EFFECT OF CROP RESIDUE BURNING OVER NORTH INDIA

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DECLARATION

I hereby declare that the project work entitled "Effect of Crop Residue Burning over North India" is an authentic record of my own work carried out at Thapar University, Patiala and National Physical Laboratory, Delhi as requirements of one year project internship for the award of degree of M.Tech.(Environment Science & Technology), Thapar University, Patiala, under the guidance of Dr. Amit Dhir and Dr. T.K. Mandal, during June 15, 2015 to June 15, 2016.

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This is to certify that dissertation "**Effect Of Crop Residue Burning Over North India**" is the original piece of work submitted at Thapar University, Patiala embodies the results of piece of bonafide research carried by Ms. Palak, Registration number 601401008 in partial fulfillment of the requirement for the Degree of Master in Technology in Environmental Science & Technology under my supervision at Radio and Atmospheric Sciences Division (RASD), National Physical laboratory. No part of the thesis has been submitted for any other degree or Diploma. She has completed the research work at RASD, NPL during the period between 15th Sept. 2015 to 15th June, 2016

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ABSTRACT

During harvesting period over north India, large amount agricultural residues are burnt in field to clear the field and prepare for next season of sowing. Biomass burning emits large amount of trace gases and particulates to the atmosphere. This emitted particulate even reaches long distance through airmass modifying the air quality at the local as well as regional level. Viewing this large impact of burning on the composition of particulates, a study was conducted to analyze the contribution of wheat and rice stubble burning practices on concentration levels of $PM_{2.5}$ which were monitored in the ambient air at several sites over North India which included Delhi, Patiala, Chandigarh, Amritsar, Nainital and Kullu. Aerosol samples were collected on Quartz filter papers of 45mm of Whattman brand using dual channel dust sampler and fine dust sampler units for a 24 h period during rice harvesting season (October,2015-November,2015). Results pointed out a distinct increase in aerosols during the crop stubble burning periods and the impact remained in the atmosphere for many days even after burning period. Total Suspended Particulate Matter (TSPM) was also measured at three different agricultural sites near Patiala during the peak time of burning for two hours and results indicated distinct increase in TSPM also. The concentration weighted trajectory (CWT) receptor model was used to identify spatial source distribution and contribution of regional-scale transported aerosols. Three-dimensional 5-day backward trajectories arriving at all the sites, 500m above ground level were calculated using HYSPLIT-4 trajectory model during burning episodes. Results indicated that states undergoing crop residue burning are potential sources contributing the major $PM_{2.5}$ in all the monitored cities. $PM_{2.5}$ samples of Delhi and Patiala were further analyzed for ionic composition using ion analyzer. High concentration levels of K^+ and Na^+ were obtained during burning season of rice crops. Although, increase in K^+ levels was observed at all the sites, but a strong association in K^+ levels and Crop Residue Burning was obtained at an agricultural site only. Using these data, PCA Model source apportionment was made to understand the depth of effect of agricultural residue burning. Principal component analysis with varimax rotation was used to qualify the source contributions to $PM_{2.5}$. Vehicular emissions and biomass burning were two major sources that contributed to $PM_{2.5}$ concentrations in Delhi, whereas in Patiala, two major sources identified were industrial pollution and biomass burning.

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CHAPTER 1

INTRODUCTION

The atmosphere is known to be a gaseous blanket around the earth and is divided into numerous concentric zones. Troposphere which is the lowest region of the atmosphere contains 80% of the total mass of air and almost all of the water vapors. Along with nitrogen & oxygen that make up around 99% of this atmosphere, there are minor amounts of various other gases, tiny droplets of different liquids and minute particles of different types of solids. Therefore, we breathe several other gases as well as particles along with oxygen and nitrogen. Sometimes the concentration of substances apart from oxygen increases in the air either due to various natural processes or anthropogenic activities, thus it results in the atmospheric pollution. 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 decay the quality of air are identified as air pollutants and these pollutants are classified as primary and secondary pollutants. The primary pollutants are detrimental chemicals that enter right away into the air due to natural human activities. A secondary air pollutant is a toxic chemical formed in the air as a consequence of chemical reaction among two or more components with a primary pollutant. Thus primary pollutant combines with several components present in the air to form a secondary pollutant. These various primary air pollutants are grouped under five main categories viz., sulphur oxides, oxides of nitrogen, oxides of carbon, aerosols and hydrocarbons. Air pollution is the significant factor for degradation of environment. Burning of biomass, burning of fuels such as coal, wood, release of smoke from industrial chimneys and the exhausts from automobiles are some of the anthropogenic sources of air pollution. In the present times, use of automobiles for transport as well as rapid industrialization to deal with the growing demands of the increasing human population have turned out to be the major sources of air pollution. In a country like India, agrarian 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 burning of crop residue takes place in the North-West region of India during the months of April-May as well as 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 nitrogen oxides (NO_x), carbon monoxide (CO), sulfur oxides (SO_x), 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. Despite global significance of biomass burning, very slight quantitative information exists about the emission of some of the harmful chemical compounds. In order to obtain more information on the effect of stubble crop burning on quality of ambient air, global air quality monitoring is needed.

1.1 CLEAN AIR REGULATIONS & CRITERIA AIR POLLUTANTS

Criteria pollutants, as selected under the Clean Air Act of 1970 (U.S.A.), consist of pollutants that are ubiquitous in the United States and are recognized 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. Following are the criteria pollutants described:

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 biotchning, necrosis and loss of yield. Sulphur dioxide is one of the main ingredients in acid rain. SO_2 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 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 (NO_2) are harmful to plants at low concentration and to animals at higher concentration. Nitric Oxide can combine with atmospheric oxygen to form Nitrogen Dioxide ($2NO + O_2 = 2NO_2$) 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 PM_{10} is used to describe particles of 10 microns or less and $PM_{2.5}$ represents particles less than 2.5 microns in aerodynamic 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. 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 AIR QUALITY STATUS IN INDIA

Rapid urbanization and industrialization has added various pollutants to the air and thus caused deterioration of air quality in India. In order to prevent, control and abate air pollution, the Air (Prevention and Control of Pollution) Act was enacted in 1981. According to Section 2(b) of Air (Prevention and control of pollution) Act, 1981 ‘air pollution’ has been defined as ‘the presence in the atmosphere of any air pollutant.’ As per Section 2(a) of Air (Prevention and control of pollution) Act, 1981 ‘air pollutant’ has been defined as ‘any solid, liquid or gaseous substance [(including noise)] present in the atmosphere in such concentration as may be or tend to be injurious to human beings or other living creatures or plants or property or environment’. The Central Pollution Control Board (CPCB) had adopted first National Ambient Air Quality

Standards (NAAQS) in 1982 to maintain the ambient air quality in India, as per the provision of the Air (Prevention and Control of Pollution) Act, 1981 and these standards have been revised by the CPCB in November 2009 as depicted in Annexure I. Therefore ambient air quality standard is developed as a policy guideline that regulates the effect of human activity upon the environment so that pollutant emission into the air can be regulated. Standards may specify a desired state or limit alterations.

Air pollutants whether man made or natural are to be monitored to know their characteristics and concentration in the ambient air. Monitoring helps us to take necessary preventive and control measures. Keeping this in view, Central Pollution Control Board initiated National Ambient Air Quality Monitoring (NAAQM) program in the year 1984 with 7 stations at Agra and Anpara. Subsequently the programme was renamed as National Air Quality Monitoring Programme (NAMP). The objectives of the NAMP are to determine status and trends of ambient air quality; ascertain whether the prescribed ambient air quality standards are violated; identify non-attainment cities where air pollutants are exceeded the prescribed standards; obtain the knowledge and understanding necessary for developing preventive and corrective measures and understand the natural cleansing process undergoing in the environment through pollution dilution, dispersion, wind based movement, dry deposition, precipitation and chemical transformation of pollutants generated. Steadily the air quality monitoring network got strengthened by increasing the number of monitoring stations from 28 to 503 during 1985 – 2011 *(CPCB, 2012)*. Under NAMP, four air pollutants, viz., sulphur dioxide (SO_2), oxides of nitrogen as (NO_X) and suspended particulate matter (SPM) and respirable suspended particulate matter (RSPM/PM10), are regularly monitored at all the locations. Besides this, additional parameters such as respirable lead and other toxic trace metals, hydrogen sulphide (H_2S), ammonia (NH_3) and polycyclic aromatic hydrocarbons (PAHs) are also being monitored in 10 metro-cities of the country since 1990. The Central Pollution Control Board collects the air quality data and brings out the annual air quality statistics. Based on such data, it has been possible to identify the polluted areas and also prepare action plans.

The air quality terms is expressed in terms of low, moderate, high and critical for various cities/towns that have been monitored. The concentration ranges for different levels have been selected based on the Notified Standards for different pollutants and area classes by calculating an Excedence Factor (the ratio of annual mean concentration of a pollutant with that of a respective standard) *(PPCB,2010).*The four air quality classifications are Critical pollution (C) when EF is more than 1.5; High pollution (H): when EF is between 1.0 - 1.5; Moderate pollution (M): when EF between 0.5 - 1.0; and Low pollution (L): when EF is less than 0.5. It is clear from the above classifications, that the locations in either of the first two categories are actually violating the standards, although, with varying magnitude. Those, falling in the third category are meeting the standards as of now but likely to violate the standards in future if pollution continues to increase and is not controlled. However, the locations in Low pollution category have a rather pristine air quality and such areas are to be maintained at low pollution level by way of adopting preventive and control measures of air pollution. The pollution control classification is given in Table 1.1.

Table 1.1: Pollution level classifications *(Source: CPCB, 2012)*

Pollution level	**Annual mean concentration range (µg/m^3)**					
	Industrial, Rural, Residential & others areas			**Ecologically sensitive area**		
	SO_2	NO_2	PM_{10}	SO_2	NO_2	PM_{10}
Low(L)	0-25	0-20	0-30	0-10	0-15	0-30
Moderate(M)	26-50	21-40	31-60	11-20	16-30	31-60
High(H)	51-75	41-60	61-90	21-30	31-45	61-90
Critical(C)	>75	>60	>90	>30	>45	>90

1.3 SYSTEM OF CROPPING IN INDIA

Two major crops grown in India are wheat and rice. The process of growing rice after wheat and then again rice forms a cycle of rice and wheat crops and known as rice-wheat cropping system (RWCS). This system is well practiced from last more than three decades in North Indian states like Punjab, Haryana, and western Uttar Pradesh which covers 12.33 million hectares (m ha) out of which about 10 m ha is in the Indo-Gangetic plains, 75% covering 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)*. This is the result of decline in fertility of soil. In past years, the crop harvesting 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. Even if RWCS has been an advantage from the food security perspective for a popular vegetarian nation, but it being an demanding cropping system is considerably demanding the two major natural resources, that is soil and water, which are necessary for the endurance of human life. As we know rice is a water consuming crop; approximately 5000 liters are required to generate 1 kg rice. Farmers are forced to immensely depend on the groundwater through tubewells for the farming of rice in the regions of non-traditional rice belt such as Punjab, Haryana and western UP where there is lack of heavy monsoon rains as compared to the traditional rice belt in the eastern India. Due to this the water table in this region has reduced considerably. This system also requires high rates of fertilizer nitrogen which has very adverse effects on the environment *(Prasad, R., 1998)*. Approximately 5-10% of the nitrogen provided to rice is lost in the environment through ammonia volatilization which could increase atmospheric levels of N, resulting in increased acid rain *(Marshal et al., 1998)*. Furthermore, burning of rice residue is so rampant that it emits great amounts of carbondioxide resulting in the global warming. Open field burning of rice stubble results in emissions of 144,719 tonnes of total particulate matter annually in India *(Gadde et al., 2009)*.

1.4 AGRICULTURAL CROP RESIDUE AND OPEN FIELD BURNING

Open burning is known as the exposed combustion of some materials in the ambient surroundings. It includes inadvertent fires like forest fires and deliberate combustion activities for example waste crop residue burning in agricultural fields to prepare the fields for the next crop. A large amount of agricultural crop stubble residues are produced every year in most of the countries. Wheat, rice, millet, maize, barley, sugarcane & sorghum are the most important crops contributing in the worldwide crop residue production. In Some countries of Southeast Asia, sugar cane and rice are major crops but in the Middle East, the crop mixture is further distinct. In the dry lands of the Near East and Mediterranean northern Africa, barley and wheat predominate. Farther south in the humid and sub-humid regions, maize is important. Open burning of crop residue is an international practice to discard leftover crop residues (rice, wheat, barley, corn, sugarcane and oats) after harvest for land clearing and hinder pest infestations. It has been predicted that humans are accountable for almost 90% of biomass burning with just a small fraction of natural fires contributing to the overall amount of vegetation burned. In Comparison to other types of biomass, crop residue has a relatively high content of inorganic compounds specially potassium compounds, that are released during combustion and form particles after flue gas cools down *(Nielsen et al., 2000, Jenkins et al., 1998)*. Although Stubble burning quickly clears the field , kills weeds, slugs and other pests, reduces nitrogen tie-up and is cheap but has a number of harmful effects on the environment such as causes pollution from smoke, increase erosion, nutrients are lost, Impacts soil microbes and fauna etc. Emissions from field burning comprise of Particulate matter, gaseous pollutants such as Carbon dioxide, Nitrogen oxides, Sulphur dioxide, methane as well as Volatile organic compounds and hydrocarbons *(Crutzen et al., 1979; Radke et al., 1988; Koe et al., 2001; Jain et al., 2014; Chanduka et al., 2015).*

Carbonaceous aerosols which form a major part of the particulate matter emitted during the crop burning process *(Susott et al., 1991)* may be broadly catergorized as organic carbon(OC) which mainly scatters solar radiation *(Novakov and Corrigan, 1996)* resulting in a net negative radiative forcing *(Bond et al., 2004)* and Black Carbon (BC) also known as elemental carbon(EC) which absorbs solar radiations resulting in a net positive radiative forcing *(Liousse et al.,1996, Haywood and Ramaswamy, 1998). Monks et al., (2009)* stated that due to the high convective activity prevalent in the tropics, the atmospheric pollutants can easily be transported to higher altitudes and then undergo long range transport. However the contribution of biomass smoke to the total particulate matter (PM) becomes difficult to delineate since the PM from biomass sources readily mix with the PM emitted from other natural and anthropogenic sources.

Levoglucosan (1,6-Anhydro-β-D-glucopyranose, $C_6H_{10}O_5$) is the most abundantly emitted anhydromonosaccharide in biomass burning PM, followed by others like mannosan (1,6-Anhydro-β-D-mannopyranose) and glactosan (1,6-Anhydro-β-D-galactopyranose) and beacause of its source specific emission and atmospheric stability, it can therefore be used as tracers in the ambient air *(Yttri et al.,2005 ; Sarrikoski et al., 2008 ; Niemi et al.,2009 ; Saarnio et al.,2010)*. It is a major degradation product of the incomplete combustion and pyrolysis of cellulose and hemi-cellulose of biomass at temperatures greater than 300^{o}C and has been recognized as a useful molecular marker for biomass burning aerosols *(Simoneit, 1999, 2002; Zhang et al.,2008 ; Kim Oanh et al., 2011).* Levoglucosan is source specific, emitted in huge amounts from biomass burning and is sufficiently stable rendering it capable of undergoing long range transport and making it superior to conventional inorganic tracers such as potassium which from the fact that it also has contributions from sea salt and soil dust.

Variation in composition of air due to biomass burning affects the energy balance of the earth and contributes to international climatic change *(Koppmann et al.,2005)*. Apart from being an irritant, smoke also contains many harmful chemicals potentially detrimental to human health. These mainly include: formaldehyde, polycyclic aromatic hydrocarbons (PAH's), carbon monoxide, nitrous oxides, dioxins, particulate matter, and volatile organic compounds (VOCs). Long exposure to these components causes various health problems such as heart disease, risk of cancer, diabetes, developmental problems in children, and harm to the immune system. Crop residue burning also leads to loss of nutrients as well as organic matter and also causes air pollution due to release of toxic and greenhouse gases such as CH_4, CO_2 and CO which cause a hazard to humans and ecosystem *(Nguyen et al., 1994).*

1.5 CROP RESIDUE BURNING IN NORTHERN INDIA

It is a common practice to burn rice and wheat crop residue post harvesting which is performed by farmers in Punjab and also in northwest region of the country *(Mittal et al., 2009; Singh et al ., 2010)*. Inspite of the fact that straw burnings are prohibited by the local administration, even now farmers feel that these practices are cost-effective and suitable for disposing of residue and preparing seedbed quickly for the upcoming crop and this practice also prevents the risk of decreased crop yields linked with late drilling. Vast amount of smoke comprising of gaseous species as well as particulate matter is generated due to Crop residue burning (CRB) practices and which leads to deterioration of ambient air quality affecting the public health *(Dennisa et al., 2002; Wiedinmyera et al., 2006)*. Aerosol is the most important criteria pollutant released during stubble crop residue burnings *(Handa et al., 1980)*. Smoke which is released from biomass burning also contains various pollutants such as toxic gases, polycyclic aromatic hydrocarbons (PAH), metal particles, etc. which have detrimental effects on human health *(Freeman and*

Catell., 1990; Godoi et al., 2004). Various scientists have reported the emissions of PAHs associated with aerosols during burning of sugarcane *(Fang et al., 1999; Godoi et al., 2004).*

Fig.1.1: Crop residue burning in field at roadside near Patiala after paddy crop harvesting

1.6 IMPORTANCE OF AGRICULTURAL CROP RESIDUE

Crop residue is an essential source of organic matter for the soil. Several 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 Carbon in the soil.

1.7 ALTERNATIVES OF CROP RESIDUE BURNING

Some of the alternatives to crop residue burning are known as follows:

a) Returning crop residue into the soil with the use of cropping devices and tormenting
b) Bale straw for use of farm animals.
c) Selling excessive straw for industrial use like ethanol production, straw particle board, etc.
d) Incorporating the residue into the soil on proper timings, or composting the residue away from the field and then returning the completed compost are various possible ways of overcoming the difficulty.
e) Residues can also be integrated into the soil as soon as the harvest is finish so that a cover crop can be seeded. This practice reduces insects and disease, weeds, minimizes erosion, captures excess nutrients and reduces the potential for odor.

1.8 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.

CHAPTER 2

REVIEW OF LITERATURE

Although, biomass burning is being ignored to some extent in managing the urban air quality, but it has drawn worldwide concerns in the past decades for its harmful effects on human health, visibility, and global climate by releasing trace gases and aerosols. Particulate matter, CO, CO_2, volatile organic compounds, polycyclic aromatic hydrocarbons, NO_x and SO_2 are some principally emitted pollutants during these operations leading to generous changes in biogeochemical processes of earth's atmosphere *(Crutzen et al., 1979; Radke, 1989; Radojevic et al., 1997; Koe et al., 2001; Crutzen and Andreae, 1990; Cofer et al., 1991; Levine, 1995; Andreae and Merlet, 2001; Andreae, 1991)*. Many polycyclic aromatic hydrocarbons (PAH) are poisonous and some of them are recognized as suspected carcinogens. A number of compounds have been recognized in smoke particles resulting from combustion of biomass of various plant species *(Hawthorne et al., 1988, Lee et al., 2005; Sheesley et al., 2003; Hays et al., 2002)*. Both particulate as well as vapor phase materials are included in biomass smoke with much of the particulate matter (PM) and that too in the $PM_{2.5}$ size range. Forest fires and savanna fires are two most important types of biomass burnings and are reported in various 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 expected to affect universal air quality as well. Estimation of the extent to which they add to the damage of air quality in urban areas becomes important in such conditions. Agriculture is under study as a cause of airborne particulate matter, but there is lack of research in quantifying the emissions of fine ($PM_{2.5}$) and coarse ($PM_{2.5–10}$) particulate matter from agricultural operations leading to ambiguity in agricultural contributions. The greater part of the available data on emissions from biomass burning sources has been of defined pollutants, including CO, SPM and oxides of nitrogen and sulfur (NO_x and SO_x). since Open burning is carried out in non ideal combustion conditions therefore it typically emits particulate matter (PM) and soot that are visible as a smoke plume, methane (CH_4) , carbon monoxide (CO), hydrocarbons, volatile organic compounds (VOCs) like benzene, and semi-volatile organic compounds (SVOCs) as well as polycyclic aromatic hydrocarbons (PAHs) such as benzo[a]pyrene. Various metals such as mercury (Hg) or lead (Pb) can also be released depending on the sources. As well as polychlorinated biphenyls (PCBs), Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDDs/Fs) can also be emitted. Carbonaceous aerosols which form a major part of the particulate matter emitted during the crop burning process *(Susott et al., 1991)* may be broadly catergorized as organic carbon(OC) which mainly scatters solar radiation *(Novakov and Corrigan, 1996)* resulting in a net negative radiative forcing *(Bond et al., 2004)* and Black Carbon (BC) also known as elemental carbon(EC) which absorbs solar radiations resulting in a net positive radiative forcing *(Liousse et al.,1996, Haywood and Ramaswamy, 1998)*. *Monks et al., (2009)* stated that due to the high convective activity prevalent in the tropics, the atmospheric pollutants can easily be transported to higher altitudes and then undergo long range transport. However the contribution of biomass smoke to the total particulate matter (PM) becomes difficult to delineate since the PM from biomass sources readily mix with the PM emitted from other natural and anthropogenic sources.

