat and rice crop changed the composition of ambient air in Patiala by increasing the concentration levels of SPM, SO₂ and NO₂. Although the levels were fluctuating at different monitoring sites, but these were greatly influenced by the WCRB and RCRB episodes during April-May as well as October-November throughout the study period. While, levels of these pollutants were high during both burning periods (April-May; wheat residue burning period, October-November: rice residue burning period), the NO₂ concentration was higher during the RCRB periods (October-November) and SO₂ concentration was higher during WCRB periods. The diesel driven equipment for threshing and harvesting and the tractors for preparing fields for the next crop contributed to the high levels of SO₂ during the WCRB periods whereas Nitrogen (N) based chemical fertilizers (NPK) contributed to the increase in NO₂ levels during burning episodes (Wang et al., 2004; Xing et al., 2002; Li et al., 1997). A very important inference can be drawn from the data that the gaseous molecules stay in the ambient air for a longer duration than those of SPM. This can be confirmed from the monthly average levels of SPM, NO₂ and SO₂ concentration. In the months of June and December, the SPM levels fall back to the baseline value, whereas, the gaseous levels tend to stay at higher

concentrations in these months as well. Though local SPM concentration obtained at all sites during non- burning months was already higher than the NAAQS (India) of $200 \mu\text{gm}^{-3}$ (for residential areas) and World Health Organization standards for most of the sampling times, during crop residue burning months a very high increment was observed in SPM level at all the sampling sites. The monthly average concentration of SO_2 and NO_2 remained below the NAAQS, India ($80 \mu\text{gm}^{-3}$).

During the study period (2006-2009), an increase in the levels of selected pollutants was noticed at urban locations indicating yearly increments in the number of vehicles plying on the roads. Meteorological factors, especially the wind direction, wind speed, temperature and rainfall have also influenced the ambient levels of these pollutants in the air. High concentrations of all parameters were observed during winter months as well as during low wind speed times. Low concentrations were obtained during high wind speed and after the rainfall. The site situated in southeast of the city and downwind in direction collected all the pollution emanating from NW due to different activities including agricultural burning practices and vehicular activities. The influence of wind direction was more prominently observed in case of gaseous levels than those of SPM levels.

References

- Andreae, M.O., 1991. Biomass burning: Its history, use, and distribution and its impact on environmental quality and global climate. In: Levine, J.S. (Ed.), *Global Biomass Burning, Atmospheric, Climatic, and Biospheric Implications*. MIT Press, Cambridge, MA, pp. 3-21.
- Andreae, M.O., Merlet, P., 2001. Emission of trace gases and SPM from biomass burning. *Global Biogeochemical Cycles* 15 (4), 955–966.
- Badrinath, K.V.S., Chand, T.R.K., Prasad, V.K., 2006. Agriculture crop residue burning in the Indo-Gangatic Plains: A study using IRS-P6 AWiFS satellite data. *Current Science* 91 (8), 1085–1089.
- CARB (California Air Resources Board), 1996. Atmospheric pollutant emission factors from open burning of agricultural and forest biomass by wind tunnel simulations. California Air Resources Board, Project No. A932/126, Final report prepared for the California Air Resources Board, Sacramento, CA.

Dhammapala, R., Claiborn, C., Corkill, J., Gullett, B., 2006. Particulate emissions from wheat and Kentucky bluegrass residue burning in eastern Washington and northern Idaho. *Atmospheric Environment* 40, 1007-1015.

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

Godish, T., 1997. Air quality. Lewis Publishers, Boca Raton, New York, pp. 137-178.

Gupta, A., Cheong, K.W.D., 2006. Physical characterization of particulate matter and ambient meteorological parameters at different indoor-outdoor locations in Singapore. *Building and Environment* 42, 237-245.

Hays, M.D., Fine, P.M., Geron, C.D., Kleeman, M.J., Gullett, B.K., 2005. Open burning of agricultural biomass: physical and chemical properties of particle-phase emissions. *Atmospheric Environment* 39, 6747-6764.

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.

Levine, J.S., Cofer, W.R., Cahoon, D.R., Winstead, E.L., 1995. Biomass burning: a driver for global change. *Environmental Science & Technology* 29 (3), 120A-125A.

Li, X., Wang, S., Duan, L.J., Li, Hao C., Chen, Y., Yang, L., 2007. Particulate and trace gas emissions from open burning of wheat straw and corn stover in China. *Environmental Science & Technology* 41, 6052-6058.

Mohanraj, R., Azeez, P.A., 2004. Health effects of airborne particulate matter and the Indian scenario. *Current Science* 87 (6), 741-748.

Nguyen, B.C., Putaud, J.P., Mihalopoulos, N., Bonsang, B., 1994. CH₄ and CO emissions from rice straw burning in South East Asia. *Environmental Monitoring & Assessment* 31, 131-137.

Oppenheimer, C., Tsanev, V.I., Allen, A.G., Mcgonigle, Andrew, J.S., Cardoso, Arnaldo, A., Wiatr, A., Paterlini, W., Dias, Cristine de Mello, 2004. NO₂ emissions from agricultural burning in Sao Paulo, Brazil. *Environmental Science & Technology* 38, 4557-4561.

Pandey, J.S., Kumar, R., Devotta, S., 2005. Health risks of NO₂, SPM and SO₂ in Delhi (India). *Atmospheric Environment* 39 (36), 6868-6874.

Patel, N., 2008. Report: Going up in smoke. *Hindustan Times Sunday Magazine*, 11 May, pp. 1-2.

Punia, M., Nautiyal, V.P., Kant, Y., 2008. Identifying biomass burned patches of agriculture residue using satellite remote sensing data. *Current Science* 94 (9), 1185-1190.

Sahai, S., Sharma, C., Singh, D.P., Dixit, C.K., Singh, N., Sharma, P., Singh, K., Bhatt, S., Ghude, S., Gupta, R.K., Tiwari, M.K., Garg, S.C., Mitra, A.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.

Schwartz, J., 1993. Particulate air pollution and chronic respiratory disease. *Environmental Research* 62 (1), 7-13.

TERI, 2003. Report No. 2003SF62, ch. 15, Patiala, DBAS (Patiala), Punjab, pp. 317-338.

Thaller, E., Hollaway, L., Mai, V., Hochman, D., Bharti, B., Brooks, E., Petronella, S., 2004. Air pollution and pulmonary function. *Journal of Allergy and Clinical Immunology* 113, 65.

Turn, S.Q., Jenkins, B.M., Chow, J.C., Pritchett, L.C., Campbell, D., Cahill, T., Whalen, S.A., 1997. Elemental characterization of particulate matter emitted from biomass burning: wind tunnel derived source profiles for herbaceous and wood fuels. *Journal of Geophysical Research* 102 (D3), 3683-3699.

WHO (World Health Organization), 2004. Systematic review of health aspects of air pollution in Europe. WHO Regional Office for Europe, June, pp. 4-16.

www.wunderground.com/global/stations/42101.html

Yang, S., He, H., Lu, S., Chen, D., Zhu, J., 2008. Quantification of crop residue burning in the field and its influence on ambient air quality in Suqian, China. *Atmospheric Environment* 42 (9), 1961-1969.

Xing, G.X., Zhu, Z.L., 2002. Regional nitrogen budgets for China and its major watersheds. *Biogeochemistry*, 57/58, 405-427.

Lee, D.S., Kohler, I., Grobler, E., Rohrer, F., Sausen, R., Gallardo-Klennerd, L., Oliviere, J. G. J., Dentenerf, F. J., Bouwmane, A. F., 1997. Estimations of global NO_x emissions and their uncertainties. *Atmospheric Environment* 31, 1735-1749

Wang, Y.X., McElroy, M.B., Wang, T., Palmer, P.I., 2004. Asian emissions of CO and NO_x: Constraints from aircraft and Chinese station data, *J. Geophys. Res.*, 109, D24304, doi:10.1029/2004JD005250

CHAPTER 5

CHARACTERIZATION OF ATMOSPHERIC PARTICULATE MATTER FROM ORGANIC TARRY MATTER AND LOSS ON IGNITION DURING CROP RESIDUE BURNING AND NON-CROP RESIDUE BURNING MONTHS

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5.1 Introduction

Suspended particulate matter (SPM) is one of the criteria pollutants emitted during crop residue burnings (Handa et al., 1980). It acts as a carrier of pollutants such as polycyclic aromatic hydrocarbons (PAH), toxic gases, metal particles, etc. which have deleterious effects on human health (Freeman and Catell, 1990; Godoi et al., 2004). Open burning activities involve incomplete burning of organic materials under sub-optimum combustion conditions. 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. Though straw burnings are banned by the local administration still farmers find these practices economical and convenient for the removal of residue and readying land for the next crop. Crop residue burning (CRB) practices generate a huge amount of smoke containing particulate matter and gaseous species which deteriorate quality of ambient air and affect public health (Dennisa et al., 2002; Wiedinmyera et al., 2006). The SPM PAH 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 tons of black smoke. Based on this and the Freeman and Catell (1990) study, approximately 6.3 tonnes of total particulates containing PAHs were released (Wild and Jones, 1995).

Organic compounds are the major components of atmospheric particulate matter in urban environments and the second most abundant fraction after sulphates at background and rural sites. The necessity to study the chemical composition of particulate matter for organic SPM is well described in literature (Jacobson et al., 2000, 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;

Rapsomanikis et al., 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 (Abase et al., 1995; Simoneit et al., 1983, 1988, 1991b, 1990, 1993).

In India, studies were carried out mainly in the Central (Pandey et al., 1999; Samal et al., 2002) and Southern parts of the country. Very few studies (Sandhu et al., 1991, 1992) are reported on characterization of atmospheric SPM in the North-Western region of India. Air pollution due to wheat and rice crop residue fires is a serious environmental problem in this North-West 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 observations provided that the SPM (particulate) pollution existed in a layer as thick as 3 kilometers (1.86 miles) and spread thousands of kilometers away from the source (Gupta et al., 2001; Verver et al., 2001). In addition to the impact on public health, the "brown cloud" (observed as widespread layers of brownish haze, are regional scale plumes of air pollutants, consisting of mainly aerosol particles, such as black carbon (BC), and precursor gases which produce aerosols and ozone) may be diminishing the monsoon-related rainfall in southern Asia and reducing crop yields through the filtering of sunlight (UNEP Assessment Report, August 2002; Ramanathan et al., 2002)

5.2 Organic tarry matter (OTM)

Organic Tarry Matter (OTM) represents the total organic matter (volatile and non-volatile, viz., aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, fatty acids and alkanols) in ambient carbonaceous SPM (Lighty et al., 2000; Johansson et al., 2003). A study conducted in Beijing to identify and estimate the contribution of biomass burning to the urban SPM organic carbon concentration indicated a high organic carbon concentration during wheat straw open fires (Duan et al., 2004). While searching for the origins of atmospheric SPM, the organic fraction may be further divided into "primary" and "secondary" materials (Stern, 1968). "Primary" material is that which is directly introduced into the atmosphere in

the particle state. Materials which condense shortly due to their low vapor pressure after introduction into the atmosphere from an elevated temperature source are also considered as Primary materials. “Secondary” material refers to particles formed as a result of homogeneous and heterogeneous reactions in the atmosphere. The carbonaceous material present in atmospheric SPM is a combination of elemental carbon, organic (including polymeric) and inorganic compounds (e.g., carbonate salts). Considerable research efforts have been made to characterize 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 SPM (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). Extractable Particulate Organic Fractions also called extractable organic matter (EOM) have the potential to cause adverse health effects. These fractions, and many compounds within them, have been shown to be mutagenic and carcinogenic. Investigators have found that the extractable organic material (EOM) from airborne particles is carcinogenic in animal bioassays (US EPA, 1984). The presence of polycyclic aromatic hydrocarbons (PAHs) in the EOM attributed to be carcinogenic and mutagenic.

5.3 Loss on Ignition (LOI)

Methodologies to provide more detailed analyses of carbonaceous SPM species in large numbers of samples are still being developed. Several techniques have been used to determine volatilizable organic matter and elemental carbon (i.e., black, graphitic, or sooty) in ambient and source-dominated SPM samples (Cadle and Groblckl 1982). Analytical methodologies have included use of (a) solvent extraction(s) to selectively remove the organic content (Grosjean 1975; Dalsey 1979), (b) optical techniques including laser-Raman spectroscopy to determine the elemental carbon content (Rosen et al., 1972; Faxfog and Roessler 1979; Japar and Killinger 1978), and (c) thermal methods based on selective evolution of organic and elemental carbon under a variety of pyrolysis conditions (Cadle et al., 1980). Thermal evolution techniques have been used in several forms, but basically they all involve programmed thermal vaporization and oxidation steps to differentiate organic carbon compounds from elemental carbon by means of differing temperature

profiles. Simplified thermo-evolution techniques which employ flash heating of samples to thereby obtain specific determination of low microgram levels of organic and elemental carbon, respectively, in atmospheric samples have been used to minimize organic-to-elemental conversions (Tanner et al., 1982). We wish to report concentration of combustible organic matter in SPM during CRB and NCRB months using a simplified thermo-evolution technique which employs heating of samples in a muffle furnace at a temperature of $600\pm 10^{\circ}$ C. Ignitable matter is a representative of combustible or unburnt hydrocarbons and is a measure of non-volatile compounds in the atmospheric SPM. Method gives a rough indication of the organic matter (Bengtsson & Enell, 1986). Depending on the ignition temperature, various losses of volatile salts, structural water and inorganic carbon may occur (Dean, 1974; Bengtsson & Enell, 1986; Sutherland, 1998) and it is important to check the ignition temperature carefully for organic matter determination. A defective furnace may produce a strong and immediately noticeable change of LOI results, hence we decided to run several tests to reduce errors and produce loss on ignition results more accurately. Interpretation of results is then only possible if an estimate of a laboratory specific error is available and real trends in the data can be viewed in relation to measurement errors.

Present study was aimed at determining the levels of combustible matter and OTM in SPM (total suspended particulate) samples collected during crop residue burning episodes (Roger et al., 1982) to determine the contribution of crop residue burning which may be helpful in source apportionment. We have presented results of solvent extraction and thermal heating of atmospheric SPM collected at three different locations in Patiala for the determination of soluble organic fraction and ignitable fraction. Correlation between combustible matter (LOI) and OTM was also studied. Sampling locations for the study include rural-cum-agricultural, semi-urban and urban-cum-commercial sites.

5.4 Methodology

SPM samples collected during the months of September 2006 to December 2007 using high volume samplers (HVS) (Envirotech, India) equipped with glass fiber filters (Whatman, Schleicher & Schuell, GF/A, Made in England) as a filtration media at selected sites (Table

1) (IS: 5182 (Part XIV) IS Standard, 1979) were analyzed for the estimation of loss on ignition and OTM in atmospheric SPM at Patiala. Each SPM sample had been collected for 24 h by passing air through the filter with an average rate of 1.5 cubic meters per minute. All the SPM samples were cut into four parts before going for further analysis. Soxhlet extraction technique was applied to each quadrant of the SPM sample to determine the OTM concentration. A fraction soluble in organic solvents represents the OTM present in samples. Samples were extracted with dichloromethane (DCM) using a customized procedure based on various used practices (Shannigrahi et al., 2005; Stephanou and Stratigakis, 1993; Gogou et al., 1998; Alves and Duarte, 1999; Oros and Simoneit, 2001). Similarly, quadrants of SPM samples were ignited in muffle furnace for the estimation of LOI. Despite the importance and relevance of the LOI test, the LOI test results are sensitive to practical variations that are within the requirements of the ASTM C 311 test standard. When thermal treatment is applied to any particulate sample, organic matter is oxidized to carbon dioxide (CO₂) and ash. LOI tests on ambient SPM samples were performed considering cooling time, sample size, ignition duration, and ignition temperature. An electrically heated temperature controlled Muffle Furnace (Sciential, India) capable of maintaining a high temperature of 800±10° C was used for the determination of loss on ignition in SPM samples.

5.5 Results and Discussion

Suspended particulate (< 100 micrometer) samples collected at three diverse locations (urban-commercial, semi-urban and rural-agricultural) in Patiala, India were analyzed for loss on ignition (LOI) and organic tarry matter (OTM) content in ambient air during crop residue burning (CRB) episodes and non-crop residue burning (NCRB) months in 2006-2007. Results showed high levels of LOI and OTM during wheat and rice crop residue burning periods at all the sites. Higher levels were obtained during rice crop residue burning period as compared to the wheat residue-burning period. At semi-urban site, LOI varied between 53±36 µgm⁻³ to 257±14 µgm⁻³ constituting 38% - 78% (w/w) part of the SPM whereas levels of OTM varied between 0.98±0.11 µgm⁻³ to 7.93±2.76 µgm⁻³ comprising 0.42% - 3.28% (w/w) fraction. At rural-agricultural area site (SVS), levels of LOI varied between 86±40 µgm⁻³ to 293±70µgm⁻³ comprising 27% - 84% (w/w), whereas

OTM levels varied between $1.31 \pm 0.64 \mu\text{gm}^{-3}$ to $10.09 \pm 6.56 \mu\text{gm}^{-3}$ constituting 0.83% - 2.42% (w/w) fraction of the SPM. At urban-cum-commercial site, levels of LOI and OTM varied between $48 \pm 23 \mu\text{gm}^{-3}$ to $281 \pm 152 \mu\text{gm}^{-3}$ and $2.53 \pm 1.23 \mu\text{gm}^{-3}$ to $17.40 \pm 8.50 \mu\text{gm}^{-3}$, constituting 24% - 62% (w/w) part of the SPM, respectively. Results also indicated that OTM and LOI were integral parts of SPM and their concentrations were influenced by the crop residue burning practices with incorporated effect of vehicular activities in Patiala.

5.5.1 SPM concentration in the ambient air

Suspended particles in the air are generally not visible at low concentration levels but at high concentration, they can be seen in the form of fog, smoke or haze during different seasons. Glass fiber filters generally become black after 24 hour sampling (Figure). At PUS, SVS and SAS, SPM levels varied between $100 \pm 29 \mu\text{gm}^{-3}$ to $458 \pm 79 \mu\text{gm}^{-3}$, $86 \pm 40 \mu\text{gm}^{-3}$ to $496 \pm 73 \mu\text{gm}^{-3}$ and $144 \pm 85 \mu\text{gm}^{-3}$ to $623 \pm 172 \mu\text{gm}^{-3}$, respectively during different sampling periods showing higher levels in the months of October-November and April-May at all the sites. During the period of study, 95% of the samples exceed the standard level of SPM ($200 \mu\text{gm}^{-3}$ for residential areas) recommended by the Central Pollution Control Board (CPCB), India. SPM levels were significantly higher in the months of October-November and April-May, indicating a clear contribution of agricultural activities, like the dust released during the process of shredding of wheat and rice grain from their spikes and crop residue burning activities after harvesting of these crops. CRB activities remain at its peak during these periods in this region of the country (Mittal et al., 2004). Since biomass combustion particles include particulates in the accumulation mode (100-1000nm) as well, it is likely to increase the total suspended particulate concentration during crop residue burnings.

5.5.2 Organic tarry matter in SPM

Organic carbon (OC) and water-soluble potassium (K^+) are the typical components of biomass burning SPM. Close to fires, OC accounts for about two-thirds of biomass burning SPM mass (Cachier et al., 1995). In a source profile study conducted in North Carolina, USA (Sheesley, 2007), the biomass burning contribution was found to be 30%-50% of the

annual OC concentration. K^+ has been used as a tracer element for the qualitative identification of biomass burning in many source apportionment studies (Lewis et al., 1988, Cachier et al., 1991, Chow, 1995).

In the present study, OTM concentrations of SPM were analyzed and found to be associated with agricultural waste fires. Variations in the levels of OTM of SPM are shown in Figures 1, 2 and 3. Monthly average absolute amounts of OTM are plotted for each site. Results indicate that the OTM content is dependent on the concentration of SPM and is an essential component of it. OTM levels are known to depend on vehicular exhaust (Li et al., 2009; Zheng et al., 1997), but CRB practices have greatly influenced the OTM levels in and around Patiala city indicating a great association with SPM levels except observations in July 2007 at PUS. Sandhu and Gehlan (1991) have reported similar results in a study conducted in Amritsar, India.

Table 5.1 Concentration levels of OTM in SPM samples during CRB and NCRB months at different sites

Year	Episode	Month	Concentration in μgm^{-3} $\pm$ standard deviation					
			PUS		SVS		SAS	
			OTM	SPM	OTM	SPM	OTM	SPM
2006	NCRB	Sep	--	--	3.59 $\pm$ 1.36	341 $\pm$ 143	--	340 $\pm$ 186
	CRB (Rice)	Oct	4.4$\pm$0.4	344$\pm$45	10.1$\pm$6.6	445$\pm$105	8.9$\pm$7.8	571$\pm$127
		Nov	6.4$\pm$1.7	381$\pm$120	9.3$\pm$8.8	460$\pm$165	6.7$\pm$3.6	348$\pm$232
	NCRB	Dec	2.0 $\pm$ 0.4	269 $\pm$ 73	3.3 $\pm$ 0.8	192 $\pm$ 16	7.0 $\pm$ 0.8	269 $\pm$ 10
2007	NCRB	Jan	1.0 $\pm$ 0.9	193 $\pm$ 184	5.9 $\pm$ 1.1	277 $\pm$ 54	4.9 $\pm$ 0.4	179 $\pm$ 31
		Feb	2.3 $\pm$ 1.0	230 $\pm$ 112	1.9 $\pm$ 1.5	206 $\pm$ 103	5.3 $\pm$ 2.6	231 $\pm$ 108
		Mar	1.9 $\pm$ 1.4	139 $\pm$ 34	1.6 $\pm$ 1.2	186 $\pm$ 72	6.6 $\pm$ 1.2	144 $\pm$ 85
	CRB (Wheat)	Apr	2.7$\pm$2.2	321$\pm$98	5.2$\pm$2.0	488$\pm$168	11.2$\pm$3.6	474$\pm$88
		May	2.7$\pm$2.0	277$\pm$74	2.9$\pm$2.3	387$\pm$72	7.2$\pm$4.5	386$\pm$139
	NCRB	Jun	1.1 $\pm$ 0.4	200 $\pm$ 142	1.3 $\pm$ 0.6	125 $\pm$ 4	2.6 $\pm$ 1.5	272 $\pm$ 239
		Jul	1.0 $\pm$ 0.1	293 $\pm$ 202	2.8 $\pm$ 0.1	266 $\pm$ 138	2.5 $\pm$ 1.2	175 $\pm$ 40
		Aug	1.6 $\pm$ 0.4	122 $\pm$ 22	1.4 $\pm$ 0.5	111 $\pm$ 22	4.0 $\pm$ 1.6	209 $\pm$ 89
		Sep	1.3 $\pm$ 0.1	100 $\pm$ 29	2.3 $\pm$ 0.7	141 $\pm$ 18	--	205 $\pm$ 73
	CRB (Rice)	Oct	7.9$\pm$2.8	458$\pm$79	8.4$\pm$7.2	442$\pm$112	8.1$\pm$4.8	441$\pm$91
		Nov	3.2$\pm$0.1	320$\pm$39	5.8$\pm$4.2	432$\pm$170	17.4$\pm$8.5	623$\pm$172
	NCRB	Dec	2.9 $\pm$ 0.8	210 $\pm$ 143	1.9 $\pm$ 0.6	248 $\pm$ 45	8.2 $\pm$ 5.8	257 $\pm$ 118

N.B. Values in bold indicate levels of OTM and SPM during CRB episodes, -- data not available

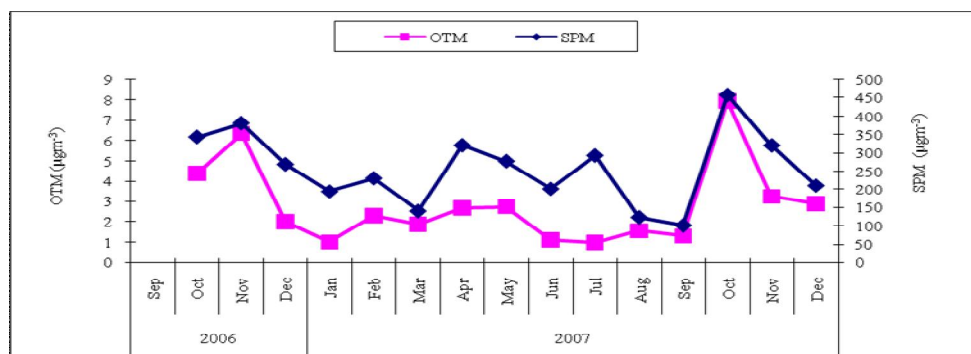


Figure 5.1 Variation in OTM concentration levels with respect to SPM levels at Punjabi University Site (semi-urban area site)

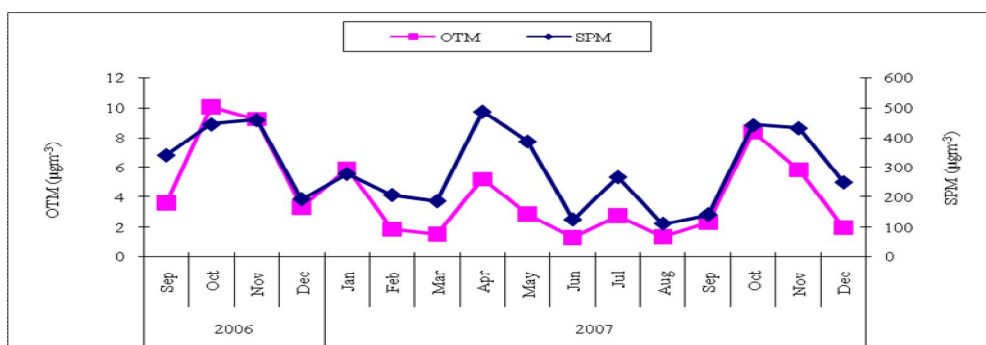


Figure 5.2 Variation in OTM concentration levels with respect to SPM levels at Sidhuwal Village Site (rural area site)

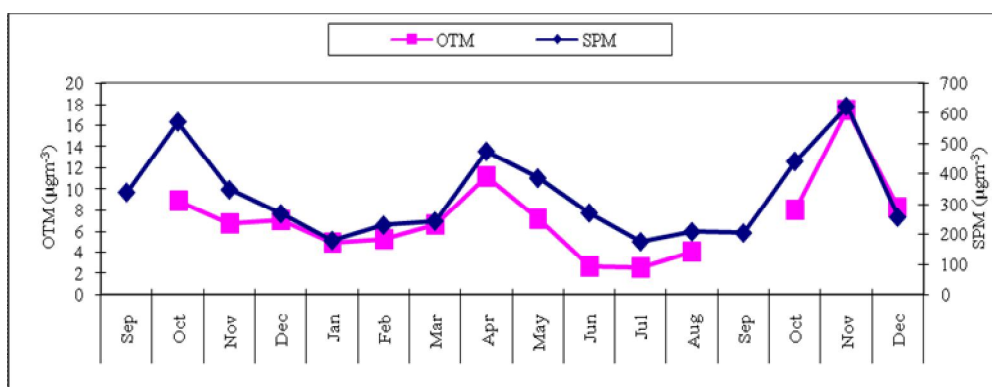


Figure 5.3 Variation in OTM concentration levels with respect to SPM levels at Sanauri Adda Site (commercial area site)

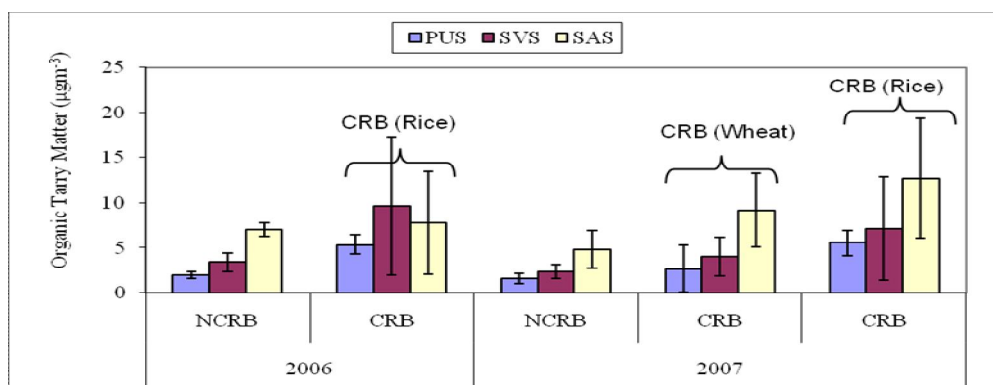


Figure 5.4 Variation in OTM concentration levels during crop residue burning (CRB) and non-crop residue burning (NCRB) episodes

During the study period, OTM concentration varied between $1.0 \pm 0.1 \mu\text{gm}^{-3}$ (lowest) to $17.4 \pm 8.5 \mu\text{gm}^{-3}$ (highest). Higher concentration was obtained in October-November and April-May as these were the months during which farmers burn rice and wheat crop residues after harvesting of the crops. Average levels of OTM during CRB months [$8 \mu\text{gm}^{-3}$ (rice season, 2006); $5 \mu\text{gm}^{-3}$ (wheat, 2007); $8 \mu\text{gm}^{-3}$ (rice, 2007)] were found higher as compared to that of the average OTM levels during NCRB ($4 \mu\text{gm}^{-3}$, 2006; $3 \mu\text{gm}^{-3}$, 2007) (Figure 4). However, levels were higher during rice CRB periods ($8 \mu\text{gm}^{-3}$) as compared to that of wheat CRB ($5 \mu\text{gm}^{-3}$) in 2006-2007. At PUS, levels of OTM varied between $1.0 \pm 0.1 \mu\text{gm}^{-3}$ to $7.9 \pm 2.8 \mu\text{gm}^{-3}$ with highest concentration in the month of October 2007 ($7.9 \pm 2.8 \mu\text{gm}^{-3}$) and lowest in the month of July 2007 ($1.0 \pm 0.1 \mu\text{gm}^{-3}$). Concentration of OTM was found dependent on the levels of SPM in these months and helps in retaining particulate matter in the lower ambient environment hence, OTM concentration was higher during high SPM load. In terms of percentage of SPM, OTM constituted only 0.4% - 3.3 % (w/w) fraction of SPM at this site (Figure 5, Table 2).

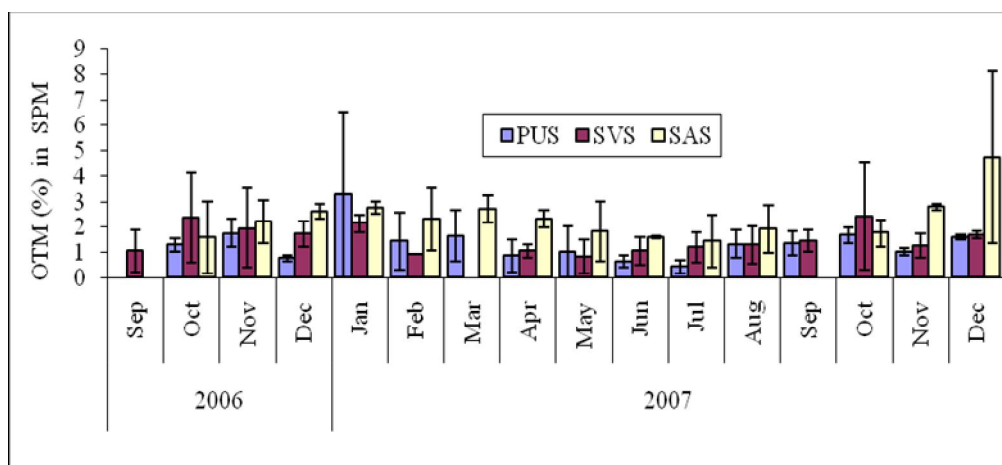


Figure 5.5 Monthly variations of OTM concentration levels in SPM at different monitoring sites

At SVS, OTM levels (Table 2) varied between $1.3 \pm 0.7 \mu\text{gm}^{-3}$ to $10.1 \pm 6.6 \mu\text{gm}^{-3}$ showing the highest concentration in October 2006 ($11.0 \pm 6.7 \mu\text{gm}^{-3}$) and lowest in June 2007 ($1.3 \pm 0.7 \mu\text{gm}^{-3}$). Concentration levels of OTM varied in association with the concentration of SPM. OTM in SPM samples varied between 0.8% - 2.4% (Figure 5). Similarly, OTM concentration varied at SAS and the levels were found higher during October-November and April-May in 2007. Peak concentration was obtained in November 2007 ($17.4 \pm 8.5 \mu\text{gm}^{-3}$) whereas, the lowest concentration was observed in July 2007 ($2.5 \pm 1.2 \mu\text{gm}^{-3}$). Higher levels during October-November and April-May again indicated that the effect of CRB on OTM levels were higher in the rice CRB events in October than in wheat CRB months (April-May) as the former events occur at lower temperature (Mittal et al., 2009) than the later events and eventually resulting in generation of particulates rich in carbon contents. Higher concentration of OTM during wheat CRB months is a clear result of the proposed hypothesis. This effect is compounded due to lower ambient temperatures. Although OTM levels were higher at all the sites during CRB, but peak concentration was obtained at SAS. In terms of total mass of SPM, OTM ranged between 4.74% - 1.44% (w/w) at this site. Meteorological parameters like wind speed, wind direction, temperature and rainfall play important role on the levels of ambient air particulates or SPM concentration. Trends of monthly variation in OTM concentration were observed similar to the trends of variation in SPM concentration, being higher, when SPM concentration was

high and lower during low SPM levels. Effect of meteorological parameters on SPM concentration has been discussed in another chapter (Chapter 7) and the effect of meteorological parameters on OTM shall also be similar to that on SPM levels.

5.5.3 Loss on ignition in SPM

SPM samples collected during September 2006 to December 2007 were analyzed to determine the combustible matter in the form of LOI levels. LOI in the SPM samples collected at PUS varied between $53 \pm 36 \mu\text{gm}^{-3}$ to $257 \pm 14 \mu\text{gm}^{-3}$ (Figure 6). Higher LOI was obtained during Rice CRB and Wheat CRB months as compared to that during NCRB months. LOI in SPM samples varied between 38%-78% (w/w) at SVS (Figure 10). At this site, LOI in SPM samples varied between 86 ± 40 to $293 \pm 70 \mu\text{gm}^{-3}$ indicating higher levels in April-May and October-November (Figure 7) as compared to the rest of the months of a year. In terms of percent weight, LOI at SVS varied between 27%-84% (w/w) of the SPM mass while at SAS, it varied between $48 \pm 23 \mu\text{gm}^{-3}$ to $281 \pm 152 \mu\text{gm}^{-3}$ and 24%-62% (w/w) during 2006-2007.