Levoglucosan (1,6-Anhydro-β-D-glucopyranose, $C_6H_{10}O_5$) is the most abundantly emitted anhydromonosaccharide in biomass burning PM, followed by others like mannosan (1,6-Anhydro-β-D-mannopyranose) and glactosan (1,6-Anhydro-β-D-galactopyranose) and beacause of its source specific emission and atmospheric stability, it can therefore be used as tracers in the ambient air *(Yttri et al.,2005 ; Sarrikoski et al., 2008 ; Niemi et al.,2009 ; Saarnio et al.,2010)*. It is a major degradation product of the incomplete combustion and pyrolysis of cellulose and hemi-cellulose of biomass at temperatures greater than 300ºC and has been recognized as a useful molecular marker for biomass burning aerosols *(Simoneit, 1999, 2002; Zhang et al., 2008; Kim Oanh et al., 2011)*. Levoglucosan is source specific, emitted in huge amounts from biomass burning and is sufficiently stable rendering it capable of undergoing long range transport and making it superior to conventional inorganic tracers such as potassium which from the fact that it also has contributions from sea salt and soil dust. Water soluble potassium (K^+) and Organic carbon (OC) are main components of the aerosols released from biomass fires. Ratio of Elemental carbon (EC) by organic carbon is known to be a good tracer of smoke from biomass fires *(Cachier et al., 1995; Ames et al., 2004; McDonald et al., 2000; Spracklen, et al. 2007; Park, et al. 2003)*. 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; Dall’Osto et al., 2013; Viana et al., 2013)*.

2.1 INTERNATIONAL SCENARIO

Crop residue burning practices are worldwide *(Andreae., 2001; Yongtaohu et al., 2009; Prasad, 2008)*. It helps growers stay competitive as it is a reasonable and efficient method to eliminate surplus residue and also it quickly clears the field, kills weeds, slugs and other pests, reduces nitrogen tie-up. It also provides a temporary ash fertilization effect. Annual cropland burning (1,239,000 hectares) have been observed corresponding 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. In countries like Mexico, neighboring 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. Several American states including California, Washington, Idaho, Arkansas, Colorado, Oregon, Florida, Kansas, Louisiana, North and South Dakota, Oklahoma, and Texas experience high levels (> $3\text{x}10^4$ ha/ yr) of CRB *(McCarty et al., 2009)*. In the past decade, agricultural field burning has been the topic of investigation and public discussions in several countries.

In northern Idaho and eastern Washington, farmers set up their fields for seeding, their practices include the use of fire to discard waste residue. In Europe and North America, deliberate agricultural burning in order to rapid residue and vegetation clearing operations largely adds in the emission of pollutants after wildfires. These sources compose approximately 30% of identified sources of atmospheric carbon monoxide (CO). Recent reductions in concentrations of atmospheric carbon monoxide (CO) in these regions have been recognized in part to decelerate in the rate of tropical burning of biomass *(Levine, 1991; Khalil and Rasmussen, 1994)*. The mutagenic activities and characteristics of PAH derived from biomass burning are described in the literature but there are lesser reports on open burning *(Bjorseth and Ramdahl, 1985; Nielsen et al., 1992; Elomaa et al., 1991; Mast et al., 1984)*. In the United States, biomass burning contributes around 35% of the primary fine particulate matter ($PM_{2.5}$) emissions and a significant fraction of these emissions are carbonaceous (70- 95%) *(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 are usually burned all over the world. Rice and wheat straw consist of 95% of the agricultural biomass, exclusive of wildfires and set forest fires, candidly burned in the state of California *(Jenkins et al., 1992)*. Release of total PAH depends mainly on conditions of burning and to a lesser extent on type of fuel and these emissions varied from 5 to 683 mg/ kg. Decrease in combustion efficiency and increase in emission rates of particulate matter increased the emission rates of total PAH *(Jenkins et al., 1996)*. In a Georgia case study *(Yongtaohu et al., 2009)*, biomass burning was identified as a major and growing contributor to $PM_{2.5}$. Specific impacts from each burning sources were quantified with the use of Community Multiscale Air Quality (CMAQ) Model which is a chemical transport model (CTM) and it was found out that the Impacts of approved burning dominated biomass burning impacts, and they contributed approximately 55% and 80% of $PM_{2.5}$ in January and March, respectively.

Various studies show that fires in the Canada and Western U.S. have increased in duration as well as in frequency, over the last few decades. These fires have resulted in universal climate change, which has led to reduced winter snow packs and warmer temperatures *(Westerling et al., 2006; Gillett et al., 2004)*. Jenkins and Turn measured particulate and gaseous emissions due to agricultural burning by developing a wind tunnel to imitate burnings *(Turn et al., 1997; Jenkins, 1996)*.

Dhammapala et al., (2007) quantified emission factors of Polycyclic aromatic hydrocarbons(PAHs), Methoxy phenols, Levoglucosan, Organic Carbon & Elemental Carbon from Kentucky bluegrass and wheat stubble burns. *Hays and coworkers (2005)* presented the chemical and physical characterization of particulate emissions by simulating agricultural fires in an enclosure. Similarly, *Zarate et al., (2000)* predicted emission factors from cereal waste burning by performing combustion chamber experiments and a field burning experiment in Spain. *Nguyen et al., (1994)* calculated CO_2, CO and CH_4 emissions from burning of rice straw by conducting field experiments in Vietnam. Several other environmental media like surface water are also affected from air emissions from open burning as well as the sensitive species that occur in those media are also impacted *(Barber et al., 2003)*.

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 in comparison to the urban and suburban sites. 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, in consequence of changes in agricultural practices because of an imposed ban on the burning of crop residue *(Samara et al., 2003)*. In Brazil Sugar cane is the major agricultural crop which is affected by agricultural crop residue burning. Burning is applied broadly and this extremely increases concentrations of particulate matter, O_3, CO and other trace gasesin the atmosphere, although to uncertain levels *(Kirchhoff et al., 1991; da Rocha, 2003)*.

Brazil is the chief sugar cane exporter, followed by India and Australia, and responsible for 25% of the international $19.5*10^6$ ha harvest. Approximately half (52%) of the Brazil's harvest is known to come from Sao Paulo, making the state an internationally significant source of emissions from agricultural biomass burning. In rural Sao Paulo State of Brazil, the composition of the lower troposphere represents a subtropical and tropical region having low population density and an agriculture based economy. Here sugar cane production constitutes the sole largest agricultural entrepreneur with greater than 75% of the area planted. In situ burning of the crop is performed by farmers prior to harvest which releases massive amount of gases and aerosols into 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 µm), accumulation mode (0.1-2 µm), and nuclei mode (< 0.1 µm) particles (Finlayson-Pitts et al., 2000). 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)*. According to Recent surveys 54% of rural population practices open burning in the Mexico, and 16-48% of all population does so in United States *(Neurath,2003)*.

As far as Asia is concerned, Rice is extensively grown crop in Asia. India (21%) and China (30%) contribute approximately half of the world's entire rice production whereas the Philippines and Thailand contribute 2% and 4% of the world's rice production correspondingly. 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 projected that almost 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 mostly 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 contribution of green house gas emissions through burning of rice straw in open fields in India, Thailand, and the Philippines were calculated 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 $PM_{2.5}$, PM_{10}, SO_2, 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 leading contributor to the total emissions, particularly during the dry season in the middle part of the Thailand. Very few studies are reported for open crop residue burning for the country with significant discrepancy *(Kanabkaew et al., 2010)*.

Rice-wheat cropping system is also 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 show that the health impacts of outdoor air pollution are more severe in Asia as compared to Europe and North America due to the degree of the air pollution, the basic health status of the population and the amount of exposure to pollution,. The biomass burning occurs in small patches, covering larger area, for the reason of land clearing. Through rapid financial growth, China has faced serious air pollution harms mainly in urban areas with particulate matter (PM) as the leading pollutant in the majority of cases. Burning of crop residues in field is a typical way to discard waste after harvesting and also it is an important type of biomass burning in China. Many studies have been conducted in China in last one decade to estimate the contribution of biomass burnings in air pollution. Various studies projected 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)*. A great amount of pollutants are released due to open burning of agricultural residues during harvest season, including particulate matter (PM), CO, hydrocarbons, and others resulting in serious local as well as regional environmental impacts *(Guo et al., 2004; Duan et al., 2004)*. In June 2006, wheat straw field burning caused crucial air pollution in Beijing *(The Global Fire Monitoring Center, GFMC)*.

Crop residue burned in the field and fuel wood burned as fuel are the major types of biomass burning in China, consisting around 90% of the complete biomass burning on dry weight base. According to statistical data forest fires in China have decreased considerably since the 1980s. Carbon monoxide (CO) emission were quantified from open biomass burning and was found to be 16.5 Tg in 2000, with a 90% uncertainty ranging from 3.4-34 Tg *(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 CO, CO_2, NO_2,NO, and NO_x were reported and it was found that the fraction of CO, CO_2, and NO_x to the sum of emissions were maximum for corn straw followed by wheat straw and rice straw, respectively *(Zhang et al., 2008)*. In an another research emission factors of element carbon (EC), organic carbon (OC), particulate matter (PM), SO_2, NO_x, CO, CO_2, and some particular ions were calculated from the domestic burning of generally produced crop residues in rural China. To calculate the emission factors, a combustion tower was built to imitate conditions of cooking under which the growers in rural China burned their crop residues. Maximum emission factor for the total PM (8.75 g/kg) were observed for the wheat straw among the four crop residues, maximum emission factor for EC (0.95 g/kg) and OC (3.46 g/kg) were observed for corn stover and wheat straw, respectively. The highest emission factors of NO, NO_x, and CO_2 were observed for corn strover, whereas the highest emission factors of NO_2, SO_2, and CO were observed for wheat straw, rice straw and cotton stalk respectively. All the crops had the maximum emission factors of water soluble ions, Cl^- and K^+. Relatively greater emission factor of some anions like F^-, Cl^-, $NO_2{}^-$ and some cation species were observed for wheat straw in comparison to other residues *(Cao et al., 2008)*.

System of double cropping of wheat-rice is widely adopted in Suqian, China with 4523 km^2 of total area under cultivation. The average amount of Crop residue produced annually according to the data of crop output from 2001 to 2005 was calculated as 3.04×10^6 t. Around 37% of rice straw and 82% of wheat straw is being burnt in the field, therefore the percentage of crop residue being burnt in the field is around 43%. Combine harvester, according to survey conducted in fields, play an important role in burning of crop residues in the field *(Yang et al., 2008)*. Emissions from burning of crop residues were estimated in China *(Street et al., 2003; Yan* *et al., 2006)* mainly by adopting the emission factors described by *Andreae and Merlet (2001)*. A set of emission factors for various species emitted from different types of biomass burning were presented by Andreae and Merlet . Agricultural field crop residue burning during the harvesting period significantly affects the air quality. Therefore source profiles for particulate matter from agricultural fire are required to find out its contribution to ambient air quality *(Zhang et al., 1998)*.

According to various previous studies the most important contributors to worldwide emissions of carbonaceous aerosols is China *(Bond et al., 2004, Chameides and Bergin, 2002)* and major proportion of carbonaceous aerosol emissions in China are caused by bio-fuel combustion contributing for 55% of organic carbon and 30% of black carbon out 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 worldwide climate effects and the level of China's carbonaceous aerosol emissions, it is significant to have more precise estimates of emissions *(Roden et al., 2006)*. The biomass burning material releases CO_2 and water vapors (H_2O) if the conditions for combustion are ideal *(Levine, 1991)*. But it is not possible to achieve the complete combustion under any given conditions of biomass burning therefore various other carbon species including methane (CH_4), carbon monoxide (CO) as well as non methane hydrocarbons (NMHCs) are also released due to 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.

2.2 NATIONAL SCENARIO

Rice, wheat and sugarcane are three major crops grown in Northern India. The harvesting of these crops leaves a huge amount of crop residue in the fields. Wheat and rice straw burning results in the decline in fertility of soil and also cause atmospheric pollution due to release of great amounts of Suspended particulate matter (SPM) as well as gases such as CH_4, CO, NO_x, SO_x, etc. which are a cause of several health problems like eye, respiratory and skin diseases. Thorough agricultural burning also adds to various greenhouse gasses (GHG) such as CO_2, CH_4,

N_2O resulting in climate change. In India out of the aggregate national emissions, 28% emissions are reported from the agricultural sector. Punjab state of India produces around 17 million tons of wheat straw and 23 million tons of rice straw, annually. Almost 50% of wheat straw (8.5 million tons) and more than 80% of paddy straw (18.4 million tons) produced are being burnt in the fields every year. The wheat and paddy straw which are burnt are very much rich in phosphorus, nitrogen and potassium contents. This straw should be recycled into the soil by the process of mulching but unfortunately it is burnt resulting in elevation of the top 3 inches of soil temperature. As a result C/N ratio in soil is disturbed, nitrogen being converted to nitrate and carbon being lost into the atmosphere as CO_2 is lost to atmosphere and therefore 0.824 million tons of Nitrogen, Phosphorus & Potassium are lost from the soil. This constitutes around 50 percent of total consumption of fertilizers in the state. According to the agriculture experts, residue burning in the fields is also beneficial in destroying friendly bacteria and pests *(PAU, 2006)*. Straw burning results in more than 1.83 million tons per year loss of carbon which is damaging the environment of the area, human health as well as the fertility of soil *(Sidhu, 2002)*.

Gupta et al., (2004) quantified emissions from burning of crop residue and total emissions were calculated as 3 kg particulate matter, 1460 kg CO_2, 60 kg CO, 2 kg SO_2 and 199 kg ash per ton straw burning. Total emissions in Punjab due to paddy and wheat crop residue burning were calculated and it was observed that paddy crop residue burning released emissions almost as twice that of wheat crop residue burning. Emissions from paddy fields burning were quantified to be 261 Gg of CO, 3 Gg of CH_4, 19.8 Gg of NOx, 28.3 Gg of $PM_{2.5}$ and 30 Gg of PM_{10} during October 2005 and from wheat crop residue burning emissions were calculated as 113 Gg of CO, 1.33 Gg of CH_4, 8.6 Gg of NO_x, 12 Gg of $PM_{2.5}$ and 13 Gg PM_{10} during May 2005 *(Badrinath et al., 2006)*.

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. It has been reported that the emissions of aerosols consisting of carbonaceous particles are not certain in Southeast Asia, because the information about emissions from fossil fuels and burning of biomass is limited and confined *(Streets et al., 2003)*. Even the key research priority is given to the transport process of black carbon and its emission rates in Southeast Asia *(Ramanathan et al., 2001)*. Usually the evaluation of aerosol released emissions from biomass burning is puzzled by the major fossil fuel combustion, vehicular emissions and industrial pollution in Southeast Asia; therefore concentration of carbonaceous aerosols should be analyzed with temporal and spatial patterns of biomass burning so that uncertainties can be reduced *(Chin et al. 2002)*. Aerosols are removed from the atmosphere by precipitation, but sometimes presence of large amount of aerosols suppresses the precipitation, resulting in increased residence time of aerosols in the air. Now drier conditions further increase smoke and dust resulting in the disturbance of hydrological cycle of that region *(Ramanathan et al., 2001; Jacobson, 2001)*. Various factors affect the severity and extent of biomass burning such as density of the vegetation, temperature, humidity and wind speed *(Schultz 2002)*.

Ground reaching solar irradiance and aerosol optical depth were measured using synchronous satellites in central region of India and high aerosol layers up to 3 km on definite days during October 2007 were observed. Therefore the observations on properties of aerosol showed the transport of particles in Indo- Gangetic Plains over large regions due to agriculture crop residue burning in *(Badarinath et. al., 2009)*. In India 40% of 284 Tg crop residue was generated due to stubble of wheat in the year 2000, out of which around 7.5% of the total produced wheat stubble was subjected to burning on the field site itself resulting in release of larger amounts of particulate matter (PM) and trace gases into the atmosphere. The Emission Factors (EFs) reported for wheat stubble burning in India addressed important information gap on open crop stubble burning in the region *(Sahai et al., 2007; Gupta et al., 2004)*.

Usually crop residue is burnt by double-crop grain farmers so that they can prepare seedbed and avoid reductions in yield but this residue burning leads to loss of nutrients from soil as well as soil organic matter (SOM). Various studies reported that if crop residue is incorporated in a rice-wheat system then it may lead to rise in soil organic matter and can also maintain high grain yields *(Aulakh et al., 2001)*. Biomass open burning also exhibited a major impact on dibenzofurans and polychlorinated dibenzo-p-dioxins concentration levels in ambient air *(Shih et al., 2008)*. It was found that increase in the concentration of aerosols, SO_2 & NO_2 due to crop stubble burning in Patiala performed after the rice and wheat crop harvesting changed the ambience of the city and also gaseous molecules had longer residence time than aerosols in air *(Mittal et al., 2009)*. *Sharma et al., (2010)* studied atmospheric aerosol loading due to agricultural crop residue burning in Punjab and higher values of aerosol index and nitrogen dioxide were reported. Agricultural crop residue burning also affects the concentration levels of different sized particulate matter. $PM_{2.5}$ contributed almost 55-64% of the total RSPM during burning episodes in Patiala *(Awasthi et al., 2011)*.

Kaskaoutis et al.,(2014), with the use of satellite observations and the synergy of ground based measurements examined the impact on modification of aerosol properties, altitude characteristics and long range transport of smoke plumes over northern India during post monsoon (October – November 2012) due to paddy crop residue burning. The size of aerosols shifted from coarse mode towards the fine – mode fraction. *Chanduka et al., (2015)* calculated the impact of stubble burning on quality of ambient air in Mandi Gobindgarh and it was found to be more for agricultural sites as compared to other sites during harvesting periods.

2.3 MULTIVARIATE RECEPTOR MODEL (PCA) & BACKWARD TRAJECTORY RECEPTOR MODEL (CWT) STUDIES

In order to reduce the air pollution, understanding the potential source categories and their contributions (source apportionment) is necessary *(Zheng et al., 2005)*. The result of source apportionment can provide the scientific supporting for air quality management decisions. Receptor models, the useful tools for source apportionment, utilize the chemical composition of receptors for identification and apportionment of sources of PM in the atmosphere *(Zheng et al., 2007; Ke et al., 2008; Kong et al., 2010; Pant and Harrison, 2012)*. Among several receptor models, two main classes of models have been employed widely over the world. That is, i) Chemical Mass Balance (CMB) model and ii) multivariate factor analysis models (including Principal Component Analysis (PCA), UNMIX, and Positive Matrix Factorization (PMF)). The first class of models need both the input data of receptor and the source profiles; while the later class of models extracts source profiles and their contributions over sets of receptor samples *(Hopke, 2003)*. The detailed introductions of the principle and applications for CMB, PCA, UNMIX and PMF models have been presented in literature *(Watson, 1984; Paatero and Tapper, 1994; Lee et al., 1999; Watson and Chow, 2001; Song et al., 2006; Chen et al., 2007; Zheng et al., 2007; Begum et al., 2010; Harrison et al., 2011; Gugamsetty et al., 2012)*. The strengths and weaknesses for the two classes of receptor models have been summarized in literature *(Hopke, 2003; Pant and Harrison, 2012)*.

PCA, as a technique which attempts to explain the statistical variance in a number of original variances by a minimum number of significant components, has often been employed in the source apportionment of air pollutants measured at a receptor site *(Harrison et al., 1997)*. Many studies have been conducted to identify and quantify source contributions to atmospheric particulate matter concentrations using PCA. Studies were conducted in locations throughout the world including Europe, United States, Canada, Africa, India, Greece *(Xhoffer et al., 1991; Kulshrestha et al., 1995; Harrison et al., 1996; Swietlicki et al., 1996; Armanino et al., 1996; Rocha et al., 1997; Cardoni et al, 1998; Beceiro-Gonzalez et al., 1998; Balachandran et al., 2000; Prati et al., 2000; Kendall et al.,2001; Ruuskanen et al, 2001)*. Most of the studies identified a factor/component that was representative of anthropogenic combustion sources (e.g., coal combustion, vehicular, industrial, biomass burning, and waste incineration emissions) regardless of whether the studies were conducted in urban, rural, and coastal locations. This component generally consisted of high component loadings on air pollutant markers, such as NO_x, SO_2, O_3, $PM_{2.5}$, black carbon, CO, and/or trace metals *(Li et al., 2008; Kim et al., 2011; Wan et al., 2009; Majewski et al., 2013; Xu et al., 2015)*. Principal component analysis, are based on the idea that the time dependence of a chemical species at the receptor site will be similar to that of other species from the same source *(Chueinta et al. 2000)*.

A Common and simple method for tracing the Origin of the observed aerosols is the calculation of back trajectories using Langranian trajectory models. With this method, a few trajectories directed backwards in time are started from the monitoring location and evaluated a few hours or days back in time. The resulting trajectories roughly show the direction from where the air masses arrived at the observation site during the observation time period. For many years trajectories have frequently been used for the interpretation of individual flow situations. However more recently statistical methods for large sets of trajectories have been developed and implemented. Over the last several decades trajectory statistical analysis methods have been used to examine transport patterns and dynamical processes of the air masses *(Stohl, 1998; Dvorska et al., 2009)*. It has been demonstrated that clusters of back trajectories arriving at a specific location can serve as a surrogate of different synoptic circulation patterns, hence many researchers have applied cluster analysis techniques to categorize back trajectories *(Moody and Galloway, 1988; Dorling et al., 1992; Jorba et al., 2004; Markou and Kassomenos, 2010)*. These statistical clustering techniques have also been used to identify synoptic weather regimes and long range transport patterns that affect air pollution *(Cape et al., 2000; Salvador et al., 2007; Kassomenos et al., 2010).*

Hybrid receptor modeling, such as potential source contribution function (PSCF) model and concentration weighted trajectory (CWT) method, has been used successfully for potential source region identification for Particulate matters and other pollutants *(Xu et al., 2010). Hsu et al., (2003)* employed three different trajectory methods – the Potential Source Contribution Function (PSCF), Concentration Weighted Trajectory (CWT) and Residence Time Weighted Concentrations (RTWC) – to hunt for sources of PCBs to the air of Chicago, USA, and found that while results were partly consistent, no one model produced as complete information as the three together. CWT was chosen by Hafner and Hites to search for sources of a host of SVOCs to the Great Lakes basin, and they found that while pesticides had identifiable source regions and showed long-range transport, PAHs had much less distinct sources *(Hafner et al., 2003)*. Hoh and Hites used PSCF to pinpoint cotton farming regions as the chief sources of the pesticides they measured at three sites in a north-south transect in the United States (*Hoh et al., 2004)*. Dvorská et al. used CWT with HYSPLIT trajectories and found that sources of industrial pollutants were differentiable from sources of agricultural chemicals in Kosetice, Czech Republic (*Dvorska et al., 2008)*. Sofowote and his coworkers applied PSCF to measurements of PAHs and found clues that some PAHs in Northern Canadian air can be traced to forest fires in California and others to oil exploration throughout the Northern Hemisphere *(Sofowote et al., 2011). Ubl et al., (2012)* applied a hybrid receptor type approach to week-long measurements collected at three Arctic stations to search for sources of PCBs.

2.4 HEALTH EFFECTS OF BIOMASS BURNING SMOKE

Burning of crop residue is not a recommended practice to manage crop stubble. Burning may appear like an easy method of discarding crop residue, but it is in fact expensive and detrimental Fine particulate matter i.e. $PM_{2.5}$ is the most important air pollutant which shows various health symptoms and problems. Toxic air pollutants emitted during crop residue burnings can travel long range distances and therefore affect the distant regions. Hence air quality of the particular region deteriorates, resulting in irritation of the airway tract, burning and itching of throat and nose *(Prasad, 2008)*. Biomass burning smoke emits aerosol particles which have potentially detrimental impacts on human health from both acute and chronic exposures. Exposure to biomass burning smoke results in the depression of immune system, reduction in lung function and increasing the risk of respiratory diseases *(Long et al., 1998; Sutherland and Martin, 2003; Sutherland, 2004)*. Even smoke from stubble burning can lead to irritation in the nose, eyes and throats of healthy adults; it can prove worse for the elderly, small children, and people with lung problems like chronic obstructive pulmonary disease (COPD) or asthma *(Romieu et al., 1996; Peters et al., 1997)*. The reason behind this is that the visible smoke from biomass burning constitutes of completely minute particles that can get deep into lungs and cause problems like wheezing, coughing, shortness of breath and chest pain. Crop residue burning causes problems in many ways. 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. Smoke emitted from crop residue open burning, in an extreme case had drastically reduced the visibility resulting in the closing of an airport and highways temporarily. Study conducted in Brazil has shown the harmful impacts on the health of the population due to sugarcane burning emissions. Increased levels of fine particulate matter were associated with the child and elderly respiratory hospitals admissions. *(Cancado et al., 2006)*. Various respiratory diseases such as asthama, emphysema, bronchitis etc., as well as eye irritation are result of air pollution, resulting in decrease in productivity at work and increasing individuals' diseases mitigation expenses. While it is known that many of the components of agricultural smoke may cause health problems under certain conditions *(Long et al. 1998)*, to date most studies valuing the health impacts of air pollution remain confined to urban areas as air pollution is considered mainly an urban problem in developing countries. Various studies have been reported developed valuing the harmful health impacts of air pollution in developed countries *(eg., Gerking and Linda1986, Schwartz, 1993, Pope et al. 1995 etc)*. Similarly various studies are available from India and various other developing countries *(eg., Cropper et al. 1997, Kumar and Rao 2001, Gupta 2008, Alberini and Krupnick 2000)*. These studies have used either damage functions, household health production models, or cost of illness approaches to calculate approximately the economic value of health damages resulting from ambient air pollution. *Cropper et al (1997)* found that there was 2.3 percent increase in trauma deaths due to100 $\mu g/m^3$ increase in total suspended particulate matter (TSPM) in New Delhi by using a dose-response model. *Jayaratne and Verma (2001)* studied the visibility impact (aerosol concentration) from biomass burning in Gaborone, Botswana in South Africa. The visibility in this city dropped to less than a kilometer at times during the winter, due to particles from biomass burning. This problem was enhanced when inversion impeded pollutant dispersion. Open burning emissions are disturbing from a public health viewpoint because they are usually released near ground level instead of tall stacks which facilitate dispersion and also because they are non-point sources, therefore, regulatory approaches such as flue gas cleaning devices, cannot be applied to these sources. Crop residue burning remains a hot issue due to the ensuing air pollution and threats to human health. Alternatives to open burning have long been investigated and debated.

2.5 RESEARCH GAPS

Studies suggest that crop residue burning is a potential source of air pollutants such as suspended particulate matter, gases like CO_2, CO, CH_4 , NO_x, SO_x, Volatile Organic Compounds and Poly Aromatic Hydrocarbons(PAH) etc. From the detailed literature review, the following lacunae have been observed.

1) Few reports highlight the monitoring of air pollution during the stubble burning episode in India but still study is incomplete as well as partial in comparison to global scenario.
2) Studies on simultaneous monitoring of particulate matter in different cities at a given time frame are missing.
3) Few scattered reports exist on the characterization of particulate matter arising from stubble burning episodes, so detailed investigations are required in this direction.
4) Limited studies have been reported on the quantification of emission factors of various ions.
5) Use of backward trajectory model to locate the source areas in Patiala has not been reported so far.
6) Study on source apportionment of $PM_{2.5}$ of Patiala is missing.

2.6 OBJECTIVES

The objectives of this project are as follows:

1. Monitoring of particulate matter ($PM_{2.5}$) during crop residue burning episodes at selected sites
2. Characterization of particulate matter ($PM_{2.5}$) of Patiala , Agricultural site in Punjab and Delhi
3. Use of backward trajectory model to identify the source areas contributing to $P_{M2.5}$ concentration in the monitored areas
4. Source apportionment studies of Delhi and Patiala during crop burning episodes

CHAPTER 3

AIR QUALITY MODELING

Air quality modeling is a mathematical tool used to predict and simulate the distribution and the behavior of air pollutants emitted to the atmosphere. It describes the causal relationship between emissions, meteorology, atmospheric concentrations, deposition, and other factors. Air pollution measurements give important, quantitative information about ambient concentrations and deposition, but they can only describe air quality at specific locations and times, without giving clear guidance on the identification of the causes of the air quality problem. Air pollution modeling, instead, can give a more complete deterministic description of the air quality problem, including an analysis of factors and causes (emission sources, meteorological processes, and physical and chemical changes), and some guidance on the implementation of mitigation measures. Air pollution cannot be measured in every point for particular area because it requires a lot of money and time. Therefore, by the help of air pollution models, one can for example determine the suitable points for making pollution measurements. Air pollution models play an important role in science because of their capability to assess the relative importance of the relevant processes. Air pollution models are the only method that quantifies the deterministic relationship between emissions and concentrations/depositions, including the consequences of past and future scenarios and the determination of the effectiveness of abatement strategies. This makes air pollution models indispensable in regulatory, research, and forensic applications.

3.1 AIR QUALITY MODELING

The purpose of these air pollution models is to quantitatively combine the effects of source strength and meteorology to describe the resulting ambient air pollution concentration. Source strength is affected by a number of variables including the size of the source, variable emission rates, and the efficiency of air pollution control equipment employed. Meteorology is affected by wind speed and direction, atmospheric stability, inversion height, and terrain features. Ambient air pollution concentrations occurring downwind of a source consist of two components: pollution contributed directly by the source and the background pollution. Useful mathematical model must be able to account for all these parameters *(Miller and Noll, 1976).*

Most modern air pollution models are computer programs that calculate the pollutant concentration downwind of a source using information on the:

- contaminant emission rate
- characteristics of the emission source
- local topography
- meteorology of the area
- ambient or background concentrations of pollutant

A generic overview of how this information is used in a computer-based air pollution model is shown in Figure 3.1.

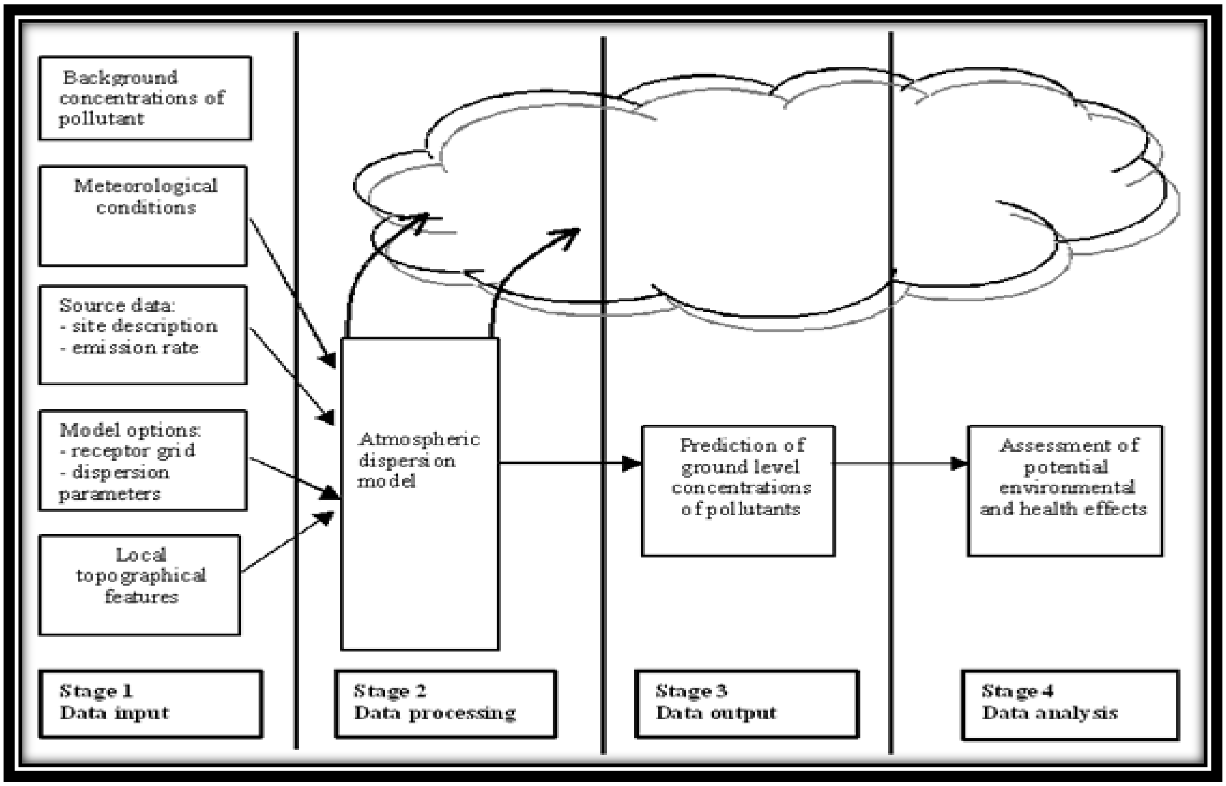


Fig.3.1: Overview of the air pollution modeling procedure

(Ministry of Environment of New Zealand, 2004)

3.2 CLASSIFICATION OF MODELS

In general, air quality models can be categorized as one of two types: steady state and non-steady state models. The movement of mass away from the source (i.e., advection) and turbulent diffusion (e.g., dispersion) are modeled in both types of models.

Steady-state models are models which assume no time-varying processes occur over the period of interest. Hence, material released travels infinitely in only one direction over the time period (e.g., one hour). Often, these models assume that the material is distributed normally (also termed a “Gaussian distribution”) and are thus called “Gaussian plume” models. The steady-state model typically uses meteorological information obtained near the source and assumes it holds true throughout the modelling region (e.g., 50 kilometre radius). This type of model is most widely used for stationary sources and for non-reactive pollutants (although models can take into account deposition and simple linear decay). Examples of steady models are Screen 3, Industrial Source Complex Short Term Version 3 (ISCST3), American Meteorological Society/Environmental Protection Agency Regulatory MODel (AERMOD) and CALINE3.

Non-steady state models are models which can simulate the effects of time- and space varying meteorological conditions on pollutant transport, transformation, and removal. These models are often used for chemically reactive pollutants or where there is complex topography or meteorology (e.g., complex sea breeze circulation). They require complex wind flow characterization and other detailed meteorological information for dispersion. For chemical transformation, they require information on the important chemical compounds as well as chemical kinetics to properly characterize the transformation and removal of air toxics. These models often take the form of grid models with the calculation of the physical and chemical processes taking place at each grid location. Other model types include “puff models”, which use a series of overlapping puffs to represent emissions. Examples of non steady models are CALPUFF, UAM-TOX.

Dispersion models are used to estimate or to predict the downwind concentration of air pollutants or toxins emitted from sources such as industrial plants, vehicular traffic or accidental chemical releases. It is based on source emission inventory and meteorological data validated by ambient data and can determine contributions of individual sources at any receptor in the airshed. Such models are important to governmental agencies tasked with protecting and managing the ambient air quality. The models are typically employed to determine whether existing or proposed new industrial facilities are or will be in compliance with the National Ambient Air

Quality Standards (NAAQS). The models also serve to assist in the design of effective control strategies to reduce emissions of harmful air pollutants.

Receptor models are source-apportionment models used to estimate the relative impact of specific types of sources at a designated location (i.e., a receptor). Chemical and physical characteristics of gases and particles that are measured at the source and receptor are used both to identify the presence and to quantify source contributions to receptor concentrations. The primary assumption of source-apportionment models is that each type of source is associated with a unique combination of pollutants (fingerprint for that source) that are measured in the ambient air. Examples include gasoline evaporation, diesel truck exhaust, tanker engine exhaust, and painting. In addition to the source fingerprints, monitoring results are used for one ambient monitoring location. Pollutants that are used in characterizing the sources must be measured in the ambient air. Two cautions apply to source-apportionment models. Firstly, speciated data are required for source apportionment modeling; measurements of total mass for particles or total hydrocarbons are insufficient. Secondly, the species used in characterizing the sources either should not participate in atmospheric chemistry or should have very long lifetimes in the atmosphere. Examples of source-apportionment models are Principal component analysis (PCA), Chemical Mass Balance model (CMB), Unmix, Positive Matrix Factorization (PMF).

3.3 OVERVIEW OF RECEPTOR MODELS

3.3.1 MULTIVARIATE MODELS

The goal of multivariate receptor modeling is to estimate the profiles of major pollution sources and quantify their impacts based on ambient measurements of pollutants. Traditionally, multivariate receptor modeling has been applied to multiple air pollutant data measured at a single monitoring site or measurements of a single pollutant collected at multiple monitoring sites. Various multivariate models are described below.

3.3.1.1 PRINCIPAL COMPONENTS ANALYSIS (PCA)

PCA is a data reduction method available in many statistical software packages. The large number of parameters observed at the receptor site are reduced to a smaller set of components or factors that explain as much of the variance in the dataset as possible *(Thurston and Spengler, 1985)*. This is based on the following mathematical model:

$$Z_{ij} = \sum_{k=1}^{p} S_{ik} L_{kj} \qquad (1)$$

Z_{ij} is the standardized observed concentration of the *j*th pollutant in the *i*th sample;
S_{ik} is the *k*th component score on the *i*th sample;
L_{kj} is the component loading for each pollutant;
k is the component;
p is the number of components which represent pollution sources.

The input variables in the dataset should have some correlations; however, the model components should be independent from each other. There are several statistics that have been determined to assess whether the dataset is suitable for PCA, such as Kaiser–Meyer–Olkin measure of sampling adequacy (> 0.5 criterion) and Bartlett's Test of Sphericity ($p < 0.05$ criterion). The number of components to retain is determined by other statistics, such as Kaiser's criterion (eigen values> 1), screen plot, analysis of variance, and/or parallel analysis, as well as achieving some minimal value of percent variance of the dataset explained by all the components (e.g. 70–80 %) and how easily the components can be interpreted *(Blanchard et al., 2002; Lynam and Keeler, 2006; Temme et al., 2007; Cheng et al., 2009)*. The number of components in a suitable solution to Eq. (1) should be less than the number of variables. Typically in PCA studies two to six components have been selected to explain the majority of the variance in the dataset. Varimax rotation is normally applied to the components in the final PCA solution so that they can be more easily interpreted *(Thurston and Spengler, 1985)*. The component loadings from PCA may be positive or negative; the sign is indicative of the association between the component and a particular parameter. Large component loadings between a component and an air pollutant marker indicate that the pollutant is a major component of that factor. Variables with component loadings greater than 0.3 or 0.5 are typically used to assign the model components to sources. The major advantage of PCA is that it is a model suitable for exploring a large dataset of environmental parameters and can gain insight about pollution sources. Although it is a statistical model, PCA has been applied in numerous air quality studies especially for the source apportionment of particulate matter; thus, it is based on well established principles, e.g. conservation of mass and mass balance analysis *(Hopke, 2003; Hopke et al., 2005)*. PCA can be readily accessed from commercial statistical software in which the detailed procedures of performing PCA are also widely available. Unlike source-based chemical transport models, PCA does not require detailed data on source emissions profiles, chemical reaction kinetics and physical processes, and meteorological forecasts *(Hopke, 2003)*.