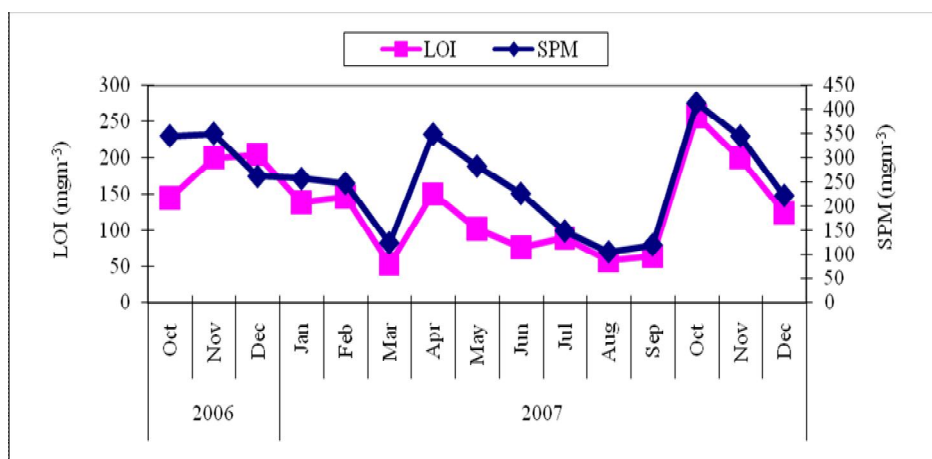


Figure 5.6 Variation in LOI concentration levels with respect to SPM levels at PUS (semi-urban area site)

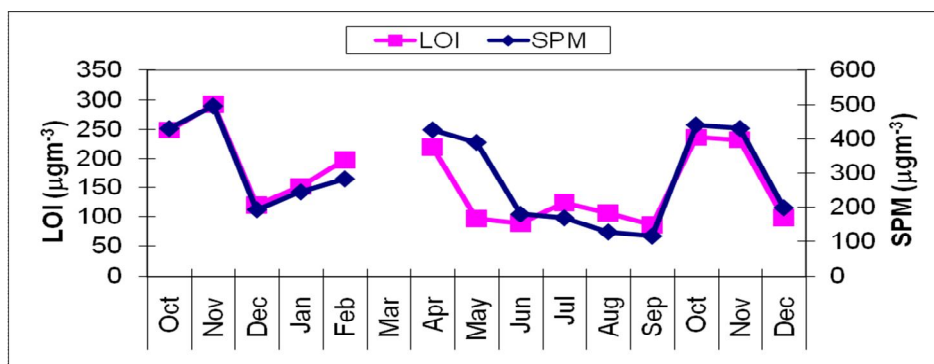


Figure 5.7 Variation in LOI concentration levels with respect to SPM levels at SVS (rural area site)

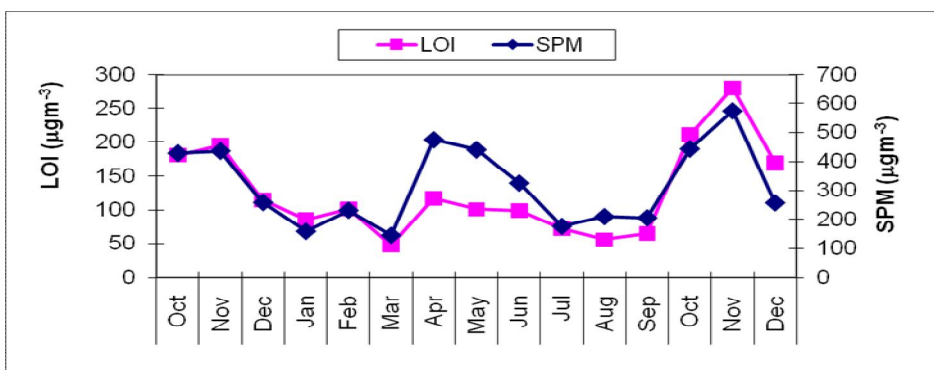


Figure 5.8 Variation in LOI concentration levels with respect to SPM levels at SAS (urban-cum-commercial area site)

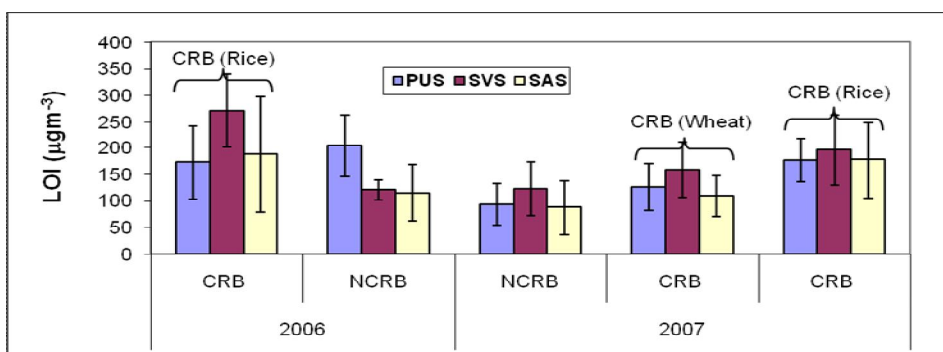


Figure 5.9 Variation in LOI concentration levels during CRB and NCRB episodes at different monitoring sites

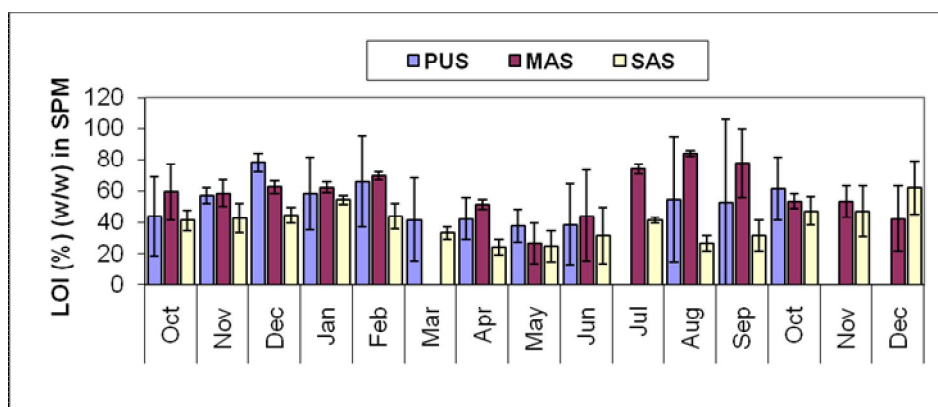


Figure 5.10 Variation in concentration levels of LOI with respect to SPM levels at different monitoring sites

Table 5.2 Concentration levels of LOI in SPM samples during CRB and NCRB months at different sampling sites

Year	Period	Month	PUS		SVS		SAS	
			LOI	SPM	LOI	SPM	LOI	SPM
2006	CRB (Rice)	Oct	145±74	345±37	249±68	430±98	181±78	429±127
		Nov	200±64	350±115	293±70	496±73	196±139	436±232
	NCRB	Dec	205±59	262±78	121±18	192±17	115±53	258±96
2007	NCRB	Jan	139±18	258±67	152±33	245±55	86±48	158±112
		Feb	146±50	248±91	198±78	283±103	102±41	231±108
		Mar	53±36	126±23	--	--	48±23	144±85
	CRB (Wheat)	Apr	150±64	349±95	219±68	426±128	117±45	475±89
		May	101±24	283±83	98±36	390±86	101±33	440±177
	NCRB	Jun	76±41	227±162	89±89	179±108	99±96	327±239
		Jul	89±32	150±60	125±20	168±74	73±36	176±56
		Aug	58±40	107±56	107±16	127±62	56±27	209±119
		Sep	64±51	121±74	86±40	115±48	65±19	205±157
	CRB (Rice)	Oct	257±14	413±47	237±69	441±110	211±58	443±88
		Nov	200±74	345±53	232±96	430±140	281±152	575±182
	NCRB	Dec	124±42	223±89	99±77	198±126	170±117	258±119

N.B. Values in bold indicate levels of LOI and SPM during CRB episodes, -- data not available

At all the sites, LOI levels increased with increase in SPM levels. Figures 6, 7, and 8 represent a clear association between LOI and SPM levels, indicating the possibility of a similar source for SPM and combustible matter at the selected locations (Sharma et al., 1992; Sillanpaa et al., 2005). LOI levels were higher at all the sites during CRB (October-November and April-May) but the highest value was obtained at SVS ($293 \pm 70 \mu\text{gm}^{-3}$). In terms of parentage, LOI levels varied between 24%-62% (w/w) of the SPM weight at SAS.

Due to agricultural fields all around the SVS sampling site, peak LOI concentration was obtained at this location (SVS), indicating a greater impact of CRB. Average concentration of combustible matter (LOI) during CRB months [$211 \mu\text{gm}^{-3}$ (rice 2006); $131 \mu\text{gm}^{-3}$ (wheat 2007); $184 \mu\text{gm}^{-3}$ (rice 2007)] was found higher when compared with the average concentration level of NCRB months ($147 \mu\text{gm}^{-3}$, 2006; $101 \mu\text{gm}^{-3}$, 2007). This clearly indicates the influence of CRB on the levels of ignitable matter in atmospheric SPM (Figure 9).

Table 5.3 Percentage of Ignitable Matter in terms of LOI and OTM in SPM samples at different sites

Year	Month	PUS		SVS		SAS	
		LOI (%)	DCM Soluble Organic Fraction (%)	LOI (%)	DCM Soluble Organic Fraction (%)	LOI (%)	DCM Soluble Organic Fraction (%)
2006	Sep	--	--	--	1.05 ± 0.83	--	--
	Oct	44 ± 25	1.3 ± 0.3	59 ± 18	2.37 ± 1.8	41 ± 7	1.6 ± 1.4
	Nov	57 ± 5	1.8 ± 0.6	59 ± 8	2.0 ± 1.6	43 ± 9	2.2 ± 0.8
	Dec	78 ± 6	0.8 ± 0.1	63 ± 4	1.8 ± 0.5	45 ± 5	2.6 ± 0.3
2007	Jan	58 ± 23	3.3 ± 3.3	62 ± 3	2.2 ± 0.3	54 ± 3	2.7 ± 0.2
	Feb	66 ± 29	1.5 ± 1.1	70 ± 2	0.92 ± 0.5	44 ± 8	2.3 ± 1.2
	Mar	42 ± 26	1.7 ± 1.0	--	--	33 ± 4	2.7 ± 0.5
	Apr	43 ± 13	0.87 ± 0.66	51 ± 3	1.1 ± 0.3	24 ± 5	2.3 ± 0.3
	May	38 ± 11	1.02 ± 1.00	27 ± 13	0.8 ± 0.7	25 ± 10	1.8 ± 1.2
	Jun	39 ± 26	0.7 ± 0.3	44 ± 29	1.1 ± 0.6	32 ± 18	1.6 ± 0.1
	Jul	--	0.4 ± 0.3	74 ± 3	1.2 ± 0.6	41 ± 2	1.4 ± 1.0
	Aug	54 ± 40	1.3 ± 0.6	84 ± 2	1.3 ± 0.8	27 ± 5	1.9 ± 0.9
	Sep	53 ± 53	1.4 ± 0.5	78 ± 22	1.5 ± 0.4	32 ± 10	--
	Oct	62 ± 20	1.7 ± 0.3	54 ± 5	2.4 ± 2.1	47 ± 9	1.8 ± 0.5
	Nov	--	1.0 ± 0.1	53 ± 10	1.3 ± 0.5	47 ± 16	2.8 ± 0.1
	Dec	--	1.6 ± 0.1	42 ± 21	1.7 ± 0.2	62 ± 17	4.5 ± 3.4

N.B. Values in bold indicate levels of LOI, OTM and SPM during CRB episodes, -- data not available, DCM: Dichloromethane (Solvent for extraction of OTM)

Quite a lot of studies have indicated significant emissions of organic material (SVOCs) like PAH from biomass burning (Masclet et al.1995; Kjallstrand et al., 2000). However, burning of crude oil and diesel fuel produced significant amounts of PAHs relative to other types of open burning, nevertheless, biomass burning is a significant source of PAH in ambient air. In the present study, significantly increased levels of OTM and LOI during biomass

burning episodes indicate the possibility of higher levels of PAH in the ambient air of Patiala during 2006-2007.

5.5.4 Relationship between OTM and LOI of SPM at different sampling sites

Linear regression analysis was performed to find out the correlation between OTM and LOI using average monthly levels of OTM and LOI obtained during crop residue burning and non-crop residue burning months. Regression coefficients were calculated for all the sites. Results from linear regression analysis showed good correlation between OTM and LOI ($R^2=0.956$, Figure 5.11) at rural-agricultural area site as compared to the semi-urban ($R^2=0.182$) and urban-commercial ($R^2=0.393$) sites. This indicated that there is a similar source of OTM and combustible matter in SPM at rural agricultural site (SVS). g

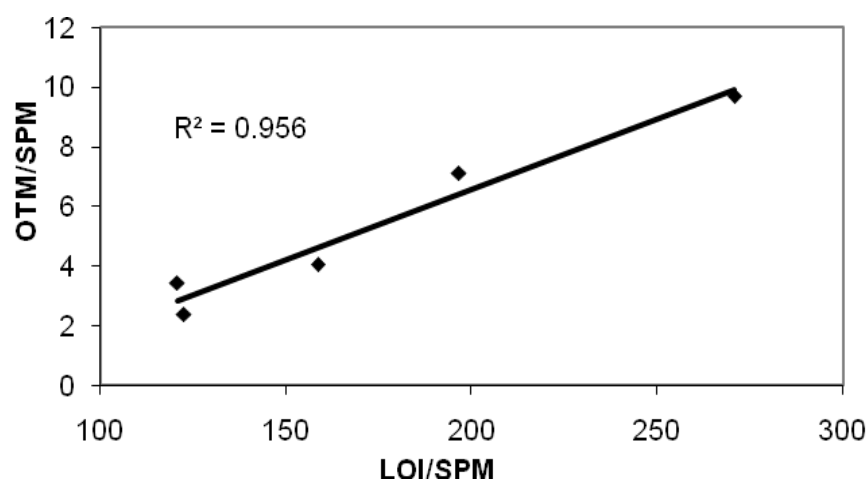


Figure 5.11 Relationship between OTM and LOI at rural-agricultural area site.
Average monthly levels of OTM and LOI during CRB and NCRB months were used for the linear regression analysis.

At, semi-urban and urban-commercial sites, a deviation in the values of OTM and LOI indicate different sources of OTM and combustible matter. Automobile exhaust might be contributing to OTM levels in addition to that of CRB episodes.

Higher levels of LOI were observed in the samples of rural-agricultural (SVS) site as compared to those of semi-urban site (PUS) and urban-commercial site (SAS). All levels of
[117]

OTM and LOI were higher in the SPM samples collected during CRB months in 2006 and 2007, which were due to CRB in the corresponding harvesting seasons. Similar sources of LOI were reported by Sandhu and Gehlan (1991) for the studies carried out at Amritsar, Punjab (India). The overall average LOI in the present study was about 50% of the SPM content as compared to 43% found at Amritsar in 1991.

5.6 Conclusions

An average level of LOI as 50% of the SPM indicated high content of combustible matter in the ambient air of Patiala during the months following the harvesting of crops. Levels of combustible matter content were found to be associated with the levels of SPM in the ambient air. Organic tarry matter (OTM) was found only 2% of the total SPM concentration. Levels of OTM was also associated with the crop residue burning episodes during 2006-2007, indicating a sizable contribution to the levels of SPM as well as OTM and combustible matter. SPM concentration level was above the $200 \mu\text{gm}^{-3}$ (National Ambient Air Quality Standards (NAAQS) for residential areas. Higher levels of combustible particulate matter and OTM increase the possibility of the presence of polycyclic aromatic hydrocarbons (PAH) in the ambient air. Determination of these components would be helpful in the study of biomass burning influences and source apportionment, as concentration of these constituents increase with the increase in the levels of SPM concentration.

References

- Abas, M.R., Simoneit, B.R.T., Elias V., Cabral, J.A., Cardoso, J.N., 1995. Composition of higher molecular weight organic matter in smoke SPM from biomass combustion in Amazonia. *Chemosphere* 30, 995-1015.
- Alves, C.P., Duarte, A., 1999. The organic composition of air particulate matter from rural and urban portuguese areas. *C Physics and Chemistry of the Earth, Part B: Hydrology, Oceans and Atmosphere* 24 (6), 705-709.
- Appel, B.R., Colodny, P., Wesolowski, J.J., 1976. Analysis of carbonaceous materials in southern California atmospheric SPM. *Environmental Science & Technology* 10 (4), 359-363.

Appel, B.R., Hoffer, E.M., Kothny, E.L., Wall, S.M., Haik, M., 1979. Analysis of Carbonaceous Material in Southern California Atmospheric SPM. *Environmental Science & Technology* 13 (1), 98-104.

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, 205-213.

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.

Bengtsson, L., Enell, M., 1986. Chemical analysis. In Berglund B.E. (ed.), *Handbook of Holocene Palaeoecology and Palaeohydrology*. John Wiley & Sons Ltd., Chichester, 423-451.

Bowyer, J.R., Pleil, J.D., 1997. Comparison of supercritical fluid extraction and Soxhlet extraction of organic compounds from carpet samples. *Journal of Chromatography A* 787 (1-2), 171-179.

Boyle, J.F., 2004. A comparison of two methods for estimating the organic matter content of sediments: comment. *Journal of Paleolimnology* 31 (1) 125-127.

Cachier, H., Ducret, J., Bremond, M.P., Yoboue, V., Lacaux, J.P., Gaudichet, A., Baudet J., 1991. Biomass burning SPM in a Savannah region of the Ivory Coast. In: Levine J.S. (Ed.), *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*. The MIT Press, Cambridge, London, pp. 174-180.

Cachier, H., Lioussé, C., Buat-Menard, P., Gaudichet, A., 1995. Particulate content of Savanna fire emissions. *Journal of Atmospheric Chemistry* 22, 123-148.

Cachier, H., Lioussé, C., Buat-Menard, P., 1995. A Gaudichet. Particulate content of Savanna fire emissions. *Journal of Atmospheric Chemistry* 22, 123-148.

Cadle, S.H., Grobllckl, P.J., In "Particulate Carbon: Atmospheric Life Cycle"; Wolff, O. T., Kllmisch, R. L., Eds.; Plenum: New York, 1982; pp 89-108.

Cadle, S.H., Qroblckl, P.J., Stroup, D.P., 1980. *Anal. Chem.*, 52, 2201-2206.