3.3.1.2 POSITIVE MATRIX FACTORIZATION (PMF)

The PMF model is accessible from the USEPA website. The principle behind PMF is that every concentration is determined by source profiles and source contributions to every sample. The model equation is given by Eq. (2):

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad (2)$$

x_{ij} is the concentration of the j^{th} pollutant at the receptor site in the i^{th} sample;
g_{ik} is the contribution of the k^{th} factor on the i^{th} sample;
f_{kj} is the mass fraction of the j^{th} pollutant in the k^{th} factor;
p is the number of factors which represent pollution sources;
e_{ij} is the residual for each measurement or model error (difference between observed and modeled concentrations).

PMF has numerous applications in the source apportionment of particulate matter *(Lee and Hopke, 2006; Lee et al., 2008; Viana et al., 2008b; Tauler et al., 2009)* and volatile organic compounds *(Song et al., 2008)*. Similar to PCA, the PMF model is used when sources are unknown since it does not require the input of source profile data. However, knowledge of potential sources is necessary to interpret model results *(Watson et al., 2008)*. PMF is ideal for a dataset with a large number of samples e.g., > 100 *(Watson et al., 2008)*. The PMF model also requires a dataset of uncertainties corresponding to the receptor measurements or estimated from equations, which are used to assess the variables and/or samples that should be down-weighted or excluded from the model *(Reff et al., 2007; USEPA, 2014b)*. Other input requirements include the number of runs, starting seed, and number of factors to compute. The model determines the optimal non-negative factor contributions and factor profiles by minimizing an objective function, which is the sum of the square difference between the measured and modeled concentrations weighted by the concentration uncertainties *(Liu et al., 2003; Reff et al., 2007; Watson et al., 2008; USEPA, 2014b)*. In general, the strengths of the PMF model are similar to those of PCA described in the previous section. However, the major advantage of PMF over PCA is the inclusion of measurement uncertainties in the PMF model, which ensures measurements with large uncertainties have less influence on the model results.

3.3.2 BACK TRAJECTORY RECEPTOR MODELS

Back trajectory receptor models simulate the movement of air parcels from the receptor site, which represents the potential pathway for transporting air pollutants from sources to the receptor site. Back trajectories are often included in source apportionment studies to supplement the multivariate models previously described because the simulated airflows incorporate meteorological data *(Hopke and Cohen, 2011)*. The HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) model *(Draxler and Rolph, 2014)*, has often been used in source–receptor studies *(Han et al., 2004, 2005; Lynam and Keeler, 2005; Liu et al., 2007; Rutter et al., 2007; Abbott et al., 2008; Choi et al., 2008; Li et al., 2008; Lyman and Gustin, 2008; Sprovieri and Pirrone, 2008; Cheng et al., 2009; Peterson et al., 2009; Sigler et al., 2009; Kolker et al., 2010)*. The HYSPLIT model simulates the transport of an air parcel by wind and estimates the position of the parcel using velocity vectors that have been spatially and temporally interpolated onto a grid *(Han et al., 2005)*. The inputs to the HYSPLIT model include the number of trajectory start locations, type of trajectory, location of the receptor site, and meteorological data source *(Draxler and Rolph, 2014; Rolph, 2014)*. The model parameters selected by the user are the type of model to simulate vertical motion, starting time and height of the trajectories, total duration of the trajectories, and number of trajectories. The input data and model parameters for back trajectory simulations depend on the sampling location and the back trajectory receptor model selected as discussed below. The output from back trajectory models includes the hourly locations of the trajectory segment endpoints, altitude, and other meteorological variables along the trajectory.

3.3.2.1 POTENTIAL SOURCE CONTRIBUTION FUNCTION (PSCF)

PSCF is the probability that a source area contributes to elevated pollutant concentrations, as defined by a concentration threshold, at the receptor site. Airflows are simulated using back trajectory models. PSCF is mathematically expressed as the ratio of the total number of trajectory segment endpoints in a grid cell (i,j) that is above a concentration threshold (m_{ij}) to the total number of trajectory segment endpoints in a grid cell (i,j) over the entire sampling period (n_{ij}) as shown in Eq. (3) *(Hopke, 2003;Watson et al., 2008)*. W_{ij} is a weighting function used to adjust for a small number of trajectory endpoints in grid cell (i,j). Grid cells are color-coded based on the PSCF value and are plotted on a map to highlight potential sources areas affecting the receptor measurements.

$$\mathrm{PSCF}_{ij} = (m_{ij}/n_{ij})W_{ij} \tag{3}$$

The advantage of PSCF over the multivariate receptor models is that it provides the spatial distribution of potential source areas contributing to the receptor site. In contrast, multivariate models infer potential types of sources, but do not provide information about where the sources are located. PSCF also do not require ancillary pollutant measurements. The disadvantages with PSCF are related to back trajectory modeling. In the PSCF studies for the back trajectory models oversimplified the source–receptor relationship because they did not account for chemical reactions, gas-particle partitioning processes, and deposition. There are also uncertainties with the distance travelled by single back trajectories *(Stohl, 1998; Watson et al., 2008)*.

3.3.2.2 GRIDDED FREQUENCY DISTRIBUTIONS (GFD)

GFD is another back trajectory receptor model which involves calculating the average number of trajectory segment endpoints in each grid cell based on an ensemble of trajectories generated using the HYSPLIT model. The average number of trajectory points in all the grid cells is plotted on a map to show the spatial distribution of the average trajectory residence time. The trajectory ensemble consists of multiple trajectory starting locations and heights. The advantage of GFD over other back trajectory models is the use of multiple trajectory starting locations and starting heights. Ensemble trajectories illustrate the variability in the pollutant transport pathways, which indicates how uncertain a single trajectory can be *(Stohl, 1998; Hegarty et al., 2009; Sexauer Gustin et al., 2012)*. Some of the disadvantages of PSCF also apply to GFD. In the GFD the back trajectory models do not account for chemical reactions, gas-particle partitioning, and deposition.

3.3.2.3 CONCENTRATION-WEIGHTED TRAJECTORY (CWT)

CWT is also common back trajectory receptor model and the most apparent difference between CWT and previously described back trajectory receptor models is that the trajectory residence time in the grid cells have been weighted by the observed pollutant concentrations corresponding to the arrival of each trajectory. CWT can be summarized by Eq. (4) *(Kabashnikov et al., 2011)*:

$$P_{ij} = \sum_{l=1}^{L} C_l T_{ijl} \;/\; \sum_{l=1}^{L} T_{ijl} \qquad (4)$$

P_{ij} represents the source intensity of a grid cell (i,j) contributing to the receptor location;

C_l is the pollutant concentration corresponding to the arrival of back trajectory l;

$T_{i\,j\,l}$ is the number of trajectory segment endpoints in grid cell (i,j) for back trajectory l divided by the total number of trajectory segment endpoints for back trajectory l (i.e., residence time of a trajectory in each grid cell);

L is the total number of back trajectories over a time period (e.g., entire sampling period or a season) *(Cheng et al., 2013b)*.

As shown in the model equation, higher pollutant concentrations would lead to higher source intensity if the trajectory residence time were the same. The advantage of CWT over PSCF and GFD described in previous sections is the integration of the receptor concentrations in the back trajectory model as evident in Eq. (4). This is important because the observed concentrations account for the various physical and chemical processes as an air pollutant is transported from sources to the receptor site *(Jeong et al., 2011)*. Another advantage of CWT is that the source intensity of the grid cells is normalized by the trajectory residence time, which reduces the bias due to increasing trajectory residence time near the receptor location.

CHAPTER 4

MATERIALS & METHODOLOGY

Air pollution monitoring studies need to be designed to accomplish specific objectives i.e. 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 this chapter, materials and methods used in this study are described in details, including instruments, selection of sampling sites, procedures used for sampling as well as characterization of particulate matter and statistical method used for source apportionment.

4.1 SELECTION OF STUDY AREA AND SAMPLING SITES

Patiala was chosen for monitoring because there are limited industries in the vicinity of the city and hence, there are few point sources of air pollution in the city. However, there is a main 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. Patiala is located in the southeastern part of the Punjab state of India. The region around Patiala city is largely agricultural (rural) with rice (paddy) and wheat as the two most important 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). Therefore, one agricultural site village Kherijattan (10 km form Patiala) was chosen. The climate here in Patiala is representative of the Punjab plain, i.e., very hot in summer (average maximum temperature 43±2° C) and very cold in winter (average minimum temperature 2±2°C). For most of the time period, wind direction of Patiala is North-West (NW). Other land stations were chosen on the basis of air mass forward and backward trajectory analysis of Patiala using HYsplit_4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) model conducted for the months of October and November for 2013 and 2014 in order to get an idea about the potential sources contributing to aerosol loading. Other than

Patiala, few other sites in northern India were chosen for monitoring which include Chandigarh, Amritsar, Delhi, Nainital and Kullu. Specifications of all the monitoring sites are given in Table 4.1.

Table 4.1: Specifications of all monitoring sites

S.No	City	Site Name	Lat/Long
A	Delhi	National Physical Laboratory (NPL), New Delhi	28°38'12.94" N,77°10'19.69" E
B	Patiala	Village Kherijattan, Patiala, Punjab	30°28'06.62" N,76°17'04.01" E
		Thapar university (TU),Patiala	30°21'05.42" N,76°21'57.93" E
C	Chandigarh	School of Public Health, PGIMER, Chandigarh	30°21'05.42" N,76°21'57.93" E
		CHC Khera Institute, Chandigarh	30°43'45.53" N,76°46'21.44" E
		Centre for Public Health, Panjab University, Chandigarh	30°45'25.86" N,76°46'05.82" E
D	Amritsar	Guru Nanak Dev University (GNDU), Amritsar	31°38'08.73" N,74°49'32.12" E
E	Nainital	Aryabhatta Research Institute of Observational Sciences (ARIES), Nainital	29°21'32.79" N,79°27'32.10" E
F	Kullu	G.B. Pant Institute of Himalayan Environment, Kullu	30°54'54.22" N,77°07'27.93" E

Table 4.2: List of equipments used at various places

S.No	Location	PM_{10}	Make/Model	$PM_{2.5}$	Make/model
1	Delhi	APM550	Envirotech	APM550	Envirotech
2	Patiala			IPM-FDS 2510, IPM-FDS 2.5u/10u	Instrumex
3	Chandigarh			APM550	Ecotech
4	Amritsar			APM550	Envirotech
5	Nainital	APM550	Envirotech		
6	Kullu			APM550	Envirotech

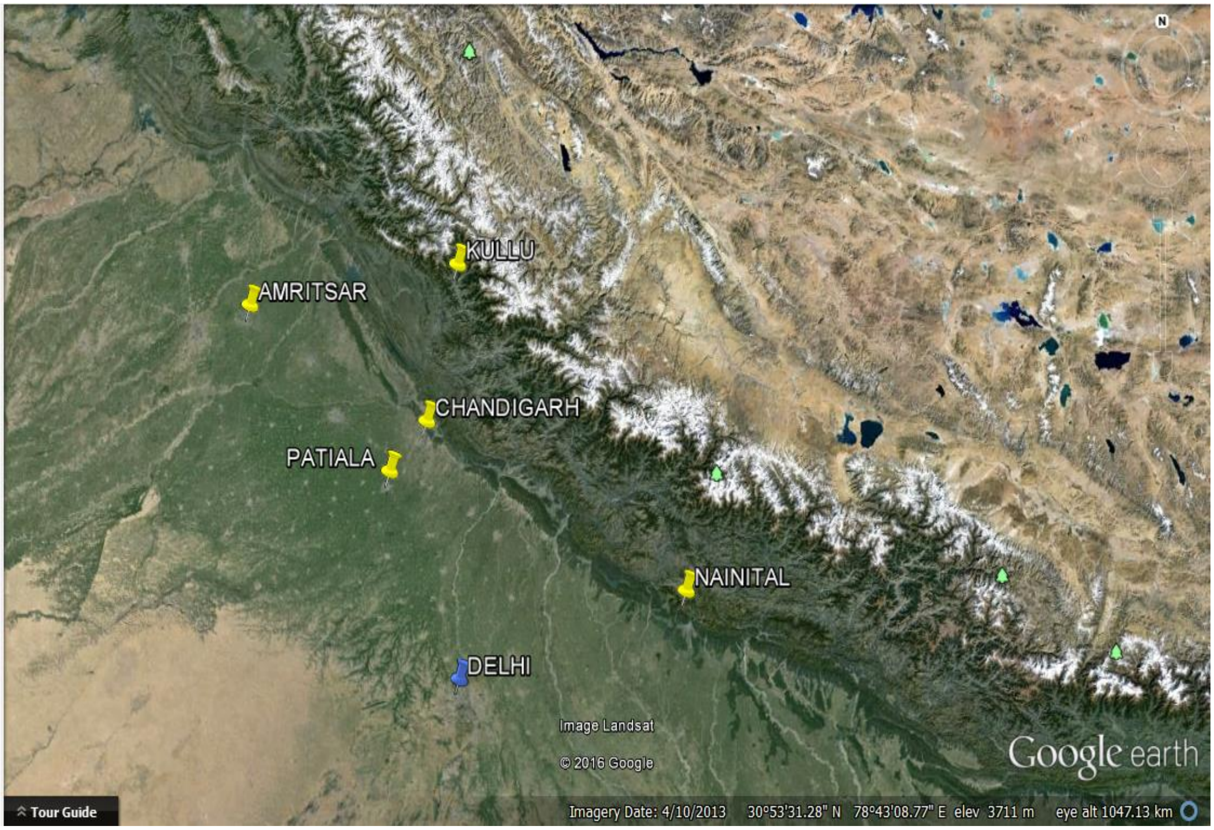


Fig.4.1: Location map of all the sites

(Downloaded from Google Earth software)

4.2 INSTRUMENTS

Various instruments were used in the study for monitoring as well as characterization of samples. Simultaneous monitoring of $PM_{2.5}$ was done at three different sites. Therefore at the same time three samplers were running at three sites. Instruments used in the study are described below.

4.2.1 Automated Weather Monitoring Station (AWS)

The weather monitoring station used in this study was Watch Dog of Spectrum Series 2000. The Watch Dog weather station is a multifunction device which allows detecting as well as store seven parameters including wind speed, wind direction, temperature, relative humidity, dew point, pressure and solar radiations using different sensor for each. The Watch Dog weather station is used in agriculture and gardening as well as in industry, and in the research sector. Its measurement ranges are wind speed: 0 to 281 Km/hr; wind direction: 0 to 360^0; air temperature: -20 to $+70^0$; air humidity: 20 to 100% and rainfall: 6.5cm measurement period. Weather monitoring station must be installed at site where there is no obstruction in path of wind so that correct data can be collected. It consist of lightweight three cup type anemometer for measuring wind speed ranging from 0 to 150 mph and wind vane for the determination of wind direction. Interval for the data collection can be chosen between 1 to 60 minutes. Data logger allows storage of data for 6 months at a time and the stored data can be transferred to computer using data cable.

Fig. 4.2: Weather monitoring station

4.2.2 Dual channel dust sampler (IPM-FDS 2510)

Dual Channel enables measurement of PM_{10} & $PM_{2.5}$ simultaneously without deviating from USEPA and CPCB norms. This model is designed for the measurement of mass concentration of particulate matter having aerodynamic diameter less than or equal to nominal 2.5 micrometer ($PM_{2.5}$) and also particulate matter of size of size 10 microns at the same time. The instrument has been specifically designed to meet or exceed the operational requirements EPA designated reference method for the determination of particulate matter. The IPM-FDS 2510 Dual channel dust sampler uses two inlet channels each standardized and documented by USEPA to separate dust particles of PM10 & PM2.5 from the air stream. The system comprises of an omni directional air inlet, impactor for particles larger than 10 microns and a $PM_{2.5}$ impactor separated by a length of the tube. The system has all provisions specified by UESPA for measurement control recording of the following parameters:

1. Actual volumetric flow rate :- Measured by flow sensor
2. Flow rate :- Maintained constant at 16.67 LPM $\underline{+}$ 5% ($1m^3/hr$)
3. Volume of sampled air :- In m^3
4. Ambient barometric pressure and temperature :- Average, Minimum & Maximum
5. Filter temperature :- Average, Minimum & Maximum
6. Filter and ambient temperature difference :- >5^{o}C maintained by fans

Fig. 4.3: Instrumex Dual channel dust sampler

4.2.3 Fine dust sampler (IPM-FDS 2.5u/10u)

This model is designed for the measurement of mass concentration of particulate matter having aerodynamic diameter less than or equal to nominal 2.5 micrometer ($PM_{2.5}$). The instrument has been specifically designed to meet or exceed the operational requirements EPA designated reference method for the determination of particulate matter. Ambient fine dust sampler has single inlet which can monitor either PM2.5 or PM10 but not at the same time. The system has all provisions specified by UESPA for measurement control recording of the following parameters:

1. Actual volumetric flow rate :- Measured by flow sensor
2. Flow rate :- Maintained constant at 16.67 LPM ± 5% ($1m^3$/hr)
3. Volume of sampled air :- In m^3
4. Ambient barometric pressure and temperature :- Average, Minimum & Maximum
5. Filter temperature :- Average, Minimum & Maximum
6. Filter and ambient temperature difference :- >5°C maintained by fans

Fig. 4.4: Instrumex Ambient fine dust sampler

4.2.4 Ion Chromatograph (DIONEX-ICS-3000)

An Ion chromatograph (DIONEX-ICS-3000, USA) with an IonPac-AS11-HC analytical column (4*250mm), a guard column (IonPac AG11-HC, 4*50 mm), ASRS-300 4 mm anion micro-membrane suppressor, 20 mM NaOH (50% w/w) eluent and triple distilled water as regenerator was used for the determination of concentration of anions viz. F^-, Cl^-, SO_4^{-2},NO_3^-,PO_4^{-2},NO_2^- and Br^-. Cations viz. Na^+,NH_4^+,K^+,Ca^{+2} and Mg^{+2} concentrations were estimated utilizing a seperation column (IonPac CS17-HC, 4*250 mm) along with a guard column (IonPac CG-HC, 4*50 mm), suppressor CSRS-300 (4mm, Dionex) and 5 mM eluent. The ICS-3000 system is controlled by a PC configured with Chromeleon Chromatography Management System (version 6.7 or later). The Chromeleon Chromatography Management System provides complete instrument control, data acquisition, and data management.