Chow, J.C., 1995. Measurement methods to determine compliance with Ambient Air Quality Standards for suspended particles. *Journal of Air & Waste Management Association* 45, 320-382.

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, 935-942.

Dalsey, J.M., Leyko, M.A., Klelnman, M.T., Hoffman, E. Ann. N.Y. Acad. Sci. 1979, 322, 125-141.

Dean, W.E., 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. *Journal of Sedimentary Research* 44, 242-248.

Dennisa, 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., Yuc, T., Cachier, H., 2004. Identification and estimate of biomass burning contribution to the urban SPM organic carbon concentrations in Beijing. *Atmospheric Environment* 38, 1275-1282.

Fang, M., Zheng, M., Wang, M., To, K.L., Jaafar, A.B., Tong, S.L., 1999. The solvent extractable organic compounds in the Indonesian biomass burning SPM characterization studies. *Atmospheric Environment* 33, 783-795.

Fartas, F.M., Othman, M.R., Latif, M.T., 2009. Qualitative Analysis of Dominant Organic Compounds in PM10 and Burning Residue of Selected Plants. *Research Journal of Agriculture and Biological Sciences* 5 (4), 452-457.

Faxfog, F.R., Roessler, D.M., *J. Appl. Phys.* 1979, 50, 7880-7882.

Folliard, K.J., Harris, N.J., Hover, K.C., Ley, T., 2006. Variables Affecting the ASTM Standard C 311 Loss on Ignition Test for Fly Ash. *Journal of ASTM International* 3 (8), 1-12.

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

Godoi, A.F.L., Ravindra, K., Godoi, R.H.M., Andrade, S.J., Santiago-Silva, M., Vaeck L.V., Grieken, R.V., 2004. Fast chromatographic determination of polycyclic aromatic hydrocarbons in SPM samples from sugar cane burning. *Journal of Chromatography A* 1027 (1-2) 49-53.

Gogou, A., Apostolaki, M., Stefanou, E.G., 1998. Determination of organic molecular markers in marine SPM and sediments: One-step flash chromatography compound class fractionation and capillary gas chromatography analysis. *Journal of Chromatography* 799, 215-231.

Grosjean, D., 1975. Solvent extraction and organic carbon determination in atmospheric particulate matter: The organic extraction-organic carbon analyzer (OE/OCA) technique. *Analytical Chemistry* 47, 797-805.

Handa, T., Kato, Y., Yamamura, T., Ishii, T., Suda, K., 1980. Correlation between the concentrations of polynuclear aromatic hydrocarbons and those of particulates in an urban atmosphere. *Environmental Science & Technology* 14 (4) 416-422.

Hays, M.D., Fine, P.M., Geron, C.D., Kleeman, M.J., Gullett, B.K., 2005. Open burning of agricultural biomass: Physical and chemical properties of particle-phase emissions. *Atmospheric Environment* 39 (36), 6747-6764.

Heiri, O., Lotter, A.F., Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Journal of Paleolimnology* 25, 101-110.

IS: 5182 (part XIV) IS Standard, 1979. Guidelines for planning and sampling of atmosphere.

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

Jacobson, M.Z., 2001. Strong radiative heating due to the mixing state of black carbon in atmospheric SPM. *Nature* 409, 695-698.

Japar, S.M., Killinger, D.K., 1978. *Chem. Phys. Lett.*, 66, 207-209.

Johansson, L.S., Tullin, C., Leckner, B., Sjobvall, P., 2003. Particle emissions from biomass combustion in small combustors. *Biomass and Bioenergy* 25 (12) 435-446.

Li, X., Guo, X., Liu, X., Liu, C., Zhang, S., Wang, Y., 2009. Distribution and sources of solvent extractable organic compounds in PM_{2.5} during 2007 Chinese Spring Festival in Beijing. *Journal of Environmental Sciences* 21 (2) 142-149.

Lighty, J.S., Veranth, J.M., Sarofim, A.F., 2000. Combustion SPM: Factors governing their size and composition and implications to human health. *Journal of the Air & Waste Management Association* 50, 1565-1618.

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

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.

Masclet, P., Cachier, H., Liousse, C., and Wortham, H., 1995. Emissions of Polycyclic Aromatic Hydrocarbons by Savanna Fires. *Journal of Atmospheric Chemistry*, 22, (1-2) 41-54

Mazzoleni, L.R., Zielinska, B., Moosmuller, 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.

Mittal, S.K., Goyal, S., 2004. SPM levels of an urban area (Patiala City) and its relation to automobile exhaust. *Clean Technology Environment Policy* 6, 263-267.

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

Oros, D.R., Simoneit, B.R.T., 2001. Identification and emission factors of molecular tracers in organic SPM from biomass burning Part 1: Temperate climate conifers. *Applied Geochemistry* 16 (13), 1513-1544.

Pandey, V., Kumar, A., Pal, A., Singh, N., Yunus, M., 1999. Status of ambient air quality in Lucknow City. *Indian Journal of Environmental Protection* 19, 181-184.

Peters, A.J., Lane, D.A., Gundel, L.A., Northcott, G.L., Jones, K.C., 2000. A Comparison of High Volume and Diffusion Denuder Samplers for Measuring Semivolatile Organic Compounds in the Atmosphere. *Environmental Science & Technology*, 34 (23), 5001-5006.

Roger, L.T., Jeffrey S.G., Phillips, M.F., 1982. Determination of organic and elemental carbon in atmospheric SPM samples by thermal evolution. *Anal. Chem.*, 54 (9), 1627-1630.

Rosen, H., Hansen, A.D.A., Gundel, L., Novakov, T., *Appl Opt*, 1978, 17, 3859-3861.

Rukmangad, P.P., 1991. Particle size distribution and its elemental composition in the ambient air of Nagpur City. *Indian Journal of Environmental Protection* 11 (6) 409-412.

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 OTM 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 (10), 733-739.

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, 1821-1832.

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

Shannigrahi, A.S., Fukushima, T., Ozaki, N., 2005. Comparison of different methods for measuring dry deposition fluxes of particulate matter and polycyclic aromatic hydrocarbons (PAHs) in the ambient air. *Atmospheric Environment*, 39, 653-662.

Sharma, V.K., Patil, R.S., 1992. Size Distribution of Atmospheric SPM and their Source Identification using Factor Analysis. *Atmospheric Environment* 26B (1), 135-140.

Sheesley, R.J., Schauer, J.J., Zheng, M., Wang, B., 2007. Sensitivity of molecular marker-based CMB models to biomass burning source profiles. *Atmospheric Environment* 41 (39), 9050-9063.

Sillanpaa, M., Frey, A., Hillamo, R., Pennanen, A.S., Salonen, R.O., 2005. Organic, elemental and inorganic carbon in particulate matter of six urban environments in Europe. *Atmospheric Chemistry and Physics* 5, 2869-2879.

Simoneit, B.R.T., 2002. Biomass burning a review of organic tracers for smoke from incomplete combustion. *Applied Geochemistry* 17 (3), 129-162.

Simoneit, B.R.T., Cardoso, J.N., Robinson, N., 1990. An assessment of the origin and composition of higher molecular weight organic matter in SPM over Amazonia. *Chemosphere* 21, 1285-1301.

Simoneit, B.R.T., Cox, R.E., Standley, L.J., 1988. Organic matter of the troposphere IV: Lipids in Harmattan SPM particles of Nigeria. *Atmospheric Environment* 22, 983-1004.

Simoneit, B.R.T., Mazurek, M.A., Reed, W.E., 1983. Characterization of organic matter in SPM over rural sites: Phytosterols. In: *Advances in Organic Geochemistry 1981*, M. Bjoroy et al. (eds.), J. Wiley and Sons Ltd., Chichester, pp. 355-361.

Simoneit, B.R.T., Rogge, W.E., Mazurek, M.A., Standley, L.J., Hildemann, L.M., Cass G.R., 1993. Lignin pyrolysis products, lignans and resin acids as specific tracers of plant classes in emissions from biomass combustion. *Environmental Science & Technology* 27, 2533-2541.

Simoneit, B.R.T., Sheng, G., Chen, X., Fu, J., Zhang, J., Xu, Y., 1991b. Molecular marker study of extractable organic matter in SPM from urban areas of China. *Atmospheric Environment* 25A, 2111-2129.

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* 644, 141-151.

Stern, A.C., 1968. Air Pollution. Vol. I, p 149, Academic Press, New York.

TERI 2003. Report No. 2003SF62, ch. 15, Patiala, DBAS (Patiala), Punjab, pp. 317-338.

UNEP Assessment Report, The Asian Brown Cloud: Climate and Other Environmental Impacts, August 2002, UNEP/DEWA/RS.02-3; Available at www.rrcap.unep.org/abc/impactstudy/.

Ramanathan, V., Crutzen, P.J., Mitra, A.P., Sikka, D., 2002. The Indian Ocean Experiment and the Asian Brown Cloud, *Current Science*, 83, 8 (25).

Vale, M.G.R., Luz, L.P., Martins, A.F., Caramao, E.B., Dariva, C., de Oliveira, J.V., 1998. Extraction of organic material in mineral coal by using supercritical fluid extraction, soxhlet, and sonication methods. *Journal of Microcolumn Separations* 10 (3), 259-263.

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.

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

Wild, S.R., Jones, K.C., 1995. Polycyclic Aromatic Hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget. *Environmental Pollution* 88, 91-108.

Williamson, S.J., 1973. "Fundamentals of Air Pollution", Ch. 2, Addison-Wesley, Menlo Park, California.

Zheng, M., Wana, T.S.M., Fang, M., Wang, F., 1997. Characterization of the non-volatile organic compounds in the SPM of Hong Kong-identification, abundance and origin. *Atmospheric Environment* 31 (2) 227-237.

Gupta, P.K., Prasad, V.K., Kant, Y., Sharma, C., Ghosh, A.B., Sharma, M.C., Sarkar, A.K., Jain, S.L., Tripathi, O.P., Sharma, R.C., Badrinath, K.V.S., Mitra, A.P., 2001. Study of trace gases and aerosol emissions due to biomass burning at shifting cultivation sites in East Godavari district (A.P.) during INDOEX IFP-99, *Current Science*, 80, 186-196.

Verver, G.H.L., Sikka, D.R., Lobert, J.M., Stossmeister, G., Zachariasse, M., 2001. Overview of the meteorological conditions and atmospheric transport processes during INDOEX 1999, *Journal of Geophysical Research*, 106, D22, 28:399-28:413.

CHAPTER 6

AMBIENT AIR LEVELS OF K, Cu, Ni, AND Zn DURING CROP RESIDUE BURNING AND NON-CROP RESIDUE BURNING PERIODS AND THEIR RELATIONSHIP WITH SPM

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6.1 Introduction

In almost all major cities of India having population more than one million, ambient air pollution levels exceed National Ambient Air Quality Standards (NAAQS) and also WHO health standards. Urban air as well as rural air quality is degrading due to upward trends in power consumption, industrialization, and vehicle use (Shah et al., 2006). Crop residue burning (CRB) has also been identified as a dominating contributor of particulate and gaseous pollution in many developing and developed countries (Park et al., 2005; Yang et al., 2008; Mittal et al., 2009). Study conducted by Park and Kim (2005) has shown that major contributors to the ambient air pollution of urban atmosphere are: vehicle exhaust (26%), soil dust (13%) and field burning (4%). Begum et al in 2004 has reported that biomass burning contributed 50% towards the SPM in ambient air particulate matter collected at Rajshahi.

Particulate matter has been linked with human morbidity and mortality and weakening of environmental properties (Charlson et al. 1992; Dockery et al., 1994; Dickerson et al. 1997; Kappos et al., 2004). Since 1990, measurements carried out by National Environmental Engineering Research Institute (NEERI) in ten major cities of India as a part of National Air Quality Monitoring program of atmospheric concentration of SPM and toxic metals revealed levels of air quality parameters with respect to Respirable Suspended Particulate Matter (RSPM) in industrial locations of Kanpur, Ahmedabad, Delhi and Kolkata (NEERI, 1998, 2000, 2001). It has been experienced that the toxic metals are associated with fine dust, which remains in ambient air environment for longer duration under the prevailing meteorological conditions. These are transported from one place to other and contaminate other pristine environments (Schroeder et al., 1987; Bhanarkar et al., 2002; Negi et al., 1987; Sadasivan et al., 1990; Gajghate et al., 2005).

Long exposure to heavy metals has adverse effects on the human health and biodiversity (Khandekar et al., 1984). Copper smelters have been reported as the main source of copper emissions in the ambient air in industrial areas but recent studies (Denier van der Gon et al. 2007) have indicated that brake wear emissions may also be responsible for copper emissions to the extent of 50-75% of the total copper emissions to the ambient air for most of Western Europe regions. Some studies have also reported particle abrasion from wheels of rail and railway tracks as a source of metal pollution in ambient air (Bukowiecki et al., 2007). Presence of Cu in SPM samples is reported from Kanpur, Jaipur, Mumbai, Nagpur and Agra (Chelani et al., 2001; Sharma et al., 1983; Negi et al., 1987; Sadasivan and Negi, 1990; Kulshrestha et al., 1994).

Chemical composition and accurate determination of chemical constituents of SPM are important in understanding the origin of its sources and human health effects. The revision of long term consequences of SPM on the environment needs a profound knowledge of particulate concentration, its chemical composition and distribution in the ambient atmosphere (WHO 2000). In last many years, concern on airborne particles led to a number of studies on the characterization of SPM with reference to industrial influences. But the data on the effect of crop residue burning practices on the metal chemistry in ambient air is very scarce. Hence, a thorough study was carried out and analysis of SPM samples was done to obtain statistically significant data on trace metal levels in SPM with special reference to crop residue burning. This study explores the importance of the knowledge of total suspended particulate matter (TSP) composition, as well as their emission sources. Seasonal variations of SPM measurements and their constituents are presented for a 16-month study period covering three crop residue burning seasons (including two rice and one wheat harvesting seasons) conducted at five different locations of Patiala, India during 2006-2007. Long-term trends and short-term fluctuations in K, Cu, Ni, Zn and SPM concentrations are analyzed.

Studies reported in literature suggest that the high levels of zinc in the ambient air are associated with the increase in hospital admissions for asthma on the following day among children living in an urban area. Pulmonary toxicity from atmospheric dust samples has

also been attributed to zinc and copper (Hirshon et al., 2008; Adamson et al. 2000; Prieditis and Adamson 2002). Although Cu is an essential nutrient for plants and animals in small amounts, high levels can cause gastric problems, vomiting and liver or kidney damage depending on the exposure time. Globally, Cu takes the fourth position after Pb, Zn, and Ni in terms of atmospheric emissions from anthropogenic sources (Fergusson and Kim, 1991).

6.2 Results and Discussion

Samples collected during 2006-2007 at five different monitoring sites, were analyzed for the estimation of Potassium (K), Copper (Cu), Nickel (Ni) and Zinc (Zn) metals in the selected areas of Patiala using the atomic absorption spectrophotometer (AAS) and flame photometric methods.

SPM concentration levels obtained in CRB and NCRB months were compared with the levels of K, Cu, Ni and Zn. A positive association has been obtained between the levels of K and SPM. Significant spatial variation was obtained in the ambient air levels of SPM, K, Cu, Ni and Zn. Similar to the trend of variation of SPM levels, the concentration levels of K were higher during April-May and October-November sampling periods. Concentration of the heavy metals like Cu, Ni and Zn varied between $0.05 \mu\text{gm}^{-3}$ - $1.45 \mu\text{gm}^{-3}$ while that of K concentration levels varied between $4.5 \mu\text{gm}^{-3}$ - $20.2 \mu\text{gm}^{-3}$ with 60% samples having concentration $>10 \mu\text{gm}^{-3}$.

During the study period, average monthly concentration of SPM at different sampling sites varied between $117 \mu\text{gm}^{-3}$ to $488 \mu\text{gm}^{-3}$ with higher levels in CRB months. About 80% samples were loaded with SPM $>200 \mu\text{gm}^{-3}$ (NAAQS, India). During the crop residue burning (CRB) episodes, higher levels of SPM and K was observed at all the sites. However, concentration levels of Cu, Ni, and Zn were not associated with the levels of SPM and K. Concentration levels of K and SPM were inclined with the residue burning activities during wheat and rice harvesting months.

6.2.1 Levels of SPM in the ambient air

Particulate samples were collected from different sampling sites during the study period 2006-2007. The monthly average SPM concentration varied between 117-488 μgm^{-3} during the study period. SPM levels obtained during October-November and April-May in 2006-07 at all the sites, were higher than those collected in other months due to CRB activities after harvesting of crops.

Higher levels of SPM were obtained at SAS (commercial site) due to the mixed influence of CRB and commercial activities. The levels of SPM were high during the burning months and exceeded the maximum permissible limit set by the government regulatory bodies. Vehicular activities and domestic emissions might have contributed to high levels of SPM at this location. Variations in the monthly average concentration levels of SPM observed at different monitoring sites are shown in Figure 6.1 and Tables 6.1-6.4. During CRB months, an increase in the concentration of SPM was observed at SVS (agricultural site) as compared to other sampling sites. Though, levels of SPM were higher during both the burning periods i.e., RCRB and WCRB, but levels were higher during RCRB episodes, probably due to the burning of large amount of rice crop residue as compared to the wheat crop residue.

6.2.2 Levels of potassium (K) in the ambient air

Balanced amount of mineral fertilizers play an important role in improving crop yields. During cultivation of wheat and rice crops, nitrogen (N), phosphorus (P) and potassium (K) are supplemented in the soil in the form of chemical fertilizers to increase the crop yield (Gurmani et al., 1996; Singh et al., 2005; Zhang et al., 2006; Obaid-ur-Rehman et al., 2006; Mehdi et al., 2008). Tracking of potassium as a marker element is the most convenient and reliable method to estimate the contribution of agricultural residue burnings (Andreae, 1983; Duan et al., 2004). Potassium (K) is one of the important elements in particulate matter emanated from open burning of crop residues (Li et al., 2007).