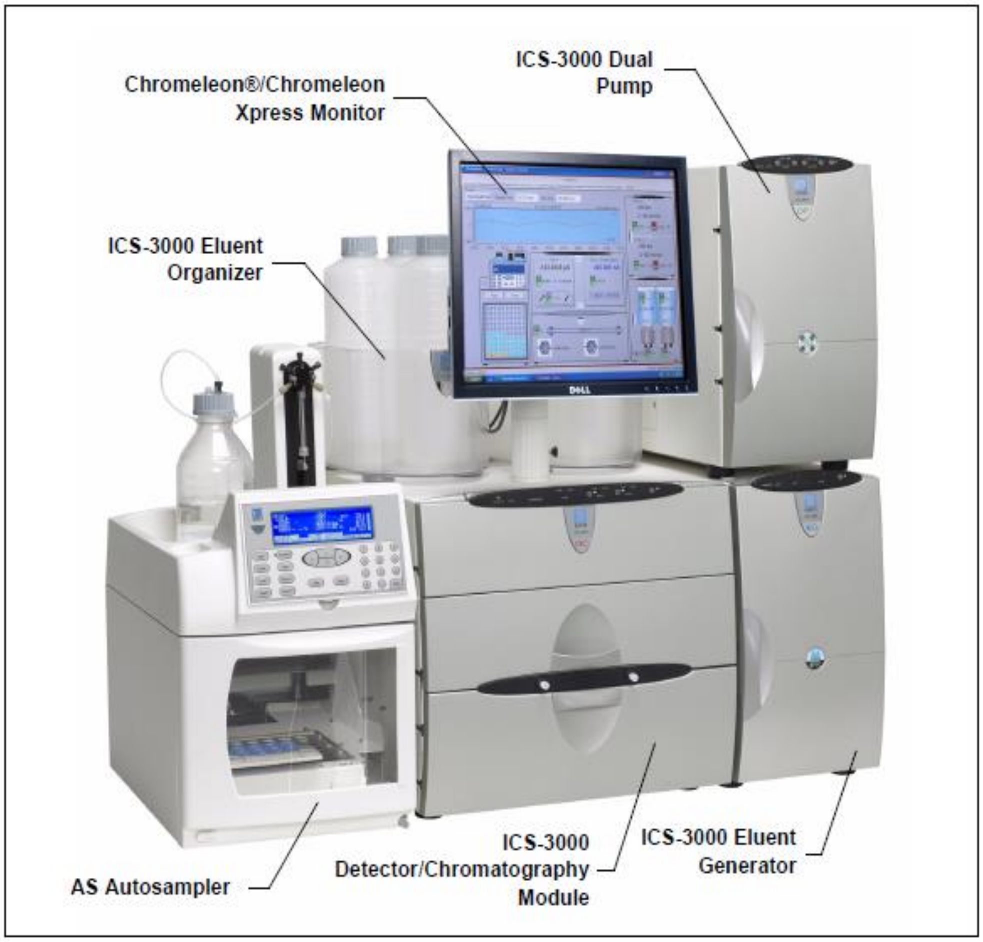


Fig. 4.5: An ion chromatograph, DIONEX-ICS-3000, USA

4.3 MATERIALS

Chemicals used for the characterization of filters were Deionized water and 50mM NaOH. For $PM_{2.5}$ monitoring filters were used, specifications of which are described below.

Filters: Quartz filter papers of 47 mm diameter of Whattman brand (Catalog number - 1820-047) were used. The specifications of filters are as follows:

a. Size: circular, 46.2 mm diameter. Medium polytetrafluoroethylene (PTFE Teflon)
b. Pore size: 2 um
c. Filter thickness: 30 to 50 um
d. Maximum pressure drop (clean filter): 30 cm H_2O column @ 16.67 LPM clean air flow
e. Collection efficiency: greater than 99.7%
f. Alkalinity: less than 25 microequivalents/gram of filter

For Total Suspended Particulate matter Quartz filter papers of 10.6 cm diameter of Whattman brand were used.

4.4 MODELS

For the simulation of trajectories and to perform cluster analysis and concentration weighted trajectories to identify the source areas contributing to $PM_{2.5}$ concentrations in selected sampling sites following air models were used. Also for the source apportionment studies PCA was used. So the air models used in the study are explained below.

4.4.1 HYsplit_4

The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) Model is a trajectory modeling tool available through NOAA Air Resources Laboratory (ARL; http://ready.arl.noaa.gov/HYSPLIT.php) that has been utilized in both operational and research applications to enhance understanding of atmospheric chemical transport, dispersion, and deposition. The HYSPLIT dispersion model has been applied towards more accurate forecasting of dust, wild fire smoke, hazardous materials, and volcanic ash emissions and transport (NOAA ARL, 2012). Additionally, the HYSPLIT trajectory model can be run both forward and backward in time, useful for source-receptor applications. Calculations in HYSPLIT are based on a hybrid combination of Eulerian and Lagrangian frameworks *(Draxler et al., 1998)*. Eulerian models focus on a specific location in space and calculate both advection and diffusion on a fixed spatial grid while Lagrangian models are applied to an air parcel moving through space, therefore calculating advection and diffusion separately. HYSPLIT utilizes the Lagrangian method for calculating advection and diffusion while chemical concentrations are calculated using a Eulerian fixed grid *(Draxler et al., 1998)*. For this study, HYSPLIT was used only for particle trajectory calculations without application of the dispersion or diffusion models. The HYSPLIT model can be run using a variety of available model meteorology datasets that have been processed into the format required by the model. The most basic meteorological inputs required to operate HYSPLIT include U and V wind components, temperature, height or pressure, and surface pressure. Vertical velocity in HYSPLIT can be assumed to be isobaric, isosigma, isopycnic, or isentropic *(Draxler et al., 1998)*. For this study, meteorological model isentropic velocity was selected to calculate trajectory motion.

4.4.2 TrajStat —Trajectory Statistics

It was developed by Yaqiang Wang and is freely available at http://www.arl.noaa.gov/ready/hysplit4.html. For air mass trajectory visualization and statistical analysis applications, a new software application called TrajStat was developed in which a geographic information systems (GIS) technique was used for spatial data management, visualization and analyses. In TrajStat, the trajectory calculation function comes from the Hybrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT) *(Draxler and Hess, 1998)*. The trajectory model, although included with the TrajStat distribution and integrated into the GIS, is an external process to the TrajStat software. Monthly trajectories could be calculated in TrajStat, and the trajectories could be converted to GIS (Geographic Information System) line shape file. Cluster analysis function is in the software. Measurement data could be added to the corresponding trajectories, so the trajectories could be selected according to the measurement data. The software also could do PSCF (Potential Source Contribution Function) and CWT (Concentration Weighted Trajectory) analysis which is useful to identify pollution sources spatially for long-term environment measurement.

4.4.3 Principal Component Analysis

PCA is a data reduction method available in many statistical software packages. The large number of parameters observed at the receptor site are reduced to a smaller set of components or factors that explain as much of the variance in the dataset as possible *(Thurston and Spengler, 1985)*. This is based on the following mathematical model:

$$Z_{ij} = \sum_{k=1}^{p} S_{ik} L_{kj} \qquad (1)$$

Z_{ij} is the standardized observed concentration of the *j*th pollutant in the *i*th sample;

S_{ik} is the *k*th component score on the *i*th sample;

L_{kj} is the component loading for each pollutant;

k is the component;

p is the number of components which represent pollution sources.

The input variables in the dataset should have some correlations; however, the model components should be independent from each other. There are several statistics that have been determined to assess whether the dataset is suitable for PCA, such as Kaiser–Meyer–Olkin measure of sampling adequacy (> 0.5 criterion) and Bartlett's Test of Sphericity ($p < 0.05$ criterion). The number of components to retain is determined by other statistics, such as Kaiser's criterion (eigen values> 1), screen plot, analysis of variance, and/or parallel analysis, as well as achieving some minimal value of percent variance of the dataset explained by all the components (e.g. 70–80 %) and how easily the components can be interpreted *(Blanchard et al., 2002; Lynam and Keeler, 2006; Temme et al., 2007; Cheng et al., 2009)*. The number of components in a suitable solution to Eq. (1) should be less than the number of variables. The component loadings from PCA may be positive or negative; the sign is indicative of the association between the component and a particular parameter. Large component loadings between a component and an air pollutant marker indicate that the pollutant is a major component of that factor. Variables with component loadings greater than 0.3 or 0.5 are typically used to assign the model components to sources.

Seinfeld and Pandis (1998) have listed several assumptions on application of PCA to source apportionment purposes: 1) the composition of emission sources is constant, 2) chemical species used in PCA do not interact with each other and their concentrations are linearly additive, 3) measurements errors are random and uncorrelated, 4) the variability of the concentrations is dominated by changes in source contributions, 5) the effect of processes that affect all sources equally (e.g. atmospheric dispersion) is much smaller than the effect of processes that influence individual sources (e.g., wind direction), 6) there are many more samples than source types, and 7) the extracted factors and rotations are physically meaningful.

The major advantage of PCA is that it is a model suitable for exploring a large dataset of environmental parameters and can gain insight about pollution sources. PCA can be readily accessed from commercial statistical software in which the detailed procedures of performing PCA are also widely available. Unlike source-based chemical transport models, PCA does not require detailed data on source emissions profiles, chemical reaction kinetics and physical processes, and meteorological forecasts *(Hopke, 2003)*. Therefore, PCA was the best suited model to apportion sources.

PCA was applied using IBM-SPSS Statistics software. It is the licensed software and the software and license key was provided by NPL, Delhi. Varimax orthogonal rotation was performed in a manner described by *Harmon (1976)* to make physical interpretation of the principal components easier *(Thurston, 1981)*. Since the originally extracted factors are often difficult to interpret, the factors are usually transformed by a specific procedure called factor rotation and the most commonly used method is known as varimax rotation, which results in orthogonal factors that are virtually uncorrelated with each other and often easier to interpret than the original factors *(Afifi and Clark 1984)*. The criteria used in selecting the optimal models: in terms of source identification (PCA), we required identification of major sources with physically reasonable principal components whose eigen values were larger than 1 after varimax rotation.

4.5 METHODOLOGY

The study was carried out in various steps. Monitoring was done at all the sites. After that characterization of sampled filter papers was done at NPL, Delhi. Also IBM SPSS Statistics software and Trajstat software were installed in PC for further source apportionment studies. Detailed methodology of the study is described below.

4.5.1 Meteorological Parameters

Since impact of crop residue burning had to be monitored therefore, wind direction and wind speed along with various other meteorological parameters like temperature, relative humidity, atmospheric pressure and rainfall were monitored during the sampling periods. Meteorological data of the area were collected from Watch-Dog Weather monitoring station installed at Thapar University, Patiala as well as all other sites. The data is valid for nearly 30 kms area. Other relevant data was collected from Indian Meteorological Department (IMD).

4.5.2 Total Suspended Particulate Matter (TSP)

Total suspended particulate matter was measured at three different agricultural sites with handy dust sampler provided by NPL, Delhi. Various sites which were measured for TSP included Village Rakhra (30^{o}21’17.09”N, 76^{o}17’52.40”E), Village Bishanpur (30^{o}32’84.38”N, 76^{o}30’19.98”E) and Sirhind road (30^{o}26’10.88”N, 76^{o}24’18.62”E). Sampling was done for 2 hours duration at the peak time of crop residue burning. Flow rate of air sampled was kept 0.5 LPM. 100 mm Whattman filter papers were used to calculate particulate matter. Weight of TSPM was estimated gravimetrically for the determination of concentration of aerosols in the ambient air. TSP were calculated as:

$$\mathrm{TSP} = \frac{(W_f - W_i) * 10^3}{V_a}$$

Where,

TSP= Total mass concentration of TSPM collected during sample period (mg/m^3)

W_f= Final mass of equilibrated filter used to collect TSPM Particle sample, g

W_i= Initial mass of equilibrated filter used to collect TSPM Particle sample, g

10^3= Units conversion (mg/g)

V_a= Total air volume sampled (m^3)

4.5.3 Particulate Matter (less than 2.5 microns) ($PM_{2.5}$)

Procedure followed for monitoring of $PM_{2.5}$ is as follows:

1. Instruments were installed in the selected fields at a height of 10m from the ground. The instrument case houses the WINS Impactor and the filter holder along with the vacuum pump and control module.
2. The WINS Impactor assembly was opened and a fresh 37 mm diameter filter was placed in the well after pouring 1 ml of silicone oil using a dropper.
3. Cover of the well was replaced and the unit was placed in WINS impactor base unit. Screwed on the cover unit of the Wins impactor.
4. The filter holder that follows wins impactor was opened and the presence of filter cassette with metal wire mesh inside it was confirmed.
5. Two sections of the filter cassette were opened by pulling them apart and the PTFE 46.2 mm filter paper was placed on it and snapped it into the filter cassette. Filter holder was covered and the entire assembly was tightened.
6. Test duration for 24 hours was set and the sampler was run for $PM_{2.5}$ sampling.

$PM_{2.5}$ samples (particles of less than 2.5 μm size) were collected for 24 hours on pre-weighed Whattman Quartz Filters at an average air flow rate of 16.67 LPM. Weight of $PM_{2.5}$ was estimated gravimetrically for the determination of concentration of aerosols in the ambient air. Before and after the sampling, each blank unexposed filter paper and exposed sampled filter paper 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 paper was removed from the sampler, placed in a filter cassette and carried into the laboratory for conditioning and weighing. Silica gel was used as a conditioning agent in dessiccator and electronic balance was used for pre- and post- weighings. Alternate day 24 hours of sampling was done consecutively during the stubble burning period from October 9, 2015 to November 30, 2015 (Rice harvesting period) at all the selected sampling locations. The $PM_{2.5}$ Concentration was calculated using the below formula.

$$PM_{2.5} = \frac{(W_f - W_i) * 10^3}{V_a}$$

Where,

$PM_{2.5}$= Total mass concentration of PM2.5 collected during sample period (ug/m^3)
W_f= Final mass of equilibrated filter used to collect PM2.5 Particle sample, mg
W_i= Initial mass of equilibrated filter used to collect PM2.5 Particle sample, mg
10^3= Units conversion (ug/mg)
V_a= Total air volume sampled (m^3)

4.5.4 Concentration Weighted Trajectory (CWT) Analysis

Back air trajectory calculations were done by using HYSPLIT model. To observe the role of long range transport, 5-day isentropic airmass back trajectories arriving at all the sites were plotted at 500m above ground level. HYSPLIT trajectories were combined with particulate matter composition observed at all the sites by matching trajectory arrival time at the receptor with the sampling time using the method of concentration weighted trajectories (CWT). This technique is especially useful for identifying sources of varying magnitudes which contribute to an observed species at a receptor site because regions which likely served as sources during high concentration events are given more weight than those regions which likely served as sources during low concentration events. Cluster analysis as well as cluster statistics for all the sites were also performed. Use of four clusters was attempted to provide the best representation of air mass classifications. Cluster statistics defined the mean and standard deviated values of $PM_{2.5}$ concentrations of four clusters. The transport distance at the regional scale or mesoscale is always within 1 to 2 km for approximately 4 to 5 days at the boundary layer. Thus, we chose a backward trajectory length of 120 h (5 days), and each trajectory consisted of 120 data pairs of latitude and longitude. 500 m as the receptor height was selected for the following reasons. First, $PM_{2.5}$ concentrations are often measured below the surface layer, typically at 500 m, and pollutants below this layer are well mixed. Second, both horizontal and vertical advections were considered when calculating the backward trajectories. Thus, air masses from higher or lower heights could reach the 500 m receptor height *(Bari et al., 2003; Zhu et al., 2011).*

4.5.5 Chemical Characterization

Quartz filters on which ambient air $PM_{2.5}$ samples were collected were analyzed for the determination of concentrations of ionic species (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}). Chemical characterization was done for three sites i.e. Village Kherijattan, Patiala; Thapar University, Patiala and National Physical Laboratory, New Delhi. TSP samples were also analyzed. Characterization of samples was done at National Physical Laboratory, New Delhi..

4.5.5.1 Extraction of Samples:

1. Sampled filter papers were cut in one fourth and further fourth part was cut into small pieces.
2. Those small pieces of filter papers were put in small conical flask.
3. 9 ml deionized water was added with glass pipette.
4. Flasks were covered with aluminium foil and kept in ultrasonicator for 45minutes to 1 hour.
5. After one hour samples were taken out and transferred to volumetric flask with the help of funnel.
6. Again 8 ml deionized water was put in the conical flask, covered with aluminium foil and kept in ultrasonicator for 45 minutes.
7. After ultrasonication samples were collected in volumetric flask and the above step was repeated.
8. Now 25 ml sample was collected in storage bottles and kept in refrigerator until it was analysed.

4.5.5.2 Ion Analysis Procedure

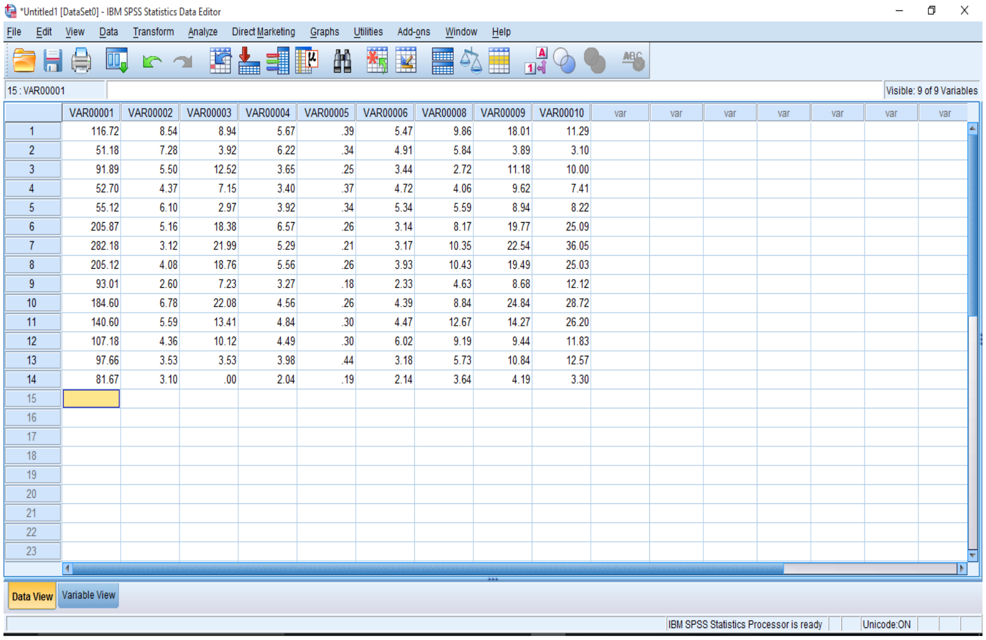
Extracted samples were filtered through 0.22 mm nylon membrane filters (millipore). After that samples were introduced manually using a 25ul sample loop fitted onto the IC. Data was collected at 5 Hz and the processing was carried out using Chromeleon software. *Leiva et al., (2012)* reported a 20% expanded uncertainty of the ion chromatograph in the determination of anion and cation concentrations. Separation was completed on Dionex carboPac PA-1 guard (4*50 mm) and analytical (4*250 mm) columns. The eluents are DI Water and 20 mM sodium hydroxide (NaOH). Each run had an eluent flow rate of 0.5 ml/min and took 25 minutes.

4.5.6 Source Apportionment using Principal Component Analysis

Source apportionment of particulate matter refers to the quantitative estimation of the contributions from different source categories to the concentrations of the measured PM in the atmosphere, based on chemical and physical characteristics of the particulate matter and temporal covariation of PM components. Principal Component Analysis technique was used for source apportionment of Delhi and Patiala. Various ionic concentrations were given as an input to the model and after that the following steps were performed to run the PCA in software to get the results.

Steps performed for PCA IN SPSS Statistics software:

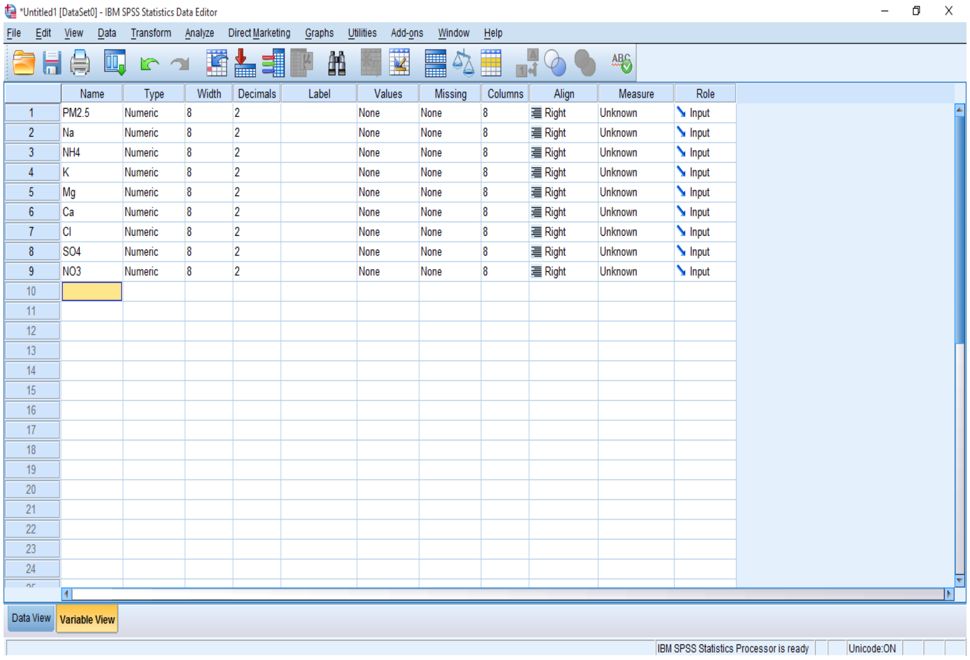
1. Copied all the data(concentrations of all the ions and $PM_{2.5}$) in data view



	VAR00001	VAR00002	VAR00003	VAR00004	VAR00005	VAR00006	VAR00008	VAR00009	VAR00010
1	116.72	8.54	8.94	5.67	.39	5.47	9.86	18.01	11.29
2	51.18	7.28	3.92	6.22	.34	4.91	5.84	3.89	3.10
3	91.89	5.50	12.52	3.65	.25	3.44	2.72	11.18	10.00
4	52.70	4.37	7.15	3.40	.37	4.72	4.06	9.62	7.41
5	55.12	6.10	2.97	3.92	.34	5.34	5.59	8.94	8.22
6	205.87	5.16	18.38	6.57	.26	3.14	8.17	19.77	25.09
7	282.18	3.12	21.99	5.29	.21	3.17	10.35	22.54	36.05
8	205.12	4.08	18.76	5.56	.26	3.93	10.43	19.49	25.03
9	93.01	2.60	7.23	3.27	.18	2.33	4.63	8.68	12.12
10	184.60	6.78	22.08	4.56	.26	4.39	8.84	24.84	28.72
11	140.60	5.59	13.41	4.84	.30	4.47	12.67	14.27	26.20
12	107.18	4.36	10.12	4.49	.30	6.02	9.19	9.44	11.83
13	97.66	3.53	3.53	3.98	.44	3.18	5.73	10.84	12.57
14	81.67	3.10	.00	2.04	.19	2.14	3.64	4.19	3.30

Fig.4.6.1: Step 1 to perform PCA

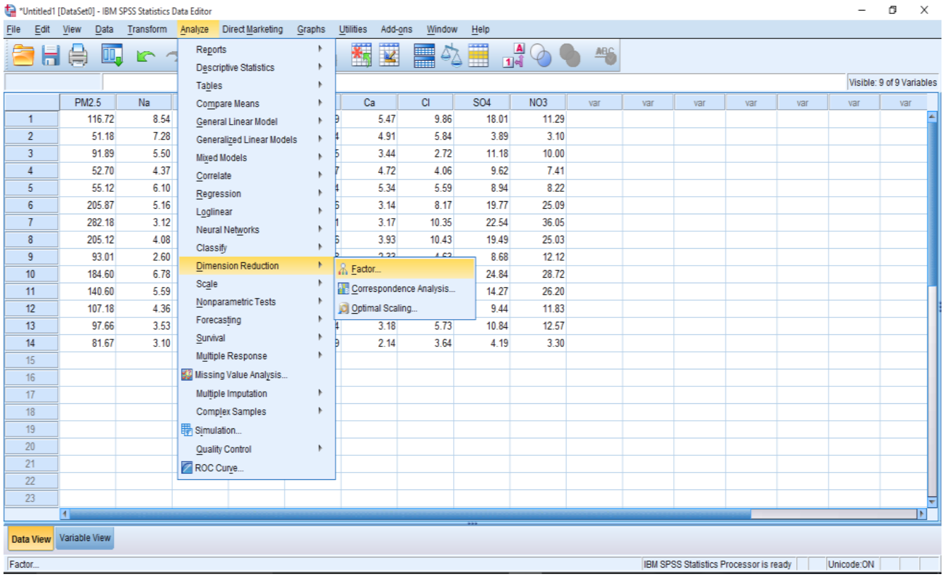
2. Then clicked variable view and defined names of the ions



	Name	Type	Width	Decimals	Label	Values	Missing	Columns	Align	Measure	Role
1	PM2.5	Numeric	8	2		None	None	8	Right	Unknown	Input
2	Na	Numeric	8	2		None	None	8	Right	Unknown	Input
3	NH4	Numeric	8	2		None	None	8	Right	Unknown	Input
4	K	Numeric	8	2		None	None	8	Right	Unknown	Input
5	Mg	Numeric	8	2		None	None	8	Right	Unknown	Input
6	Ca	Numeric	8	2		None	None	8	Right	Unknown	Input
7	Cl	Numeric	8	2		None	None	8	Right	Unknown	Input
8	SO4	Numeric	8	2		None	None	8	Right	Unknown	Input
9	NO3	Numeric	8	2		None	None	8	Right	Unknown	Input

Fig.4.6.2: Step 2 to perform PCA

3. After that went to analyze option at the top of screen and chose dimension reduction option and further chose Factors.



	PM2.5	Na	Ca	Cl	SO4	NO3
1	116.72	8.54	5.47	9.86	18.01	11.29
2	51.18	7.28	4.91	5.84	3.89	3.10
3	91.89	5.50	3.44	2.72	11.18	10.00
4	52.70	4.37	4.72	4.06	9.62	7.41
5	55.12	6.10	5.34	5.59	8.94	8.22
6	205.87	5.16	3.14	8.17	19.77	25.09
7	282.18	3.12	3.17	10.35	22.54	36.05
8	205.12	4.08	3.93	10.43	19.49	25.03
9	93.01	2.60			8.68	12.12
10	184.60	6.78			24.84	28.72
11	140.60	5.59			14.27	26.20
12	107.18	4.36			9.44	11.83
13	97.66	3.53	3.18	5.73	10.84	12.57
14	81.67	3.10	2.14	3.64	4.19	3.30

Fig.4.6.3: Step 3 to perform PCA

4. All the variable names appeared, selected and moved to variables column.

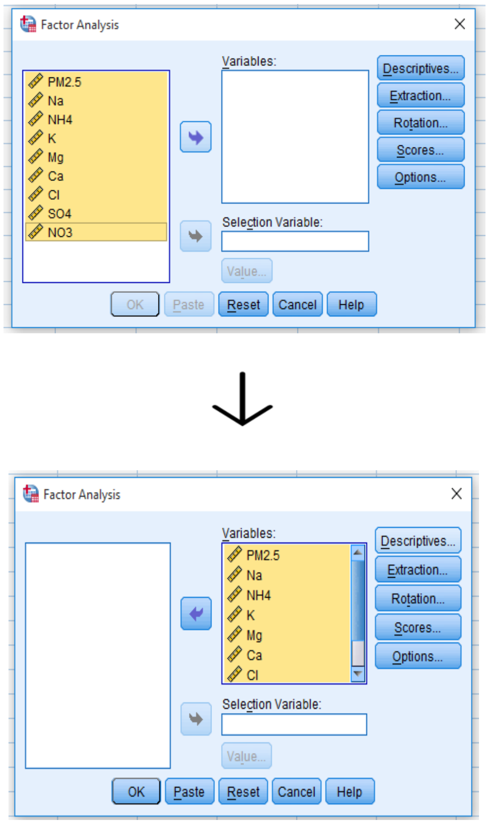
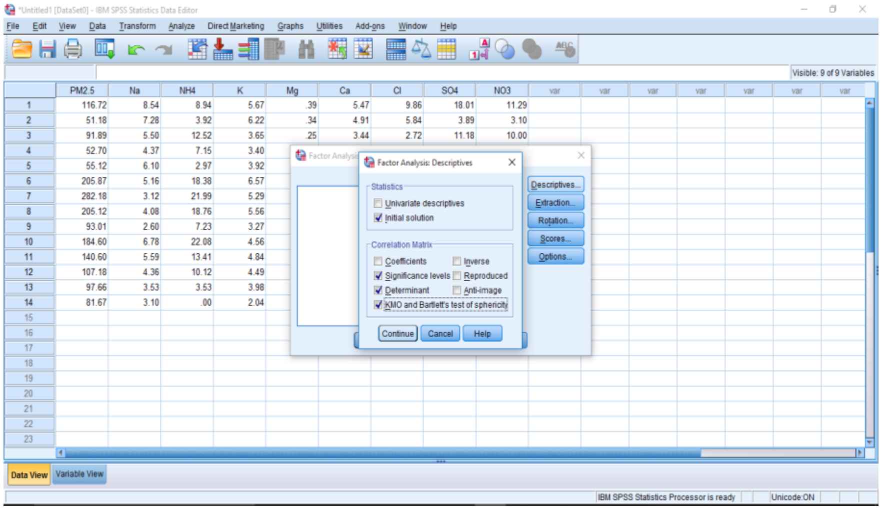


Fig.4.6.4: Step 4 to perform PCA

5. After that clicked descriptive option and three correlation matrices were chosen i.e. significance level, determinant and KMO & Bartlet's test of sphericity. And then clicked OK



	PM2.5	Na	NH4	K	Mg	Ca	Cl	SO4	NO3
1	116.72	8.54	8.94	5.67	.39	5.47	9.86	18.01	11.29
2	51.18	7.28	3.92	6.22	.34	4.91	5.84	3.89	3.10
3	91.89	5.50	12.52	3.65	.25	3.44	2.72	11.18	10.00
4	52.70	4.37	7.15	3.40					
5	55.12	6.10	2.97	3.92					
6	205.87	5.16	18.38	6.57					
7	282.18	3.12	21.99	5.29					
8	205.12	4.08	18.76	5.56					
9	93.01	2.60	7.23	3.27					
10	184.60	6.78	22.08	4.56					
11	140.60	5.59	13.41	4.84					
12	107.18	4.36	10.12	4.49					
13	97.66	3.53	3.53	3.98					
14	81.67	3.10	.00	2.04					

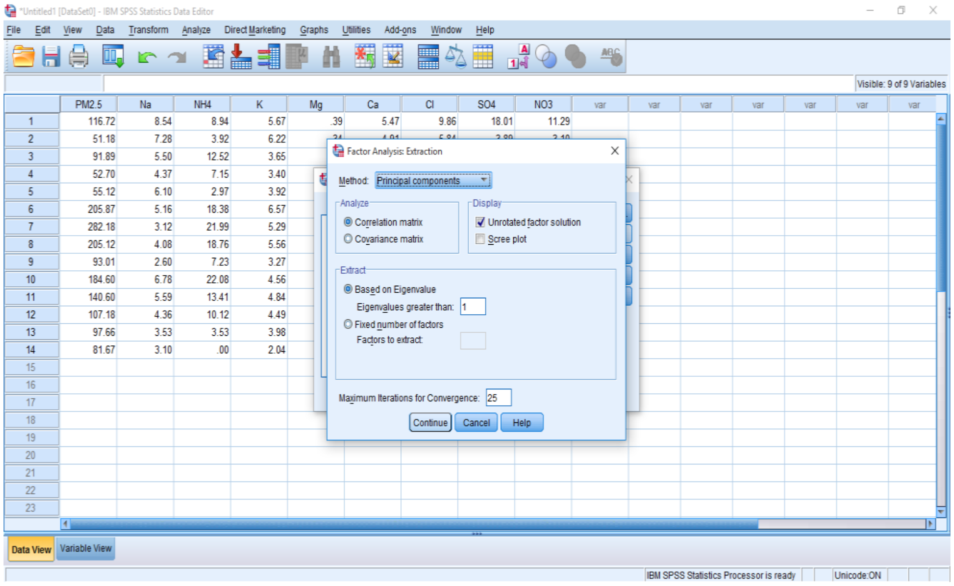
Factor Analysis: Descriptives

Statistics
☐ Univariate descriptives
☑ Initial solution

Correlation Matrix
☐ Coefficients ☐ Inverse
☑ Significance levels ☐ Reproduced
☑ Determinant ☐ Anti-image
☑ KMO and Bartlett's test of sphericity

Fig.4.6.5: Step 5 to perform PCA

6. Then clicked extraction option, in methods principal component was chosen and eigen values greater than 1 to be extracted were defined and after that clicked continue.



	PM2.5	Na	NH4	K	Mg	Ca	Cl	SO4	NO3
1	116.72	8.54	8.94	5.67	.39	5.47	9.86	18.01	11.29
2	51.18	7.28	3.92	6.22					
3	91.89	5.50	12.52	3.65					
4	52.70	4.37	7.15	3.40					
5	55.12	6.10	2.97	3.92					
6	205.87	5.16	18.38	6.57					
7	282.18	3.12	21.99	5.29					
8	205.12	4.08	18.76	5.56					
9	93.01	2.60	7.23	3.27					
10	184.60	6.78	22.08	4.56					
11	140.60	5.59	13.41	4.84					
12	107.18	4.36	10.12	4.49					
13	97.66	3.53	3.53	3.98					
14	81.67	3.10	.00	2.04					

Factor Analysis: Extraction

Method: Principal components

Analyze

● Correlation matrix
○ Covariance matrix

Display

☑ Unrotated factor solution
☐ Scree plot

Extract

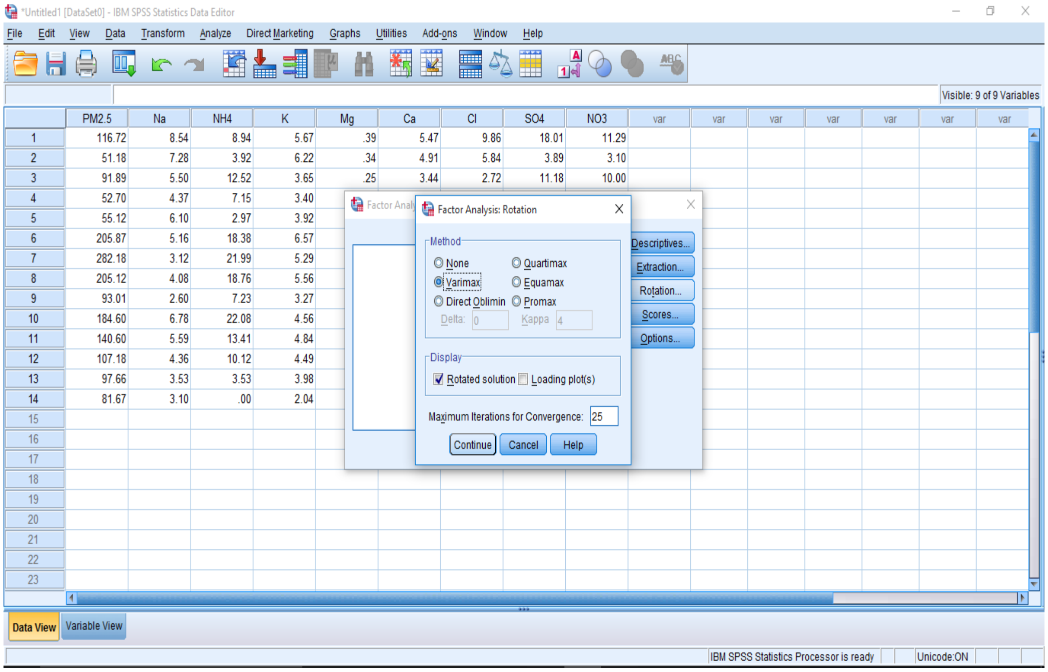
● Based on Eigenvalue
Eigenvalues greater than: 1
○ Fixed number of factors
Factors to extract:

Maximum Iterations for Convergence: 25

Continue Cancel Help

Fig.4.6.6: Step 6 to perform PCA

7. After that clicked rotation option and varimax rotation was chosen and clicked continue.



	PM2.5	Na	NH4	K	Mg	Ca	Cl	SO4	NO3
1	116.72	8.54	8.94	5.67	.39	5.47	9.86	18.01	11.29
2	51.18	7.28	3.92	6.22	.34	4.91	5.84	3.89	3.10
3	91.89	5.50	12.52	3.65	.25	3.44	2.72	11.18	10.00
4	52.70	4.37	7.15	3.40					
5	55.12	6.10	2.97	3.92					
6	205.87	5.16	18.38	6.57					
7	282.18	3.12	21.99	5.29					
8	205.12	4.08	18.76	5.56					
9	93.01	2.60	7.23	3.27					
10	184.60	6.78	22.08	4.56					
11	140.60	5.59	13.41	4.84					
12	107.18	4.36	10.12	4.49					
13	97.66	3.53	3.53	3.98					
14	81.67	3.10	.00	2.04					

Factor Analysis: Rotation

Method

○ None ○ Quartimax
● Varimax ○ Equamax
○ Direct Oblimin ○ Promax
Delta: 0 Kappa 4

Display

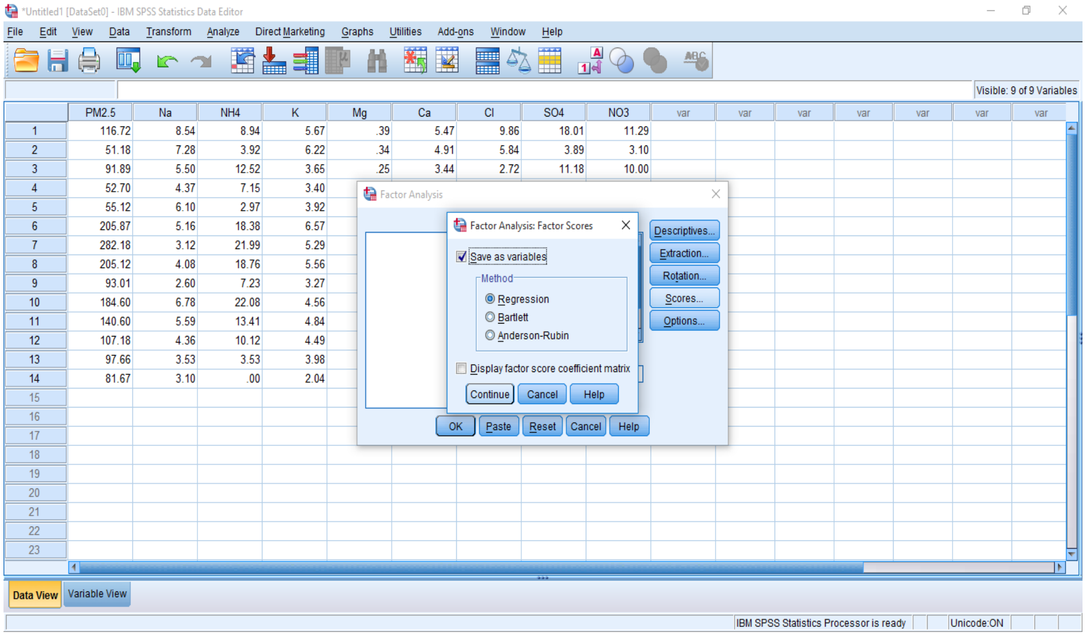
☑ Rotated solution ☐ Loading plot(s)

Maximum Iterations for Convergence: 25

Continue Cancel Help

Fig.4.6.7: Step 7 to perform PCA

8. Then chose 4th option which was scores, in that regression option was clicked and after that clicked continue.



	PM2.5	Na	NH4	K	Mg	Ca	Cl	SO4	NO3
1	116.72	8.54	8.94	5.67	.39	5.47	9.86	18.01	11.29
2	51.18	7.28	3.92	6.22	.34	4.91	5.84	3.89	3.10
3	91.89	5.50	12.52	3.65	.25	3.44	2.72	11.18	10.00
4	52.70	4.37	7.15	3.40					
5	55.12	6.10	2.97	3.92					
6	205.87	5.16	18.38	6.57					
7	282.18	3.12	21.99	5.29					
8	205.12	4.08	18.76	5.56					
9	93.01	2.60	7.23	3.27					
10	184.60	6.78	22.08	4.56					
11	140.60	5.59	13.41	4.84					
12	107.18	4.36	10.12	4.49					
13	97.66	3.53	3.53	3.98					
14	81.67	3.10	.00	2.04					