Combustion of potassium containing crop residue at high temperature originates K in the atmosphere (Chow et al., 1992; Begum et al, 2004). As K has been associated to the biomass burning events, increase in the levels of K concentration at different monitoring sites in Patiala during crop residue burning months clearly indicates that residue burning is a dominating source of particulate pollution in this region. Variations in the concentrations of K and their corresponding SPM levels with standard deviations are presented in Tables 6.1-6.4.

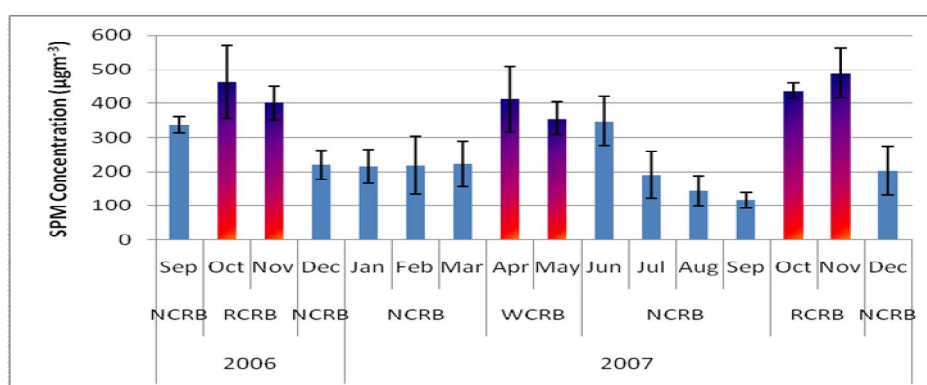


Figure 6.1 Variation in monthly average SPM concentration levels during CRB and NCRB months (Data for 2006 based on three sampling stations while for 2007 five sampling stations)

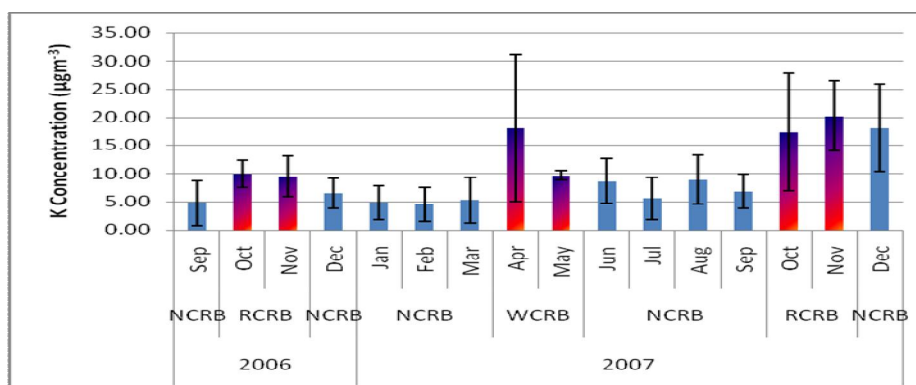


Figure 6.2 Variation in monthly average concentration levels of K during CRB and NCRB months (Data for 2006 based on three sampling stations while for 2007 five sampling stations)

Overall monthly average K concentration varied between 0.53-38.0 μgm^{-3} during the sampling period at all the sites. Levels of K showed a clear trend of variation in

concentration for different months in a year. Levels were higher by 40 % during the crop residue burning months as compared to the non-burning months. Though, K concentrations during burning months were higher at all the sampling sites but an interesting trend was noticed at SVS (agricultural site) (Table 6.2) where a significant increase in the concentration of K was observed during the burning months (October-November) in 2007 as compared to the levels in the corresponding months of 2006, indicating an increase in the production of rice crop residue as well as its burning. Peak K concentration ($37.59 \mu\text{gm}^{-3}$) was obtained at SAS (Table 6.3) in April 2007 followed by SVS in October ($31.81 \mu\text{gm}^{-3}$) and in November ($27.69 \mu\text{gm}^{-3}$) in 2007 (Figure 6.2 Table 6.2). Use of combination of Nitrogen-Phosphorus-Potassium (NPK) fertilizers for the wheat and rice crops could be the only source of K in the crop residues.

6.2.3 Levels of Cu, Ni, and Zn in the ambient air of Patiala

A study conducted by Shah et al., 2008 for seasonal variations of SPM and selected metals (Na, K, Zn, Cu, Pb, Sb, Sr, Co and Cd) showed peak levels during the winter months (November, December and January) and the levels remained low during the summer months (April, May, June and July). Ca, Fe, Mg and Mn were recorded with highest concentration during the spring (February and March). In the present study campaign, the overall monthly average concentrations of the three heavy metals Cu, Ni and Zn ranged between $0.04\text{-}1.84 \mu\text{gm}^{-3}$ during the study period in 2006-2007 without any specific order or trend of variation. However, the levels of SPM and K were associated to some extent with a similar trend of variation ($r = 0.56$).

High levels of Cu concentration were observed during the months of September 2006 to April 2007. Peak concentration was obtained in the month of December 2006 while the lowest concentration was obtained in the month of December 2007. Variation in the levels of copper was found with less degree of association with crop residue burning. The individual variability in airborne copper concentrations could be examined through either respective ranges or standard deviation (SD) values listed in Tables 6.1-6.4.

At SVS (Agricultural area) site, peak Cu concentrations were obtained in January and February 2007, whereas, in April, November and December 2007, lower Cu levels were

obtained (Fig. 4). In spite of the higher levels of SPM in December 2007, a gradual increase in the Cu concentration was observed from September 2006 to February 2007 (Table 6.2).

The monthly average levels of Ni during the study period varied between $0.32 \mu\text{gm}^{-3}$ to $1.45 \mu\text{gm}^{-3}$ with a minimum concentration in September and maximum in December in 2006. Levels of Ni in the ambient air increased from September till December, 2006 and fell down in January 2007. Almost similar levels were observed in the months of February and March and after that levels again decreased till May followed by an increased till August. Levels again fell down in the month of September 2007 and increased in October-November as shown in Figure 6.4. Thus, no even specific episodic variation was obtained in the levels of Ni.

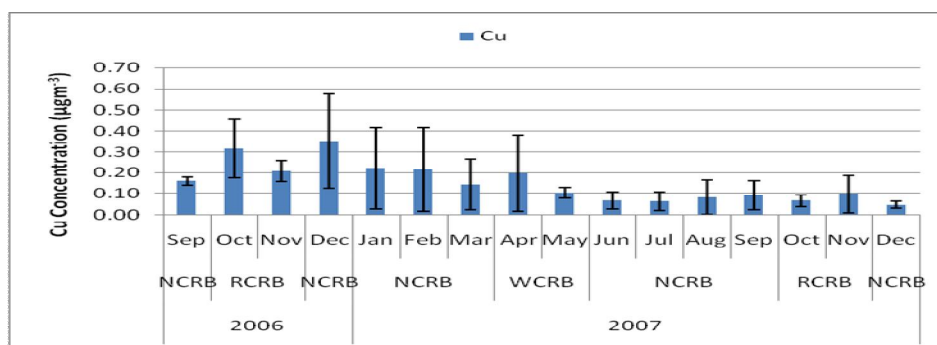


Figure 6.3 Variation in monthly average concentration levels of Cu during CRB and NCRB months

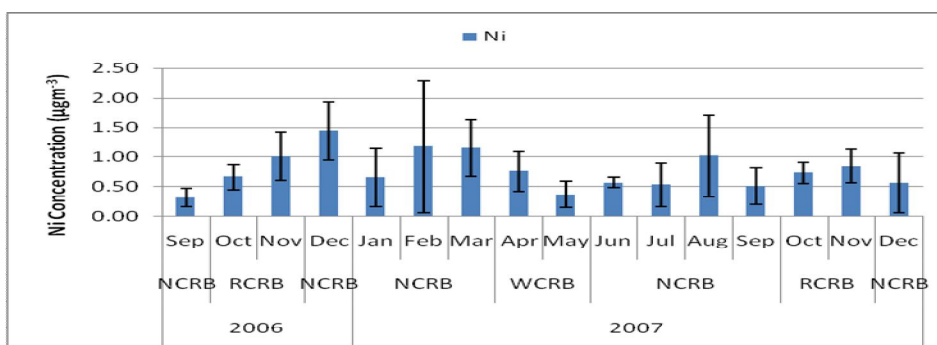


Figure 6.4 Variation in monthly average concentration levels of Ni during CRB and NCRB months

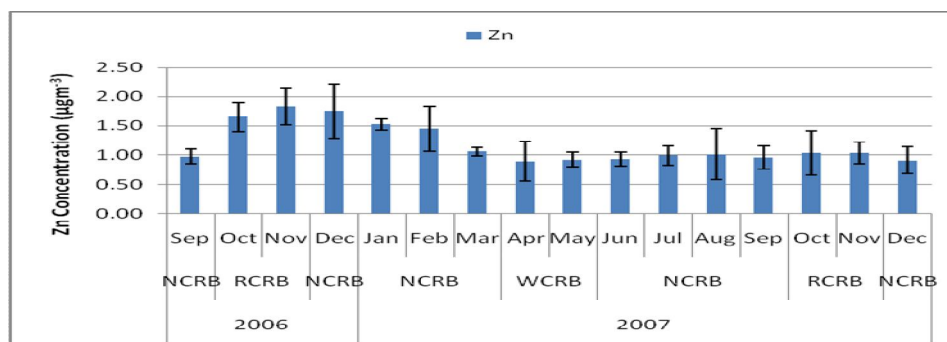


Figure 6.5 Variation in monthly average concentration levels of Zn during CRB and NCRB months

Table 6.1 Concentration levels of K, Cu, Ni, Zn and SPM at PUS during CRB and NCRB months

Year	Period	Month	Monthly average concentration in μgm^{-3} with SD				
			K	Cu	Ni	Zn	SPM
2006	CRB-R	Oct	7.44±5.82	0.48±0.02	0.43±0.26	1.38±0.38	345±37
		Nov	5.38±1.20	0.20±0.01	1.09±0.54	1.83±0.21	350±115
	NCRB	Dec	5.10±1.60	0.17±0.01	0.99±0.48	1.99±0.55	226±15
2007	NCRB	Jan	6.58±0.42	0.19±0.10	0.75±0.62	1.59±0.04	244±68
		Feb	5.49±0.37	0.12±0.06	0.39±0.19	1.72±0.40	249±122
		Mar	7.91±7.19	0.06±0.04	0.60±0.31	1.05±0.63	252±108
	CRB-W	Apr	10.77±8.79	0.05±0.01	0.54±0.30	0.91±0.35	391±86
		May	8.65±4.15	0.08±0.03	0.40±0.11	0.82±0.09	331±102
	NCRB	Jun	5.64±3.61	0.04±0.02	0.50±0.26	0.77±0.11	277±252
		Jul	3.32±0.58	0.04±0.01	0.60±0.05	0.82±0.06	130±27
		Aug	6.22±6.65	0.04±0.03	0.72±0.16	0.84±0.06	122±22
		Sep	4.64±0.10	0.04±0.01	0.18±0.08	0.75±0.05	100±29
	CRB-R	Oct	7.68±2.10	0.03±0.01	0.59±0.31	0.61±0.51	446±93
		Nov	12.74±4.82	--*	0.82±0.61	0.82±0.28	429±166
	NCRB	Dec	6.50±2.12	0.04±0.01	0.28±0.04	0.58±0.21	303±11.82

Note: --Data not available for the corresponding month

Table 6.2 Concentration levels of K, Cu, Ni, Zn and SPM at SVS during CRB and NCRB months

Year	Period	Month	Monthly average concentration in μgm^{-3} with SD				
			K	Cu	Ni	Zn	SPM
2006	NCRB	Sep	4.75±0.29	0.16±0.03	0.32±0.06	--	339±35
	CRB-R	Oct	10.08±3.17	0.22±0.06	0.84±0.98	1.68±	491±172
		Nov	11.84±2.80	0.26±0.16	0.57±0.24	--	449±131
	NCRB	Dec	9.62±7.27	0.28±0.27	1.97±0.04	3.22±	176±30
2007	NCRB	Jan	6.60±2.50	0.43±0.18	1.09±0.73	2.46±	244±68
		Feb	6.87±1.40	0.47±0.08	1.97±0.47	--	283±102
		Mar	7.25±2.50	--	--	--	268±96

	CRB-W	Apr	13.80±4.63	0.05±0.03	1.25±0.08	1.22±0.23	419±207
		May	10.24±7.26	0.14±0.11	0.36±0.32	1.03±0.54	380±64
	NCRB	Jun	5.19±3.23	0.08±0.06	0.49±0.36	0.97±0.04	296±278
		Jul	3.42±1.33	0.12±0.01	0.86±0.14	1.14±.61	267±138
		Aug	7.39±1.75	0.08±0.02	0.60±0.09	--	111±22
		Sep	8.96±5.78	0.14±0.03	0.55±0.13	1.03±.43	133±48
	CRB-R	Oct	31.81±14.19	0.07±0.04	0.65±0.57	1.50±0.67	440±116
		Nov	27.69±4.53	0.05±0.01	1.09±1.05	1.27±0.35	455±148
	NCRB	Dec	22.37±7.94	0.04±0.01	0.49±0.32	1.02±0.33	201±103

Note: --Data not available for the corresponding month

Table 6.3 Concentration levels of K, Cu, Ni, Zn and SPM at SAS during CRB and NCRB months

Year	Period	Month	Monthly average concentration in μgm^3 with SD				
			K	Cu	Ni	Zn	SPM
2006	NCRB	Sep	--	--	--	--	--
	CRB-R	Oct	12.30±1.71	0.25±0.14	0.71±0.61	1.88±0.45	551±3
		Nov	11.16±6.57	0.16±0.09	1.38±0.97	2.16±0.16	405±215
	NCRB	Dec	4.79±1.5	0.60±0.56	1.38±0.86	2.05±0.25	258±50
2007	NCRB	Jan	1.29±0.85	0.05±0.01	0.13±0.10	--	158±32
		Feb	--	--	--	--	--
		Mar	--	--	--	--	--
	CRB-W	Apr	37.59±12.04	0.49±0.19	0.65±0.43	0.55±	538±115
		May	10.47±2.32	0.09±0.06	0.63±0.63	1.04±0.07	409±147
	NCRB	Jun	9.93±1.47	0.03±0.01	0.68±0.68	0.99±0.16	398±274
		July	9.84±3.20	0.04±0.02	0.14±0.09	1.02±0.26	176±56
		Aug	15.36±1.50	0.20±0.10	4.57±1.20	1.58±0.29	209±96
		Sep	--	--	--	--	--
	CRB-R	Oct	17.38±5.98	0.09±0.04	1.00±0.56	0.90±0.33	458±96
		Nov	21.55±11.86	0.07±0.02	1.01±0.42	1.05±0.13	593±181
	NCRB	Dec	22.18±5.3	0.07±0.02	2.46±1.59	1.07±0.34	173±26

Note: --Data not available for the corresponding month

The Zn concentration varied between a minimum $0.89 \mu\text{gm}^{-3}$ to a maximum $1.84 \mu\text{gm}^{-3}$. The levels increased in September 2006 till April 2007 and after remained almost in a range of $1 \mu\text{gm}^{-3}$ till the end of the sampling campaign. There was no significant change in Zn concentration in the ambient air, as it was not associated with CRB activities. However, the background concentration level of Zn seems to decrease in 2007 as compared to that of 2006.

Table 6.4 Concentration levels of K, Cu, Ni, Zn and SPM at MAS during CRB and NCRB months

Year	Period	Month	Monthly average concentration in μgm^{-3} with SD				
			K	Cu	Ni	Zn	SPM
2007	NCRB	Jan	--	--	--	--	--
		Feb	1.14 $\pm$ 0.15	0.06 $\pm$ 0.01	--	--	123 $\pm$ 45
		Mar	0.53 $\pm$ 0.31	0.03 $\pm$ 0.02	1.35 $\pm$ 1.01	1.13 $\pm$ 0.70	147 $\pm$ 70
	CRB-W	Apr	10.02 $\pm$ 6.62	0.21 $\pm$ 0.06	0.57 $\pm$ 0.33	--	302 $\pm$ 137
		May	9.42 $\pm$ 4.14	0.10 $\pm$ 0.07	0.10 $\pm$ 0.05	0.83 $\pm$ 0.17	303 $\pm$ 70
	NCRB	Jun	13.72 $\pm$ 9.62	0.12 $\pm$ 0.02	0.59 $\pm$ 0.08	1.02 $\pm$ 0.06	424 $\pm$ 344
		Jul	--	--	--	--	--
		Aug.	6.51 $\pm$ 0.33	0.02 $\pm$ 0.01	0.71 $\pm$ 0.11	1.08 $\pm$ 0.04	137 $\pm$ 14
		Sep	--	--	0.79 $\pm$ 0.08	1.12 $\pm$ 0.56	--
	CRB-R	Oct	12.57 $\pm$ 5.29	0.08 $\pm$ 0.03	0.69 $\pm$ 0.35	1.15 $\pm$ 0.12	404 $\pm$ 61
		Nov	18.80 $\pm$ 2.77	0.05 $\pm$ 0.01	0.46 $\pm$ 0.25	1.03 $\pm$ 0.32	474 $\pm$ 194
	NCRB	Dec	21.20 $\pm$ 2.57	0.04 $\pm$ 0.00	0.02 $\pm$ 0.04	0.99 $\pm$ 0.10	135 $\pm$ 50

Note: -- Data not available for the corresponding month

Table 6.5 Inter-correlations of SPM and metals in terms of correlation coefficients

S. No.	Relative Array (x, y)	Correlation Coefficient (r)
1	SPM, K	0.56 (>0.50)
2	SPM, Cu	0.15
3	SPM, Ni	-0.15
4	SPM, Zn	0.10
5	K, Cu	-0.30
6	K, Ni	-0.11
7	K, Zn	-0.33
8	Cu, Ni	0.50
9	Cu, Zn	0.82 (>0.50)
10	Ni, Zn	0.56 (>0.50)

6.3 Inter-relationships among K, Cu, Ni, Zn and SPM

The levels of K, Cu, Ni, Zn and SPM were analyzed to check any relationship among them. Levels of K were observed higher during crop residue burning practices in association with the increase in SPM concentration levels. Potassium levels were higher during April-May and October-November, as also found with SPM. A positive correlation was obtained between the levels of Cu and Zn ($r = 0.82$) indicating a similar trend of variation during different months. A positive association was also obtained between SPM and K ($r = 0.56$), Ni and Zn ($r = 0.56$), and Cu and Ni ($r = 0.50$). There was no relationship in other combinations of arrays. The positive relationship indicates that there may be a similar

source of Cu, Ni and Zn in the ambient air. Levels of these heavy metals were also associated with a similar range of concentration. But the concentration levels of these metals were never associated with the concentration levels of SPM and K.

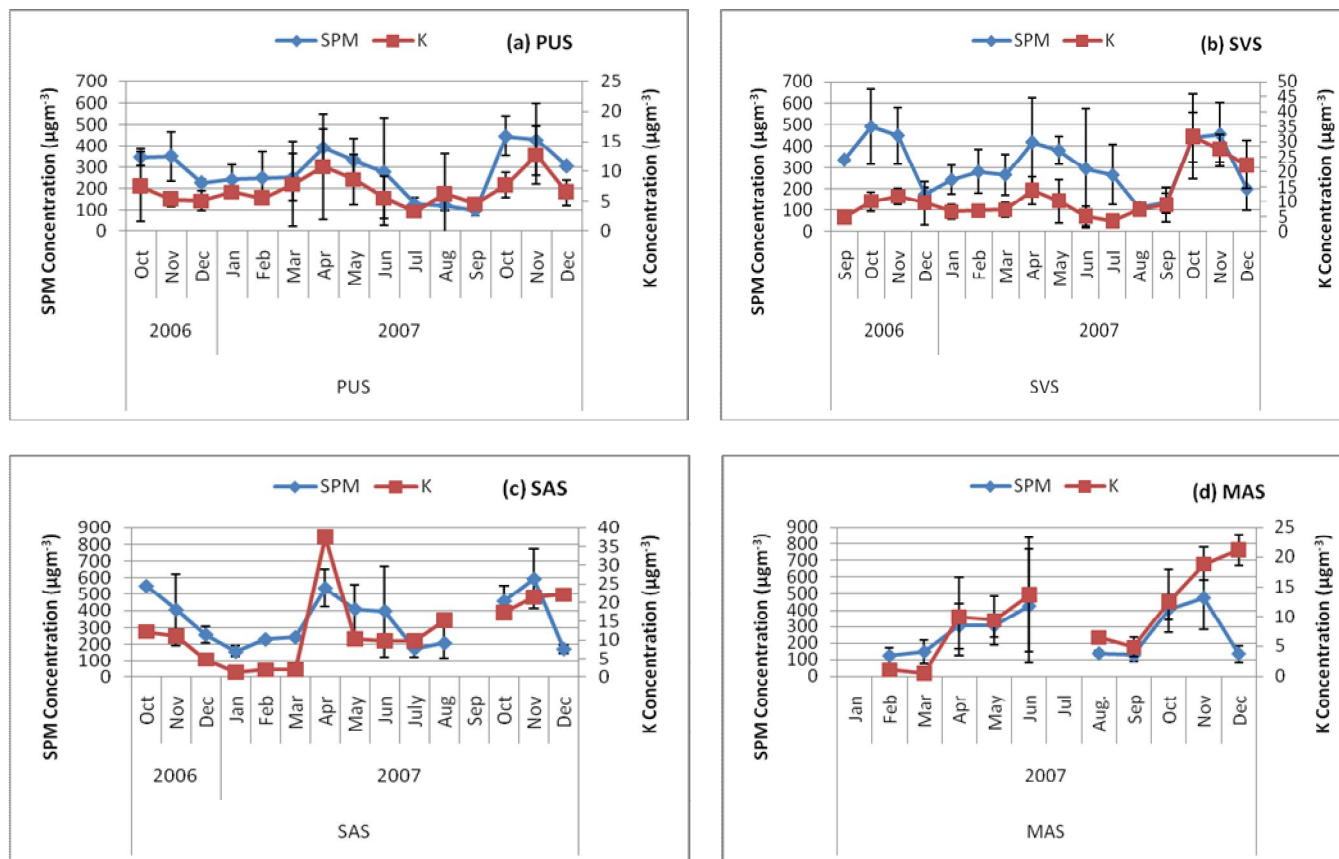
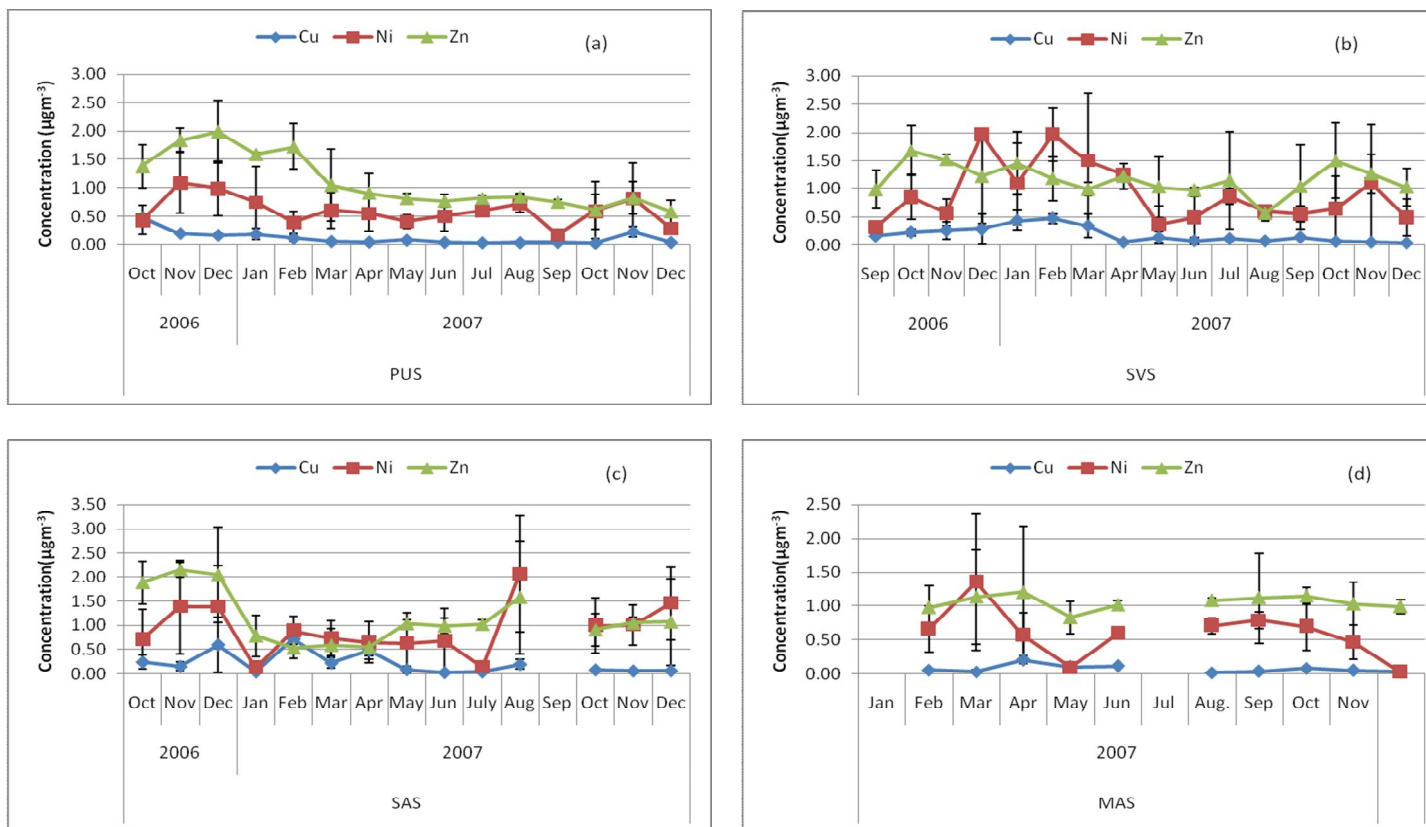


Figure 6.7 Variation in ambient air SPM and K concentration levels at PUS (a), SVS (b), SAS (c) and MAS (d)



Figures 6.8 Variations in the concentration levels of Ni, Cu and Zn at PUS (a), SVS (b), SAS (c) and MAS (d)

The levels of Ni, Cu and Zn metals were not affected by the crop residue burning practices occurred during April-May and October-November, as there was no increase in the levels during these months. While the levels of SPM and K were associated with each other and affected by the crop residue burning practices, K has been identified as a potential marker of crop residue burning activities. Various researchers have observed high K concentration levels during crop residue burning periods (Cheng et al., 2009) (Fig. 6).

6.4. Conclusions

SPM concentration levels obtained during CRB and NCRB months were compared with the levels of K, Cu, Ni and Zn in the SPM. Significant association was obtained in the ambient air levels of SPM and K. Heavy metals like Cu, Ni and Zn were associated with the similar range of concentration but any direct relationship could not be established with CRB episodes. Although, increase in K levels was observed at all the sites but strong association between K levels and CRB was obtained at SVS (Agricultural site) as compared to other monitoring sites. This indicated that CRB was a dominating source at agricultural site as compared to the other sources in the increment of SPM load. Since, K metal has been identified as a marker of crop residue burning in previous studies, as well, crop residue burning can be identified as an important source of SPM pollution in and around Patiala city integrated with the contribution of vehicular emissions.

References

- Adamson, I. Y. R., Frieditis, H., Hedgecock, C., Vincent, R., 2000. Zinc is the toxic factor in the lung response to an atmospheric particulate sample. *Toxicol. Appl. Pharm.*, 166 (2), 111-119.
- Andreae, M.O., 1983. Soot carbon and excess fine potassium: Long range transport of combustion-derived SPMs. *Science* 220, 1148-1151.
- Begum, B.A., Kim, E., Biswas, S.K., Hopke, P.K., 2004. Investigation of sources of atmospheric SPM at urban and semi-urban areas in Bangladesh. *Atmospheric Environment* 38, 3025-3038.
- Bhanarkar, A.D., Gajghate, D.G., Hasan, M.Z., 2002. Assessment of air pollution from small scale industry. *Environmental Monitoring & Assessment* 80, 125-133.

Bukowiecki, N., Gehrig, R., Hill, M., Lienemann, P., Zwicky, C.N., Buchmann, B., Weingartner, E., Baltensperger, U., 2007. Iron, manganese and copper emitted by cargo and passenger trains in Zürich (Switzerland): Size-segregated mass concentrations in ambient air, *Atmospheric Environment*, 41(4) 878-889

Chelani, A., Gajghate, D.G., Hasan, M.Z., 2001. Ambient toxic metals in air of Mumbai city, India. *Bulletin of Environmental Contamination & Toxicology* 66, 196-206.

Cheng, M.T., Horng, C.L., Su, Y.R., Lin, L.K., Lin, Y.C., Chou, C.C.K., 2009. Particulate matter characteristics during agricultural waste burning in Taichung City, Taiwan, *Journal of Hazardous Materials*, 165 (1-3), 187-192.

Chow, J.C., Watson, J.G., Lowenthal, D.H., Solomon, P.A., Mogoliand, K.L., Ziman, S.D., Richards, L.W., 1992. PM₁₀ sources apportionment in California's San Joaquin Valley. *Atmospheric Environment* 26, 3335-3354.

Denier van der Gon, H.A.C., Hulskotte, J.H.J., Visschedijk, A.J.H. and Schaap, M., 2007. A revised estimate of copper emissions from road transport in UNECE-Europe and its impact on predicted copper concentrations. *Atmospheric Environment*, 41(38) 8697-8710.

Dockery, D.W., Papes, C.A., 1994. Acute respiratory effects of particulate air pollution. *Annual Reviews of Public Health* 15, 107-132.

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

Fergusson, J.E., Kim, N.D., 1991. Trace elements in street and house dust: sources and speciation, *Science of the Total Environment*, 100, 125-150.

Gajghate, D.G., Bhanarkar, A.D., 2005. Characterisation of particulate matter for toxic metals in ambient air of Kochi city, India. *Environmental Monitoring and Assessment* 102, 119-129.

Gurmani, A.H., Bhatti, A.U., Bakhsh, A., Rehman, H., 1996. Yield response of paddy to balanced application of NPK. *Pakistan Journal of Soil Science* 11, 77-79.

Hirshon et al., 2008. Elevated Ambient Air Zinc Increases Pediatric Asthma Morbidity, *Environmental Health Perspectives*.

Kappos, A.D., Bruckmann, P., Eikmann, T., Englert, N., Heinrich, U., Hoppe, P., Koch, E., Krause, G.H., Kreyling, W.G., Rauchfuss, K., Rombout, P., Schulz-Klemp, V., Thiel, W.R., Wichmann, H.E., 2004. Health effects of particles in ambient air. *International Journal of Hygiene & Environmental Health*, 207 (4) 399-40.

Khandekar, R.N., Mishra, U.C., Vohra, K.G., 1984. Environmental lead exposure of an urban indian population. *Science of Total Environment* 20, 269-278.

Li, X., Wang, S., Duan, L.J., Li, Hao, C., Chen, Y., Yang, L., 2007. Particulate and trace gas emissions from open burning of wheat straw and corn stover in China. *Environmental Science & Technology* 41, 6052-6058.

Mehdi, S.M., Sarfraz, M., Ibrahim, M., Mahmood, K., 2008. Fertilizer requirement of different crop rotations in recently reclaimed soil. *American-Eurasian Journal of Agricultural and Environmental Science* 3 (2), 179-186.

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

NEERI: Ambient Air Quality Status in Ten Cities in India: 1996, National Environmental Engineering Research Institute, Nagpur, India (2000)

NEERI: Ambient Air Quality Status in Ten Cities in India: 1997-98, National Environmental Engineering Research Institute, Nagpur, India (2001)

NEERI: Introduction of Environmental Economics into Decision Making for Sustainable Development: Air Media Project Report Submitted to IGIDR under Capacity 21 Project, Nagpur, India (1998)

Negi, B.S., Sadasivan, S., Mishra, U.C., 1987. A composition of SPM and sources in urban area in India. *Atmospheric Environment* 21, 1259-1266.

Park, S.S., Kim, Y.J., 2005. Source contribution to fine particulate matter in an urban atmosphere. *Chemosphere* 59, 217-226.

Prieditis and Adamson 2002

Rehman, O., Zaka, M.A., Rafa, H.U. and Hassan, N.M., 2006. Effect of balanced fertilization on yield and Phosphorus uptake in wheat-rice rotation fertilizer requirement of different crop rotations in recently reclaimed soil. *Journal of Agricultural Research* 44 (2), 105-115.

Sadasivan, S., Negi, B.S., 1990. Frequency distribution in the city of Varanasi, *Atmospheric Environment* 28, 2117-2323.

Schroeder, W.H., Dobson, M., Kane, D.M., Johnson, N.D., 1987. Trace elements associated with the air borne particulate matter: A review. *JAPCA* 37, 1268-1285.

Shah, M.H., Shaheen, N., 2008. Annual and Seasonal Variations of Trace Metals in Atmospheric Suspended Particulate Matter in Islamabad, Pakistan. *Water Air Soil Pollut*, 190, 13-25.

Shah, M.H., Shaheen, N., Khalique, A., Tariq, S.R., Manzoor, S., 2006. Spatial variations in selected metal contents and particle size distribution in an urban and rural atmosphere of Islamabad, Pakistan, *Journal of Environmental Management* 78, 128-137.

Singh, K.N., Major nutrient management for sustaining rice-wheat productivity in reclaimed sodic soils. In: *Abstract of International Conference on Soil, Water and Environmental Quality-Issues and Strategies*, Organized by Indian Society of Soil Science, at I.A.R.I, New Delhi, pp: 255 (2005).

Yang, S., He, H., Lu, S., Chen, D., Zhu, J., 2008. Quantification of crop residue burning in the field and its influence on ambient air quality in Suqian, China. *Atmospheric Environment* 42 (9) 1961-1969.

Zhang, Qi-chun, Wang, Guang-huo, 2006. Effect of different fertilization treatments on ecological characteristics of microorganism in paddy soil, *J Zhejiang Univ, Science A*, 7 (Suppl. II), 376-380.

CHAPTER 7

IMPACT OF CROP RESIDUE BURNING EPISODES ON THE AMBIENT AIR LEVELS OF POLYCYCLIC AROMATIC HYDROCARBONS

CHAPTER 7

IMPACT OF CRB EPISODES ON THE AMBIENT AIR LEVELS OF POLYCYCLIC AROMATIC HYDROCARBONS

7.1 Introduction

Sources of polycyclic aromatic hydrocarbons (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). In addition, in the Indian urban and rural environment, cooking fuel combustion and biomass burning are likely sources of PAH. High concentrations of PAHs have been measured 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 (formerly Bombay) (Mohan Rao et al., 1983) and Ahmedabad (Aggarwal et al., 1982), with a view to evaluate the carcinogenic risk from PAH exposure. Studies of PAH concentrations in ambient aerosol in Ahmedabad, Mumbai, Nagpur and Kanpur show that total PAH concentrations in Indian cities 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).