Factor Analysis: Factor Scores

☑ Save as variables

Method

● Regression

○ Bartlett

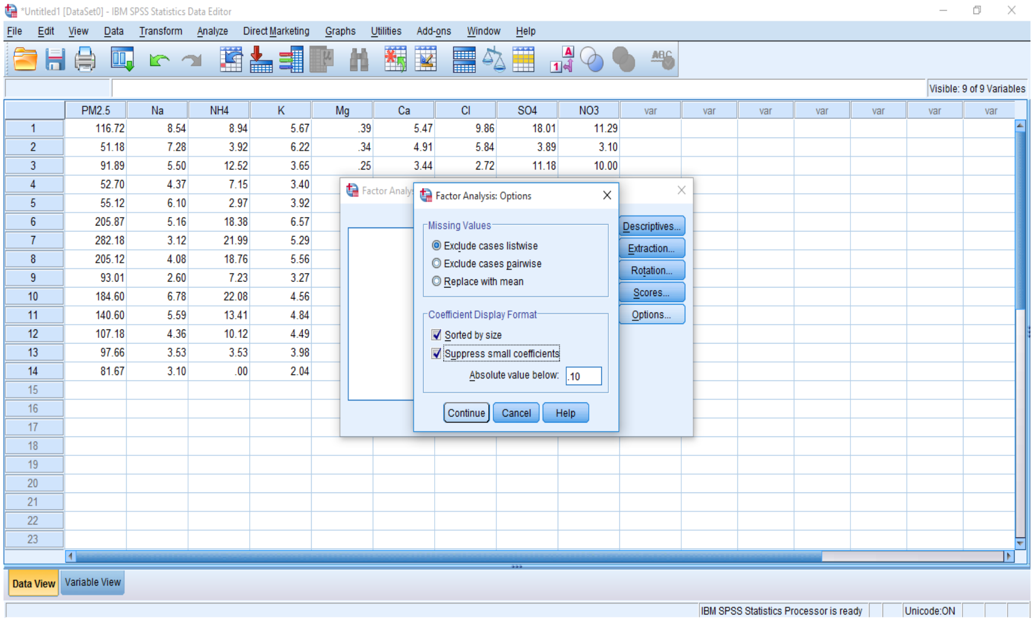
○ Anderson-Rubin

☐ Display factor score coefficient matrix

Continue Cancel Help

Fig.4.6.8: Step 8 to perform PCA

9. Finally option was chosen and both coefficient display format options were marked tick. After that click continue



	PM2.5	Na	NH4	K	Mg	Ca	Cl	SO4	NO3
1	116.72	8.54	8.94	5.67	.39	5.47	9.86	18.01	11.29
2	51.18	7.28	3.92	6.22	.34	4.91	5.84	3.89	3.10
3	91.89	5.50	12.52	3.65	.25	3.44	2.72	11.18	10.00
4	52.70	4.37	7.15	3.40					
5	55.12	6.10	2.97	3.92					
6	205.87	5.16	18.38	6.57					
7	282.18	3.12	21.99	5.29					
8	205.12	4.08	18.76	5.56					
9	93.01	2.60	7.23	3.27					
10	184.60	6.78	22.08	4.56					
11	140.60	5.59	13.41	4.84					
12	107.18	4.36	10.12	4.49					
13	97.66	3.53	3.53	3.98					
14	81.67	3.10	.00	2.04					

Factor Analysis: Options

Missing Values

● Exclude cases listwise

○ Exclude cases pairwise

○ Replace with mean

Coefficient Display Format

☑ Sorted by size

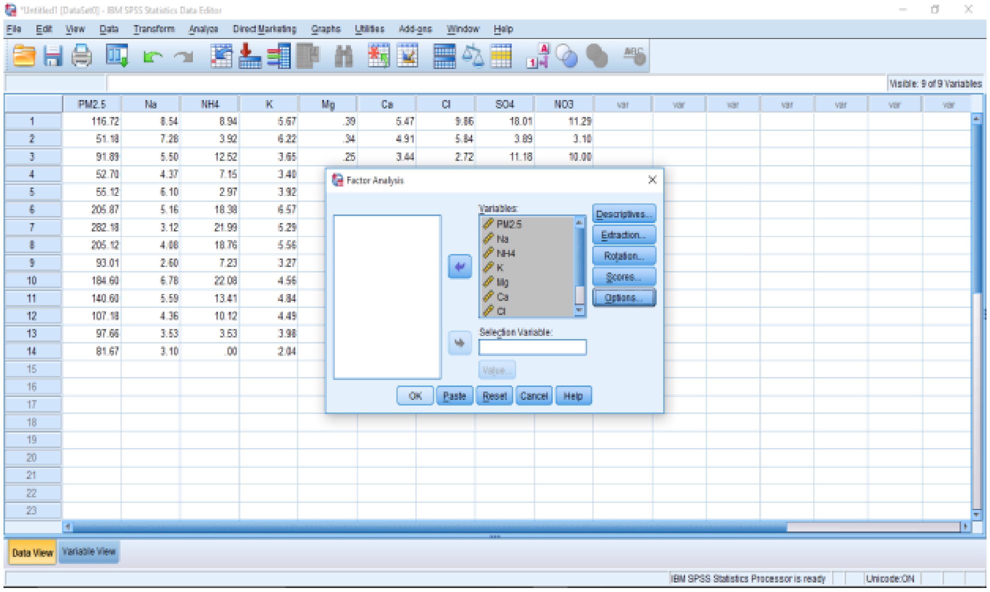
☑ Suppress small coefficients

Absolute value below: .10

Continue Cancel Help

Fig.4.6.9: Step 9 to perform PCA

10. Clicked OK and got the output.



	PM2.5	Na	NH4	K	Mg	Ca	Cl	SO4	NO3
1	116.72	8.54	8.94	5.67	.39	5.47	9.86	18.01	11.29
2	51.18	7.28	3.92	6.22	.34	4.91	5.84	3.89	3.10
3	91.89	5.50	12.52	3.65	.25	3.44	2.72	11.18	10.00
4	52.70	4.37	7.15	3.40					
5	56.12	6.10	2.97	3.92					
6	205.87	5.16	18.38	6.57					
7	282.18	3.12	21.99	5.29					
8	205.12	4.08	18.76	5.56					
9	93.01	2.60	7.23	3.27					
10	184.60	6.78	22.08	4.56					
11	140.60	5.59	13.41	4.84					
12	107.18	4.36	10.12	4.49					
13	97.66	3.53	3.53	3.98					
14	81.67	3.10	.00	2.04					

Fig.4.6.10: Step 10 to perform PCA

Since the output of Principal Component Analysis consisted of only extracted principal components and their covariance, so to interpret the results source profiling needed to be done. Various sources signature ions were found out using literature. Table 4.4 presents the signature ions for various sources.

Table 4.3: Signature ions for different sources

S.No	Signature Ion	Source	Reference
1	Na^+	Biomass burning, Marine	*Begum et al., 2007; Viana et al., 2008; Heo et al., 2009; Majewski et al., 2013; Xu et al., 2015*
2	K^+	Biomass burning	*Song et al., 2006; Lynam and Keeler, 2006; Zhang et al., 2008; Tiwari et al., 2009; Chelani et al., 2010; Dall'Osto et al., 2013*
3	NH_4^+	Secondary fine particles, Coal combustion	*Keeler et al., 2006; Sharma et al., 2007; Watson et al., 2008; Shridhar et al., 2010; Gajghate et al., 2012*
4	Mg^{+2}	Road dust, Construction activity	*Lee and Hopke, 2006; Watson et al., 2008; Zhang et al., 2008; Tiwari et al., 2009; Kim et al., 2011*
5	Ca^{+2}	Road dust, Diesel Vehicles	*Watson and Chow, 2001; Almeida et al., 2005; Lynam and Keeler, 2006; Shridhar et al. 2010; Gajghate et al. 2012*
6	Cl^-	Coal combustion Oil, biomass burning	*Kumar et al., 2001; Gupta et al., 2007; Li et al., 2008; Tiwari et al., 2009; Kim et al., 2011; Xu et al., 2015*
7	SO_4^{-2}	Secondary fine particles, Coal combustion	*Dahl, 2005; Begum et al. 2007; Shridhar et al. 2010; Owoade et al. 2015*
8	NO_3^{-2}	Secondary fine particles, Diesel engines	*Kumar et al., 2001; Maykut et al., 2003; Lynam and Keeler, 2006; Chelani et al., 2008; Owoade et al. 2015*

CHAPTER 5

RESULTS & DISCUSSION

This chapter incorporates the observations and results of $PM_{2.5}$ Monitored at all the six sites as well as Total Suspended Particulate Matter concentrations which were also monitored at three sites. Cluster analysis and Concentration Weighted Trajectories for each city are included in this chapter. Afterwards, ion analysis results of three sites are shown by graphical representations and then Principal Component Analysis model results are explained which qualified sources of pollution in Delhi and Patiala.

5.1 PARTICULATE MATTER (LESS THAN 2.5 MICRONS SIZE) ($PM_{2.5}$)

$PM_{2.5}$ samples were collected for 24 hours on pre-weighed Whattman Quartz Filters at an average air flow rate of 16.67 LPM at all the selected sites. Fine dust samplers and dual channel dust samplers were used for the monitoring of Particulate matter. Weight of $PM_{2.5}$ was estimated gravimetrically for the determination of concentration of aerosols in the ambient air. Therefore $PM_{2.5}$ concentrations were calculated using the formula mentioned in section 4.5.3. Location map marking all the sites is shown in methodology section in figure 4.5. Location map of each site followed by the graph of $PM_{2.5}$ Concentration at that site are shown below. Location maps of all the sites i.e. NPL, Delhi; Village Kherijattan, Punjab; Thapar University, Patiala; School of Public Health, PGIMER, Chandigarh; CHC Khera Institute, Chandigarh; CPH, Panjab University, Chandigarh; Guru Nanak Dev University, Amritsar; Aryabhatta Research Institute of Observational Sciences (ARIES), Nainital; G.B. Pant Institute of Himalayan Environment, Kullu are shown in figures 5.1, 5.3, 5.5, 5.7, 5.9, 5.11, 5.13, 5.15 and 5.17 respectively. In case of Nainital PM_{10} were measured instead of $PM_{2.5}$ concentrations. PM_{10} were measured using High Air Volume Sampler which was also run for 24 hours at an average air flow rate of 1.2m^3/min. Graphs of $PM_{2.5}$ Concentrations at each site and PM_{10} in case of Nainital are shown in figures 5.2, 5.4, 5.6, 5.8, 5.10, 5.12, 5.14, 5.16 and 5.18. Comparison of $PM_{2.5}$ Concentrations at all the sites is shown in figure 5.19

A. DELHI

➢ National Physical Laboratory (NPL), New Delhi

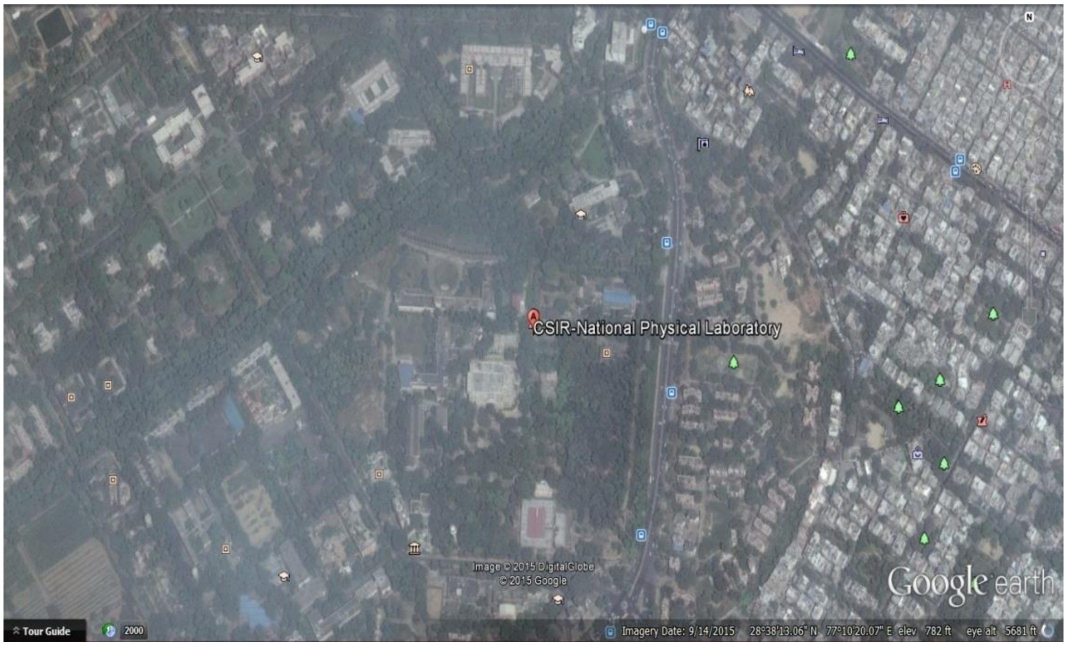


Fig.5.1: Location map of NPL, Delhi

(Downloaded from Google Earth Software)

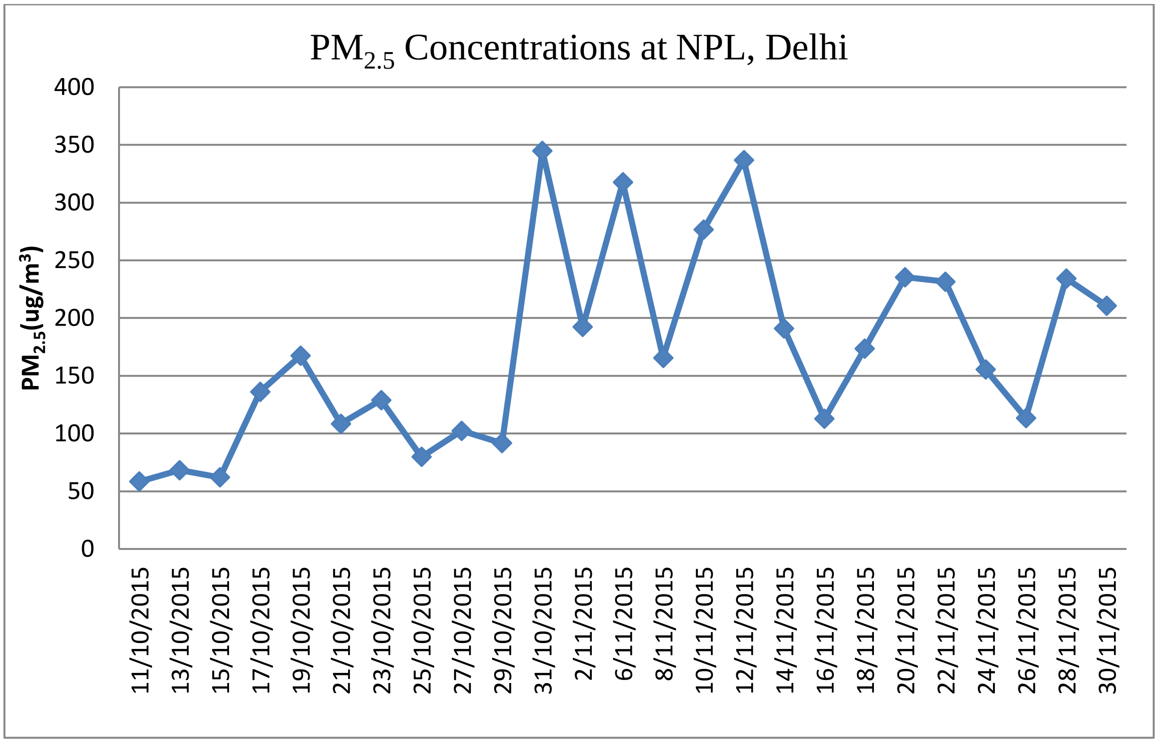


Fig.5.2: $PM_{2.5}$ concentrations at NPL, Delhi

During the monitoring period the average concentration of $PM_{2.5}$ was 172ug/m^3 in Delhi. The concentration levels varied between 59ug/m^3 to 345ug/m^3 at the site. On the day of Diwali and the next day from Diwali, $PM_{2.5}$ concentrations were much larger as compared to normal biomass burning days. Maximum $PM_{2.5}$ concentration was almost 6 times to that of National Ambient Air Quality Standards (NAAQS) $PM_{2.5}$ standards for 24 hour sampling i.e. 60ug/m^3 in Delhi during crop residue burning episodes.

B. PATIALA

➢ Location 1: Village Kherrijattan, Punjab

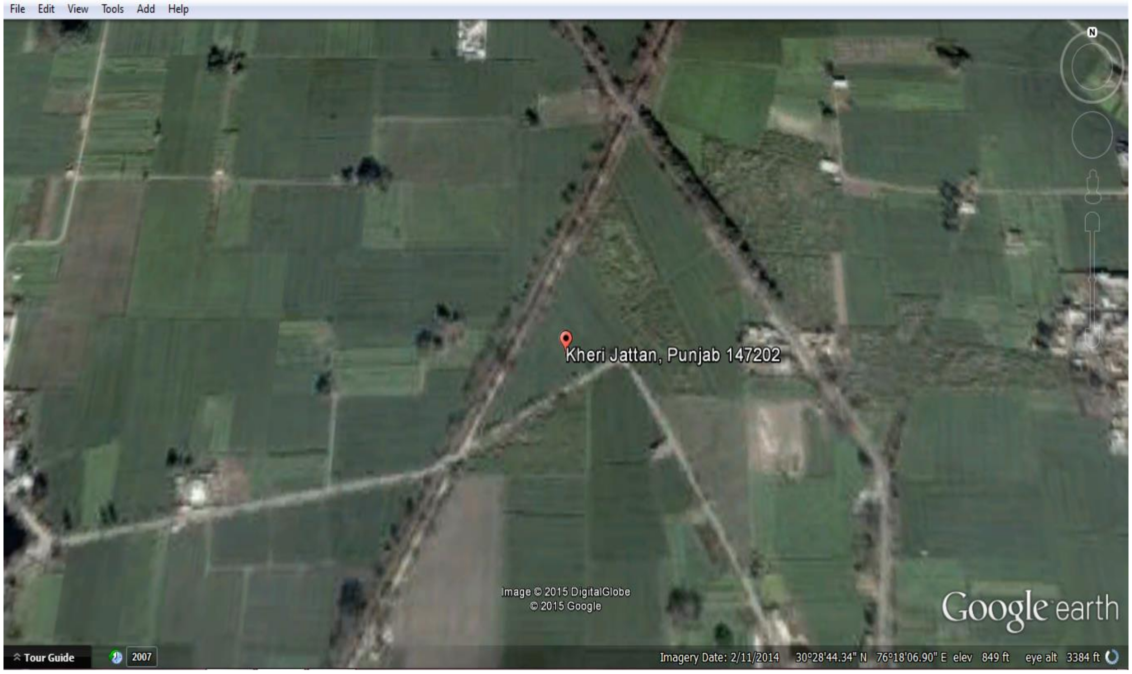


Fig. 5.3: Location map of Village Kherijattan, Punjab

(Downloaded from Google Earth Software)

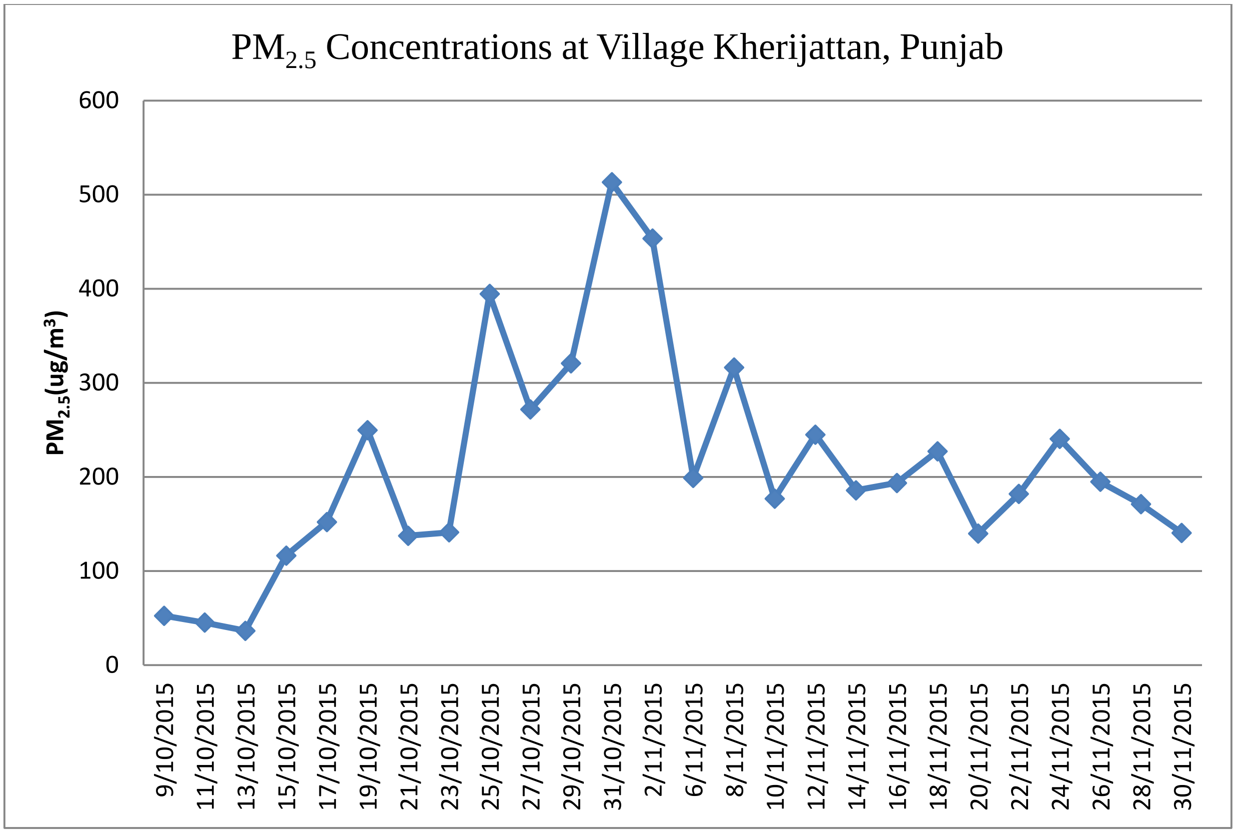


Fig.5.4: PM$_{2.5}$ concentrations at Village Kherijattan, Punjab

During the monitoring period, the average concentrations of PM$_{2.5}$ were 217.6ug/m^3 in Village Kherijattan, which is purely an agricultural site (10 Kms from Patiala). The concentration levels varied between 36ug/m^3 just before start of burning to 514ug/m^3 during burning episodes at the agricultural field. As soon the burning started, PM$_{2.5}$ concentration levels increased drastically at the site. The maximum concentration observed during burning episodes was almost 8.5 times that of the NAAQS PM$_{2.5}$ standards for 24 hour sampling i.e. 60ug/m^3. Even after burning days average concentration remained around 200ug/m^3 due to influence of biomass burning.