Aromatic hydrocarbons also referred as arenes are derived from benzene. Polycyclic or polynuclear aromatic hydrocarbons (PAHs) known as polyarenes are one of the largest classes of organic molecules found in nature. PAHs are chemical compounds with a similar structure comprising two or more (up to seven) condensed aromatic and other cyclic rings and exist under ambient environmental conditions as gases, volatile liquids, semi volatile substances and solids. They contain at least two fused benzene (six sided) rings. These are formed by the incomplete combustion of coal, oil, petrol, wood, tobacco, charbroiled meats, garbage, or other organic materials. The emissions of PAHs from incomplete combustion are of special environmental concern because of the potential carcinogenicity for some of these compounds.

The US Environmental Protection Agency in 1997 has identified 16 PAHs as priority pollutants. These compounds are: naphthalene (Nap), acenaphthene (Acp), acenaphthylene (AcPy), fluorene (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 (IND).

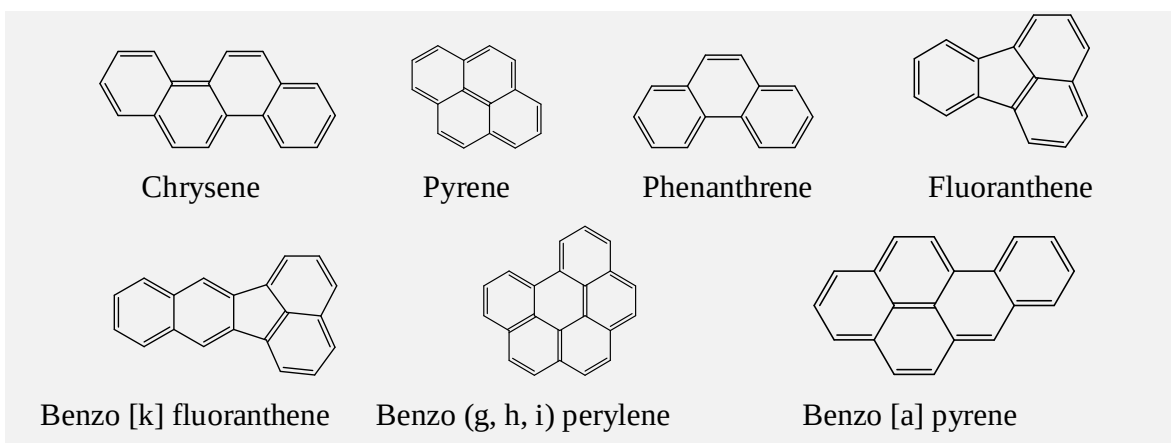


Figure 7.1 Structures of a few Polycyclic Aromatic Hydrocarbons

Particulate organic compounds play important roles in atmospheric chemistry by impacting regional air quality, climate change and human health (Crutzen and Andreae 1990; Quinn et al. 2005). Molecular markers of organic aerosols, defined as chemically inert and source-specific compounds have been applied as tracers over the past decade to quantitatively assess source contributions to particulate matter concentrations in the atmosphere (Cass 1998; Schauer and Cass 2000; Schauer et al. 1996). The objectives of the present study were to measure selected particulate PAH concentrations at ambient locations in Patiala to assess their concentrations, and to compare with the PAH levels during rice and wheat crop residue burning episodes.

7.2 Health Effects of PAHs

The PAH pollutants having high molecular mass (4 and more condensed aromatic rings) are considered to be more dangerous than two and three-ring PAHs in view of their potential

carcinogenicity (Tuhackova et al., 2001). For the past three decades, PAHs have been of environmental concern due to their toxicity and their ubiquitous presence in the environment. PAHs particularly Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(j)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Benzo(g,h,i)perylene, Chrysene, Dibenzo(a,h)anthracene, Indeno(1,2,3-cd)pyrene and Phenanthrene are known for their carcinogenic, mutagenic and estrogens disrupting properties (IARC, 2002). In general, there is an important category of emissions known as air toxics (or hazardous air pollutants); these are toxic air pollutants that are known or probable carcinogens or linked to other serious health problems such as cancer, neurological, cardiovascular, and respiratory diseases, and birth and reproductive defects (EPA, 1993b, 2000c).

7.3 Sources of Hydrocarbons

Atmospheric suspended particulate matter (SPM) acts as a carrier of pollutants such as PAH, toxic gases and metal particles etc, which have harmful effects on human health. PAH are mostly distributed among sub micron particles, which can travel far from emission sources and are subject to transformation by photochemical or dark reaction with various gases (e.g. O₂, O₃, NO, N₂O₅) in the atmosphere. Mostly PAHs are formed as products of incomplete combustion of organic materials during industrial and other human activities, such as processing of coal and crude oil, combustion of natural gas, including for heating, combustion of refuse and biomass, vehicle traffic, cooking and tobacco smoking, as well as in natural processes such as carbonization. The emissions of PAHs from incomplete combustion are of special environmental concern because of the potential carcinogenicity for some of these compounds. Polycyclic aromatic hydrocarbons will enter the body if we breathe in contaminated air, or consume food or water that has been contaminated.

7.3.1 Possible Sources of PAH emissions in the Study Area

There is no major Industry in the vicinity of Patiala city. The possible major sources of air pollution in the city are vehicular exhaust and the episodic crop residue burnings during April-May and October-November. Rice crop residue burning and wheat crop residue burning practices are among the most important waste residue disposal agricultural activities

in Punjab (India). These activities are expected to be one of the main sources of carcinogenic PAH pollution to the atmosphere in Punjab.

However, the concern and awareness of the sources and effect of PAH on human health are still very low among the people in the Punjab state. Therefore, the objectives of this study were to determine and compare the concentration of PAHs in different months of crop residue burning, and to identify the types and characteristics of PAH compounds in selected agricultural and commercial-cum-residential areas in Patiala, India. The results from this study provide a baseline reference for a global database on PAHs due to wheat and rice crop residue burnings.

7.4 Locations of monitoring sites and aerosol sampling

The particulate PAH samples were collected at two different locations in Patiala covering an agricultural area site called Sidhuwal Village Site (SVS, Latitude- $30^{\circ}22'42.14''$ N, Longitude- $76^{\circ}20'31.52''$ E) and a commercial area site named as Sanauri Adda Site (SAS, Latitude- $30^{\circ}19'23.14''$ N, Longitude- $76^{\circ}24'23.88''$ E). Patiala is located in Northwest region of the country (about 250 Km from the Capital (New Delhi) of India as shown in Figure 3.1 (For more details on land use patterns of sites see Chapter 3, Page 2). The SVS site was a rural agricultural area site and the monitoring of particulate associated PAH was considered as a measure of PAH emissions from crop residue burning during wheat and rice crop harvesting months. Being a residential-cum-commercial area with high vehicular activities and its strategic location in SE direction, SAS was considered as a mixed use urban area site. SAS is likely to collect particulates emanating from CRB practices reinforced with commercial activities from NW direction of the city, as the wind direction was from NW to SE for most of the times in a year (refer to wind rose plots in Chapter 4). In this study, the airborne samples were collected by using two high volume air samplers (HVS) each of them were placed separately at the two sites fitted with glass micro fibre (GMF/A). The samplings were carried out over a 24 hours period in the selected areas over a period of 2006-2007.

7.5 Analysis of SPM samples by Gas Chromatography (GC-FID)

Analysis of organic compounds in aerosol samples using Gas Chromatography (GC) has become widely used in air pollution studies. Samples, including ambient aerosol samples were analyzed by GC-FID. Although consistent results were obtained, the sensitivity of different compounds to analytical parameters was examined to assess analytical accuracies. US EPA Method TO-13 (USA EPA, 1999) was used as analytical method in this study. A quadrant of each aerosol sample was extracted with 150 mL Dichloromethane (Merck, India) for a period of 8 hours using a soxhlet extractor. Solvent was reduced to 5 mL using rota-evaporator (steam bath treatment of organic extracts is not expected to produce significant loss of organic aerosol constituents). The extracts were then filtered through Whatman filter thimbles and transferred to pre-weighed chromatographic amber vials. The vials were then dried at room temperature and the contents were dissolved in 1 mL of acetonitrile. The sample was then analyzed by using the gas chromatography-flame ionization detector (GC-FID) method. The gas chromatograph (NUCON, 5765) fitted with a fused silica capillary column (30 m, 0.25mm i.d., 0.25 μ m film thickness, Equity-5, SUPELCO) and a standard Flame Ionization Detector (FID) was used for the analysis of each extracted sample. A volume of 1 μ L sample was injected in the GC-FID and the quantification and identification of Pyrene and Benzo(k)fluoranthene from the fraction were made.

7.6 Results and Discussion

7.6.1 Compound Identification

Pyrene (Py) and Benzo(k)fluoranthene (B(k)F) were selected as representative PAHs in the SPM samples. These contaminants were identified for quantitative representation of PAHs as these were constantly obtained in all samples of SPM collected during CRB months. Identification of the PAH compounds was accomplished by comparing retention time of the sample with that of standard sample (Cass 1998).

7.6.2 Particulate associated PAHs at urban (SAS) and rural (SVS) sites

Pyrene in SPM samples collected from sanauri adda site (SAS, urban area site) was detected during different sampling months. The concentration levels and the variations are shown in Figures 7.2 (a-c) and in Table 7.1. The concentration of pyrene in samples collected from SAS was high during April-May and October-November. The maximum concentration of pyrene (0.58 ppm) was recorded in November 2007 which indicated that the combustion processes in the crop residue burning activities emitted pyrene into the ambient air atmosphere. In addition, the results also show that biomass fires are pyrolysis processes resulting in the formation of PAHs from natural product precursors in the source organic matter or process of recombination of molecular fragment in the smoke. There was a distinct increase in the concentration levels of Pyrene throughout the course of the study. The results can be correlated with corresponding variations in the dichloromethane (DCM) soluble fraction of SPM. Besides variations in the CRB months, a small increase in concentration of DCM soluble SPM is also observed in the NCRB months of December 2006 which could be due to organic compounds other than PAHs finding its origin in automobile exhaust emissions.

The levels become noticeable in December due to the phenomenon of temperature inversion taking place in lower ambient air environment. The temperature varied from $22\pm 1^{\circ}\text{C}$ in October and November to $(14\pm 2^{\circ}\text{C})$ in December and further $(13\pm 3^{\circ}\text{C})$ in January and February. There was a total absence of Pyrene in the ambient air till March 2007 and further in June, July, August and September months whereas, during WCRB and RCRB, the concentration levels rose at the maximum level of $0.20\ \mu\text{gm}^{-3}$ and $0.22\ \mu\text{gm}^{-3}$, respectively. Pyrene concentration has also been compared with the DCM soluble SPM content [Figure 7.2 (a)] and SPM concentration [Figure 7.2 (b)]. Values of Pyrene/DCM Soluble SPM ratio and Pyrene/SPM ratio for a period of October 2006 till December 2007 are shown in Figure 7.2 (c) and Table 7.1. The correlation of these values indicated a clear impact of CRB events to the PAHs levels in the ambient air after wheat and rice crop harvesting respectively.

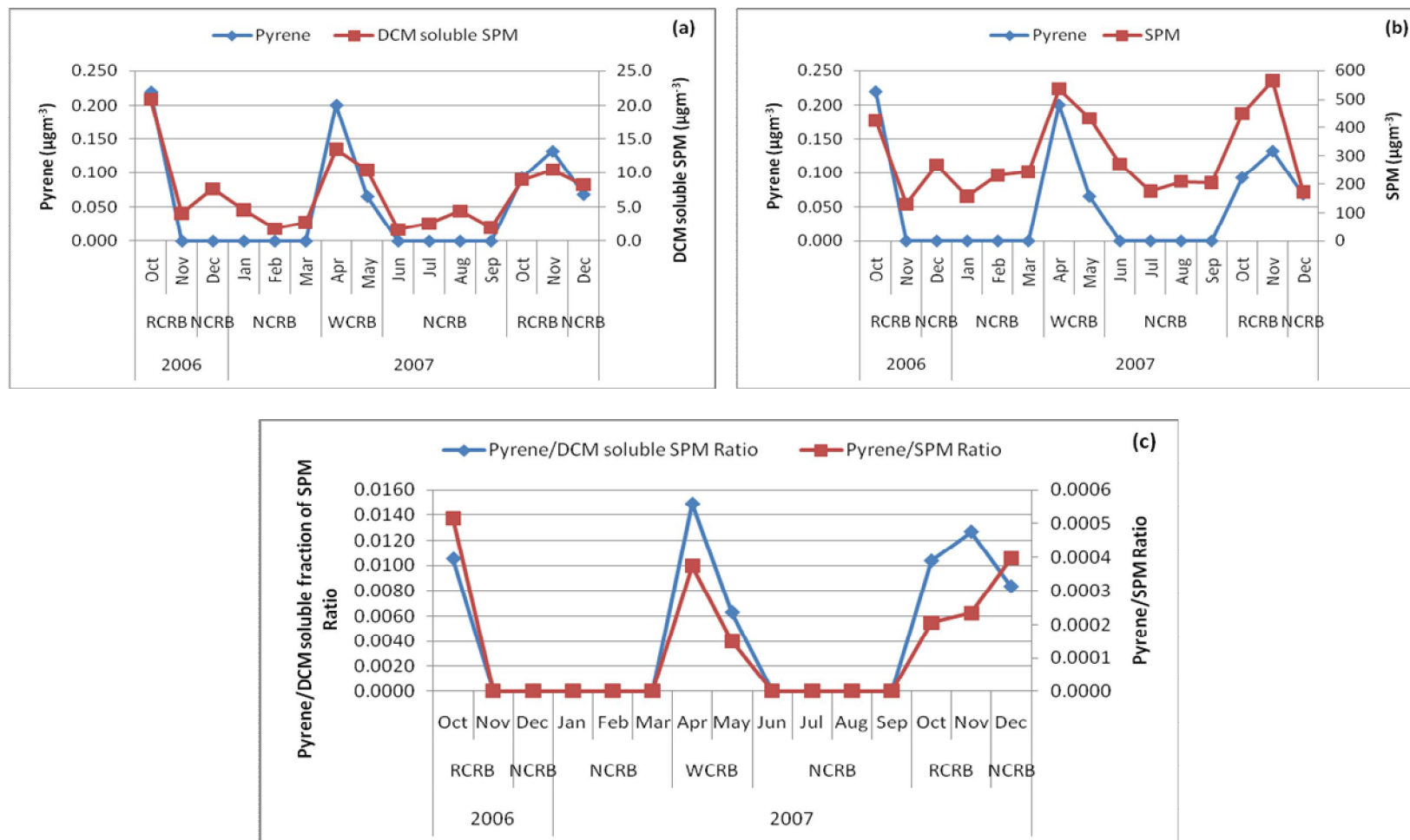


Figure 7.2 Variation in Pyrene concentration levels with DCM soluble fraction of SPM (a), with SPM (b) and variation in Pyrene/DCM soluble fraction ratio and Pyrene/SPM ratio (c) at SAS

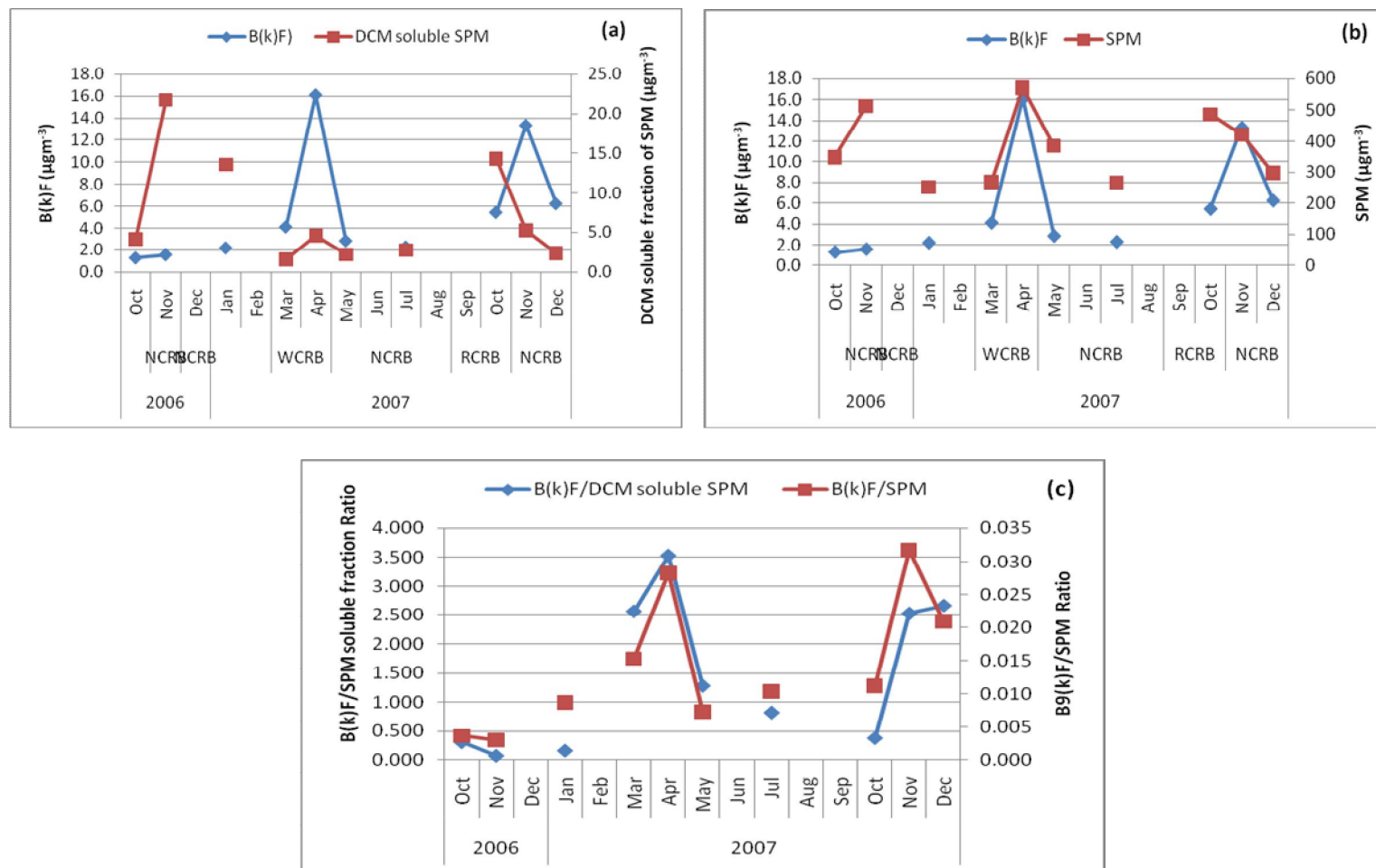


Figure 7.3 Variation in B(k)F concentration levels with DCM soluble fraction of SPM (a), with SPM (b) and variation in B(k)F/DCM soluble fraction ratio and B(k)F/SPM ratio at SVS

Table 7.1
Monthly average concentration levels of SPM, Pyrene (Py) and DCM soluble fraction of SPM at SAS

Year	2006			2007											
Period	RCRB		NCRB	NCRB			WCRB		NCRB				RCRB		NCRB
Month	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
SPM (μgm^{-3})	427	130	268	157	231	244	537	435	272	175	209	205	451	565	173
Py (μgm^{-3})	0.220	ND	ND	ND	ND	ND	0.201	0.066	ND	ND	ND	ND	0.093	0.132	0.069
DCM soluble SPM (μgm^{-3})	20.9	4.1	7.6	4.6	1.8	2.7	13.5	10.4	1.7	2.5	4.4	2.0	8.9	10.4	8.2
[Py/ DCM soluble SPM] Ratio	0.0105	0.0000	0.0000	0.0000	0.0000	0.0000	0.0149	0.0063	0.0000	0.0000	0.0000	0.0000	0.0104	0.0127	0.0083
[Py/SPM] Ratio	0.0005	0.0000	0.0000	0.0000	0.0000	0.0000	0.0004	0.0002	0.0000	0.0000	0.0000	0.0000	0.0002	0.0002	0.0004

N.B. - ND means not detected, and the sign '--' indicates no data to put.

Table 7.2
Monthly average concentration of SPM, Benzo(k)fluoranthene [B(k)F] and DCM soluble fraction of SPM at SVS

Year	2006			2007											
Period	RCRB		NCRB	NCRB			WCRB		NCRB				RCRB		NCRB
Month	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
SPM (μgm^{-3})	348	513	--	251	--	268	571	385	--	266	--	--	487	421	298
B(k)F (μgm^{-3})	1.27	1.56	--	2.18	--	4.10	16.12	2.83	--	2.27	--	--	5.43	13.34	6.23
DCM soluble SPM (μgm^{-3})	4.15	21.74	--	13.60	--	1.60	4.56	2.21	--	2.76	--	--	14.33	5.28	2.34
[B(k)F/DCM soluble SPM] Ratio	0.31	0.07	--	0.16	--	2.56	3.53	1.28	--	0.82	--	--	0.38	2.53	2.66
[B(k)F/SPM] Ratio	0.00	0.00	--	0.01	--	0.02	0.03	0.01	--	0.01	--	--	0.01	0.03	0.02

N.B. - ND means not detected, and the sign '--' indicates no data to put.

At SVS, the polycyclic aromatic hydrocarbon Benzo(k)fluoranthene [B(k)F] was detected in almost all the samples. The results of analysis and the levels obtained are shown in Figures 7.3 (a-c) and in Table 7.2. High concentration levels were obtained in April (wheat crop residue burning season) and November (rice crop residue burning season) during 2007. From the observation, it is clear that the concentration of BkF in SVS air samples shows the increase in the concentration during crop residue burning months.

7.7 Conclusions

It can be concluded that the increased crop residue burning activities during April-May and October-November increased the levels of PAHs in the ambient air particularly at SAS and SVS. Results suggest that episodic crop residue burnings and vehicular exhaust are the two major sources contributing to the presence of polycyclic aromatic hydrocarbons in the ambient air of the area. However, the variations in PAH levels could be attributed to the factors such as, site characteristics, topography of surrounding area, types and frequency of vehicles plying on the roads, types of biomass burned, etc. The meteorological factors such as wind speed and direction, relative humidity, atmospheric pressure and temperature can also impact the levels and flow of PAHs.

References

- Cass, G. R., 1998. Organic Molecular Tracers for Particulate Air Pollution Sources, *Trac-Trends in Anal. Chem.* 17(6) 356-366.
- Crutzen, P. J., Andreae, M.O., 1990. Biomass Burning in the Tropics: Impact on Atmospheric Chemistry and Biogeochemical Cycles, *Sci.* 250(4988) 1669-1678.
- Environmental Protection Agency, 1993b, 2000c
- International Agency for Research on Cancer (IARC 2002). Polynuclear Aromatic Compounds, Part 1, Supplement No. 7, Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs, Vols. 1-42.
- Oros, D.R., Simoneit, B.R.T., 2000. Identification and Emission Rates of Molecular Tracers in Coal Smoke Particulate Matter, *Fuel* 79(5) 515-536.
- Quinn, P.K., Bates, T.S., Baynard, T., Clarke, A.D., Onasch, T.B., Wang, W., Rood, M.J., Andrews, E., Allan, J., Carrico, C.M., 2005. Impact of Particulate Organic Matter

on the Relative Humidity Dependence of Light Scattering: A Simplified Parameterization, *Geophys. Res. Lett.* 32(22).

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., 1996. Source Apportionment of Airborne Particulate Matter Using Organic Compounds as Tracers, *Atmospheric Environment* 30(22) 3837-3855.

Simoneit, B.R.T., 1985. Application of Molecular Marker Analysis to Vehicular Exhaust for Source Reconciliations, *International J. Environ. Anal. Chem.* 22(3-4) 203-233.

Simoneit, B.R.T., Schauer, J.J., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge, W.F., Cass, G.R. (1999). Levoglucosan, a Tracer for Cellulose in Biomass Burning and Atmospheric Particles, *Atmospheric Environment* 33(2) 173-182.

TO-13A: Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatographic/Mass Spectrometry (GC/MS), January 1999

Tuhackova, J., Cajthaml, T., Novak, K., Novotny, C., Mertelik, J., Sasek, V., 2001. Hydrocarbons deposition and soil microflora as affected by highway traffic. *Environmental Pollution*. 113. 244-262.

U.S.EPA, Compendium method TO-13A, Determination of polycyclic aromatic hydrocarbons (PAHs) in ambient air using gas chromatography-mass spectrometry (GC-MS), 1999.

Vecchio V. Del, Valori, P., Melchiorri, C., Grella, A., 1970. Polycyclic Aromatic Hydrocarbons from Gasoline-Engine and Liquefied Petroleum Gas Engine Exhausts. *Pure and Applied Chemistry* 42, 739-748.

CHAPTER 8
CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

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

- During the study period average SPM concentration remained around $200 \mu\text{g m}^{-3}$ (NAAQS for residential, rural and other area) while the SO_2 and NO_2 concentration levels were below the safe limits of $80 \mu\text{g m}^{-3}$ recommended by NAAQS during NCRB months. However, all the levels were higher during the CRB months at all the monitoring sites.
- Monthly average concentration levels of SPM, SO_2 , NO_2 and PAH indicate a clear increase during crop residue burning months.
- Urban commercial site has highest levels of SPM due to its geographical location in south-east of the city and also due to northwestern wind direction during most of the monitoring period. Even the background values of SPM, SO_2 and NO_2 are higher than all other monitoring sites.
- Concentration levels of OTM, LOI and K was higher during the burning episodes than those in the absence of burning events in the ambient air of Patiala.
- The concentration levels of gaseous species stayed at upper levels of CRB episodes for the next two months even after the burning episodes showing that the gaseous molecules remain suspended for longer duration as compared to the SPM.
- Positive correlation was observed between SPM concentration and its constituents i.e. OTM and LOI.

- Potassium (K), taken as a tracer element for CRB practices, also has a positive correlation with SPM.
- Inverse relationship is observed between monthly average SPM concentration and ambient temperature i.e., SPM level increases with decrease in temperature.
- No direct inter-relationship was observed among the levels of Cu, Ni, Zn and SPM during CRB and NCRB Months.
- A significant increase in the concentration levels of polycyclic aromatic hydrocarbons like Benzo (k) fluoranthene and Pyrene (Pyr) were observed during the crop residue burning episodes during the study.

8.2 Further 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. Closely linked with this study, expanded (spatially and temporally) field measurement of fine particulate matter in this region would provide a great deal of policy-relevant information. Measurements presented by this thesis illustrate spatially variable SPM, SO_x, and NO_x concentrations, suggesting equally variable population exposure and location-specific source impacts.

Further monitoring of NMHC, VOCs and gases like CO, CH₄, and Ozone is also needed and linked to various radiation parameters which may result into exploring the enormous effect of crop residue burning in the NW India. 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.

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.

LIST OF PUBLICATIONS

- [1]. Susheel K Mittal, **Nirankar Singh**, Ravinder Agarwal, Amit Awasthi and Prabhat K Gupta (2009). Ambient air quality during wheat and rice crop stubble burning episodes. **Atmospheric Environment** 43, 238-244 (IF: 3.139)
- [2]. **Nirankar Singh**, Susheel K Mittal, Ravinder Agarwal, Amit Awasthi and Prabhat Kumar Gupta (2010). Impact Assessment of Rice Crop Residue Burning on Levels of SPM, SO₂ and NO₂ in ambient air of Patiala city in India. **International Journal of Environmental Analytical Chemistry** (90(10) (2010) 829-843) (IF: 1.703)
- [3]. R. Agarwal, A. Awasthi, S. Mittal, **N. Singh** and P. K. Gupta. Effects of air pollution on respiratory parameters during the wheat-residue burning in Patiala (2010). **Journal of Medical Engineering & Technology** 34 (1) 23-28 (IF: 0.526)
- [4]. **Nirankar Singh**, Ravinder Agarwal, Amit Awasthi, Prabhat K Gupta and Susheel K Mittal (2010). Characterization of atmospheric aerosols for organic tarry matter and combustible matter during crop residue burning and non-crop residue burning months in Northwestern region of India. **Atmospheric Environment** 44, 1292-1300 (IF: 3.139)
- [5]. Amit Awasthi, **Nirankar Singh**, Susheel K Mittal, Prabhat K Gupta and Ravinder Agarwal Effects of Agriculture Crop Residue Burning on Children and Young on PFTs in North West India. **Science of the Total Environment** 408 (20) 2010, 4440-4445 (IF 2.905)
- [6]. Amit Awasthi, Ravinder Agarwal, Susheel K Mittal, **Nirankar Singh**, Khem Singh, Prabhat K. Gupta. Study of size and mass distribution of particulate matter due to crop residue burning with seasonal variation in rural area of Punjab, India. **J. of Environmental Monitoring**, 2011, 13, 1073-1081 (IF: 2.225)
- [7]. **Nirankar Singh**, Susheel K. Mittal, Rishipal Singh, Amit Awasthi, Prabhat K. Gupta, Ravinder Agarwal. Characterization of crop residue burning particulate matter for K, Cu, Ni and Zn metals and their inter-relationship. (*Communicated in Atmospheric Environment*)

PRESENTATION IN CONFERENCES/WORKSHOPS

- [1]. **Nirankar Singh**, Susheel Mittal, Ravinder Agarwal, Amit Awasthi and Prabhat K Gupta. **Comparison study of ignitable material in aerosol samples collected during crop residue burning and non-crop residue burning months**, Conference on Advances in Chemical Engineering (AChemE-2009), 27-28 Feb, 2009, Dept of Chemical Engineering, Thapar University, Patiala, Punjab
- [2]. **Nirankar Singh**, Susheel Mittal, Ravinder Agarwal, Amit Awasthi and Prabhat K Gupta. **Wheat residue burning practices and its impact on ambient air aerosol, SO₂ and NO₂ levels at two different locations in Patiala, Punjab**, International conference Emerging Environmental Trends and Sustainable Development (CETAS-2009), 9-11 Feb, 2009, Dept of Environmental Science & Technology, Guru Jambheshwar University of Science & Technology, Hisar, India
- [3]. **Nirankar Singh**, Susheel Mittal, Ravinder Agarwal, Amit Awasthi and Prabhat K Gupta. **Air quality standards and the levels of SPM, SO₂ and NO₂ in the ambient air of Patiala**, National Symposium on Green Chemistry: Applications in Science & Engineering (NSGC-2009), 5-6 Feb, 2009, School of Chemistry & Biochemistry, Thapar University, Patiala, Punjab.
- [4]. **Nirankar Singh**, Amit Awasthi, Susheel Mittal, Ravinder Agarwal and Prabhat K Gupta. **Air quality of Patiala during crop residue burning and non- crop residue burning months from September 2006 to November 2007 in 11th Punjab Science Congress**, Feb 7-9, 2008. Thapar University, Patiala, Punjab, India
- [5]. **Nirankar Singh**, Susheel Mittal, Amit Awasthi, Ravinder Agarwal and Prabhat K Gupta. **Effect of crop residue burning on Air borne suspended particulate matter concentration in Patiala in International Conference on Aerosol-Climate-Interactions**, 20-22 Nov, 2007. Physical Research Laboratory, Ahmedabad, India.
- [6]. **Nirankar Singh**. "Air Pollutants: Origin, Effects on Human World and Remedies" in **National Seminar** on 'Environmental Education: Nature and Nurture' organized by Department of Teachers Education, Vardhman Post Graduate Institute, Bijnor, U.P., India 26- 27 February 2006.
- [7]. Amit Awasthi, Ravinder Agarwal, Prabhat Gupta, **Nirankar Singh** and Susheel Mittal **Effects on pulmonary functions due to rice-straw burning in Patiala**, National Symposium on Instrumentation (NSI-33), December 8-10, 2008, AU College of Engineering, Visakhapatnam.

- [8]. Amit Awasthi, Ravinder Agarwal, **Nirankar Singh**, Susheel Mittal, Khem Singh and Prabhat K Gupta, **“Size and mass distribution study of particulate matter due to ricewheat residue burning”**, 7th International Conference on Advances in Metrology (Admet-2009), Feb.18-20, 2009, New Delhi, India organized by NPLI and Metrology Society of India.
- [9]. Ravinder Agarwal, Prabhat Gupta, Amit Awasthi, **Nirankar Singh** and Susheel Mittal, **Study of human respiratory functions in relation to wheat- residue burning**, International Congress of Environmental Research [ICER-08], December 18-20, **2008**, BITS-Pilani, Goa Campus, Goa.
- [10]. Amit Awasthi, Ravinder Agarwal, **Nirankar Singh**, Susheel Mittal, Prabhat Gupta. **A review on effects of agriculture crop residue burning on respiratory system in different countries**, **11th Punjab Science Congress**, Feb. 7-9, **2008**, Thapar University, India

APPENDIX-I

National ambient air quality standards (NAAQS) for pollutants according to the Central Pollution Control Board (CPCB) India, Notification, 1998 and 2009

S.No.	Pollutant	Time weighted average	Concentration in ambient air					
			Industrial area		Residential, rural and other areas		Sensitive area	
			1998	2009	1998	2009	1998	2009
1.	Sulphur Dioxide (SO ₂), μgm^{-3}	Annual*	80	50	60	50	15	20
		24 hours**	120	80	80	80	30	80
2.	Nitrogen Dioxide (NO ₂), μgm^{-3}	Annual*	80	40	60	40	15	30
		24 hours**	120	80	80	80	30	80
3.	Suspended Particulate Matter (SPM ₁₀₀), μgm^{-3}	Annual*	360	--	140	--	70	--
		24 hours**	500	--	200	--	100	--
4.	Suspended Particulate Matter (PM ₁₀), μgm^{-3}	Annual*	120	60	60	60	50	60
		24 hours**	150	100	100	100	75	100
5.	Suspended Particulate Matter (PM _{2.5}), μgm^{-3}	Annual*	120	40	60	40	50	40
		24 hours**	150	60	100	60	75	60
6.	Nickel (Ni), ngm^{-3}	Annual*	--	20	--	20	--	20
		24 hours**	--	--	--	--	--	--

Source: CPCB (1998) Pollution Control Acts, Rules and Notifications. Pollution Control Series PCL/2/1992, Volume I, Sixth Edition, Delhi (India): Central Pollution Control Board.

*Annual arithmetic mean of 104 measurements in a year, twice a week, 24 hourly at uniform interval; and ** 24 hourly or 8 hourly values should be met 98% of the time in a year. However, 2% of the time values may be exceeded, but not on two consecutive days.

APPENDIX-II

US National Ambient Air Quality Standards (NAAQS)

The EPA Office of Air Quality Planning and Standards (OAQPS) has set National Ambient Air Quality Standards for six principal pollutants, which are called "criteria" pollutants. They are listed below.

	Primary Standards		Secondary Standards	
Pollutant	Level	Averaging Time	Level	Averaging Time
CO	9 ppm (10 mgm ⁻³)	8-hour	None	
	35 ppm (40 mgm ⁻³)	1-hour		
Pb	0.15 µgm ⁻³	3-Month Average	Same as Primary	
	1.5 µgm ⁻³	Quarterly Average		
NO ₂	53 ppb	Annual	Same as Primary	
	100 ppb	1-hour		
PM ₁₀	150 µgm ⁻³	24-hour	Same as Primary	
PM _{2.5}	15.0 µgm ⁻³	Annual	Same as Primary	
	35 µgm ⁻³	24-hour		
O ₃	0.075 ppm (2008 std)	8-hour	Same as Primary	
	0.08 ppm (1997 std)	8-hour		
	0.12 ppm	1-hour		
SO ₂	0.03 ppm	Annual	0.5 ppm	3-hour
	0.14 ppm	24-hour		
	75 ppb	1-hour	None	

“Don't judge each day by the harvest you reap, but by the seeds you plant”

-Robert Louis Stevenson