- **Location 2: Thapar university (TU), Patiala**

Fig. 5.5: Location map of Thapar University, Patiala (Downloaded from Google Earth Software)

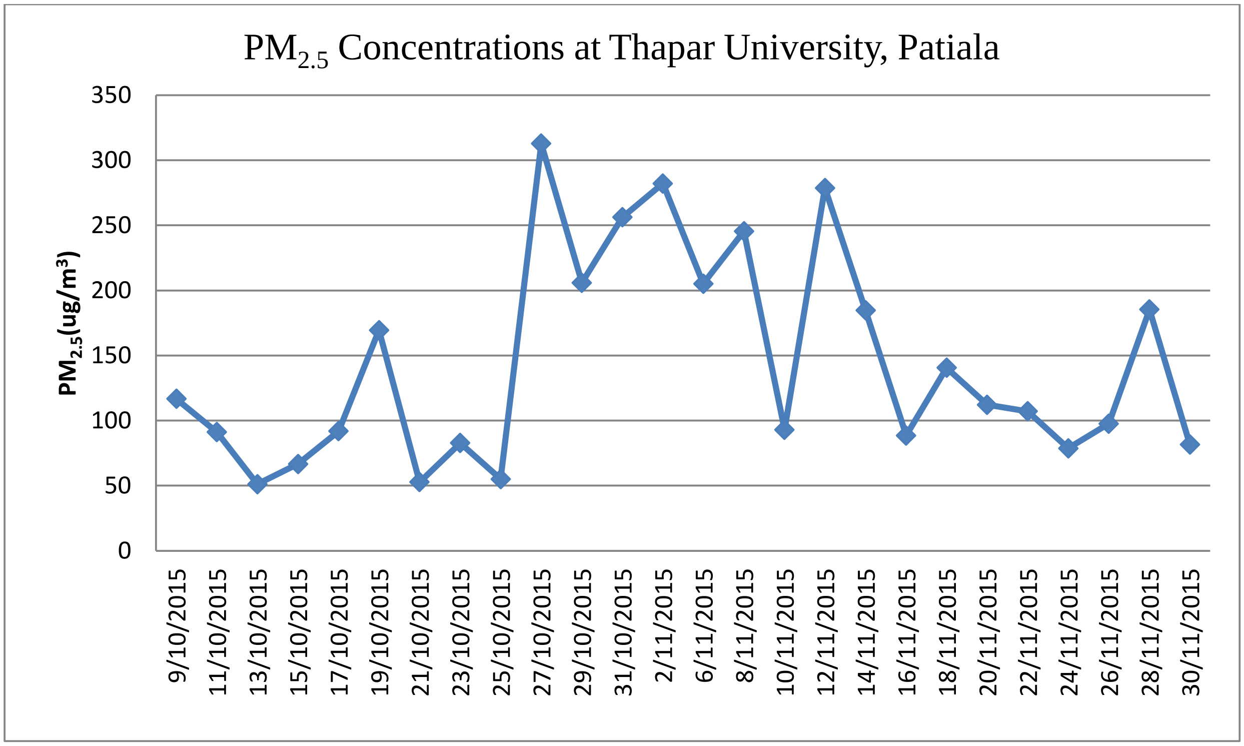


Fig.5.6: $PM_{2.5}$ concentrations at Thapar University, Patiala

During the monitoring period the average concentration of $PM_{2.5}$ was 145.134ug/m^3 at Thapar University, Patiala. The concentration levels varied between 52ug/m^3 to 314ug/m^3 at the site. After Diwali, $PM_{2.5}$ concentration was much larger when compared to normal burning days.

C. CHANDIGARH

➢ Location 1: School of Public Health, PGIMER, Chandigarh

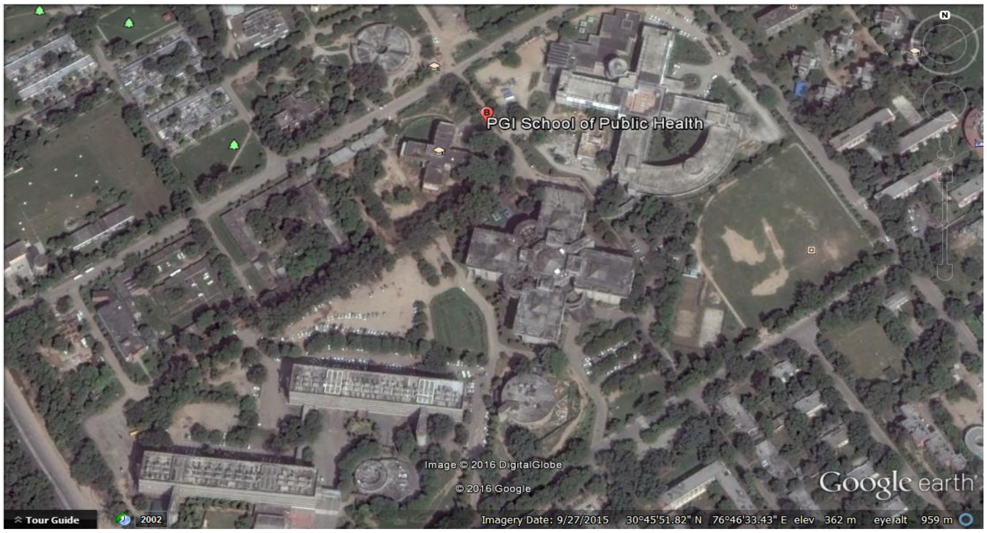


Fig. 5.7: Location map of School of Public Health, PGIMER, Chandigarh (Downloaded from Google Earth Software)

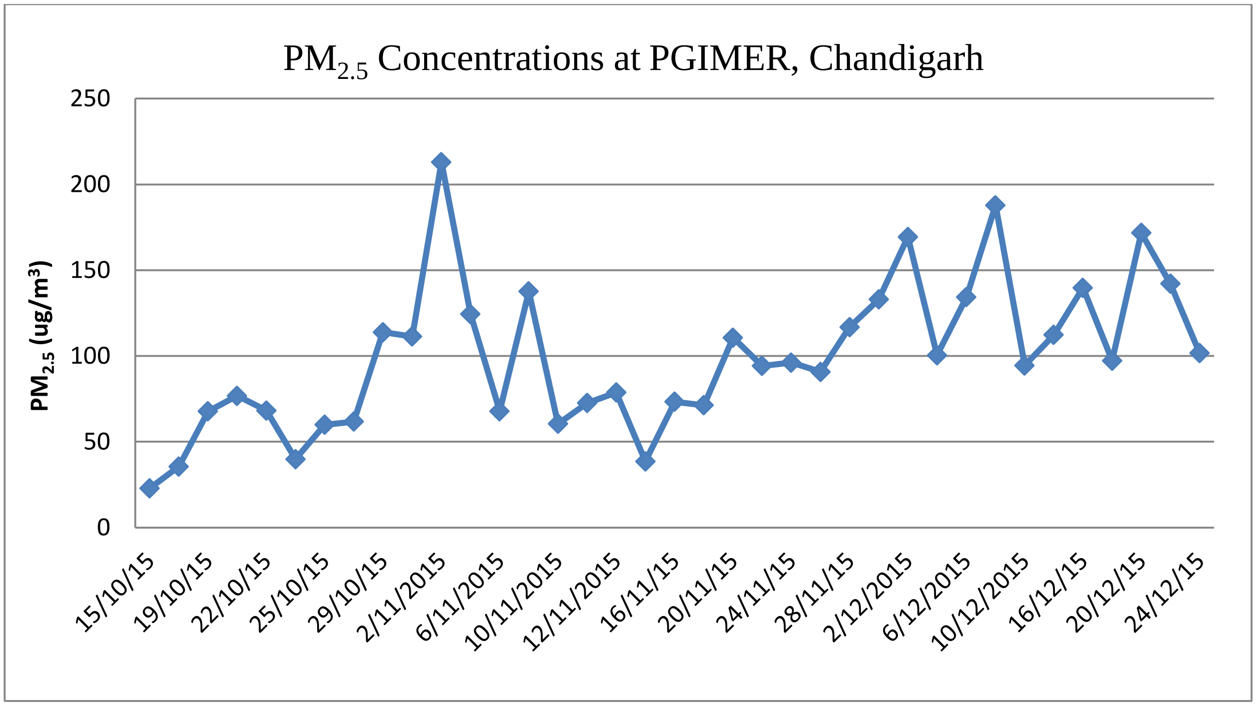


Fig.5.8: PM$_{2.5}$ concentrations at School of Public Health, PGIMER, Chandigarh

During the monitoring period the average concentration of PM$_{2.5}$ was 100 ug/m^3 at School of Public Health, PGIMER, Chandigarh. Maximum concentration was observed as 215ug/m^3 on the day of Dushehra.

➢ Location 2: CHC Khera Institute, Chandigarh

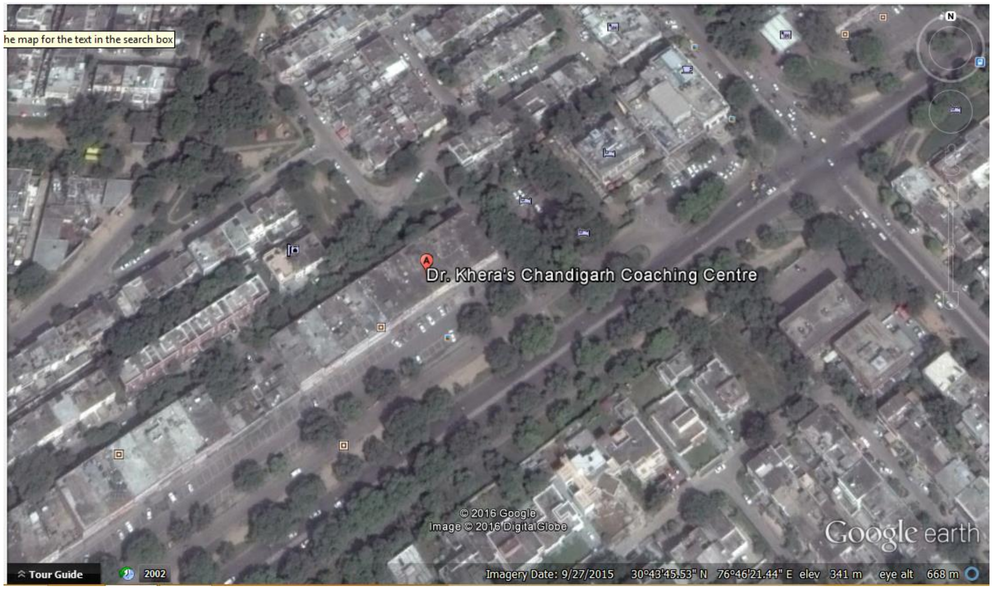


Fig. 5.9: Location map of CHC Khera Institute, Chandigarh (Downloaded from Google Earth Software)

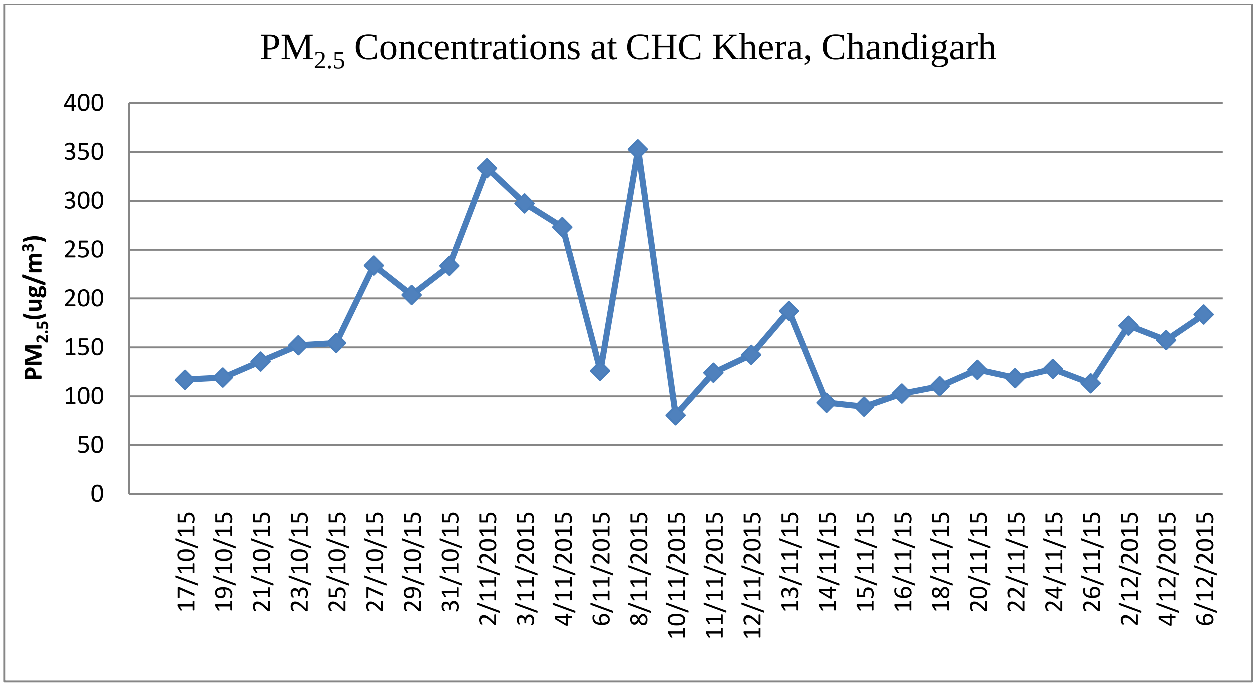


Fig.5.10: $PM_{2.5}$ concentrations at CHC Khera Institute, Chandigarh

During the monitoring period the average concentration of $PM_{2.5}$ was 167ug/m^3 at CHC Khera Institute, Chandigarh. Maximum concentration was observed as 355ug/m^3 which is almost 6 times that of NAAQS $PM_{2.5}$ standards for 24 hour sampling.

- **Location 3: Centre for public health, Panjab University, Chandigarh**

Fig. 5.11: Location map of Panjab University, Chandigarh (Downloaded from Google Earth Software)

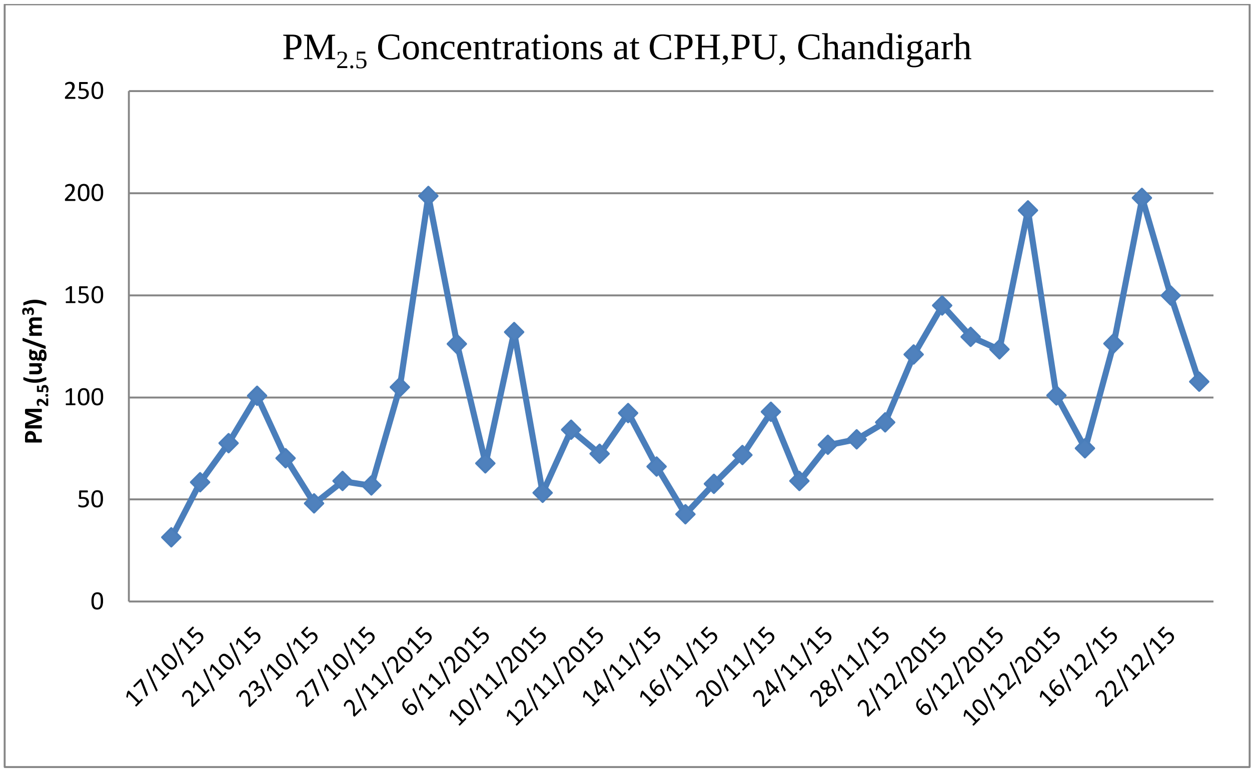


Fig.5.12: $PM_{2.5}$ concentrations at CPH, PU, Chandigarh

During the monitoring period, the average concentration of $PM_{2.5}$ was 95 ug/m^3 at CPH, PU, Chandigarh. Maximum concentration was observed as 200ug/m^3 on the day of Dushehra.

D. AMRITSAR

➢ Guru Nanak Dev University (GNDU), Amritsar

Fig. 5.13: Location map of GNDU, Amritsar
(Downloaded from Google Earth Software)

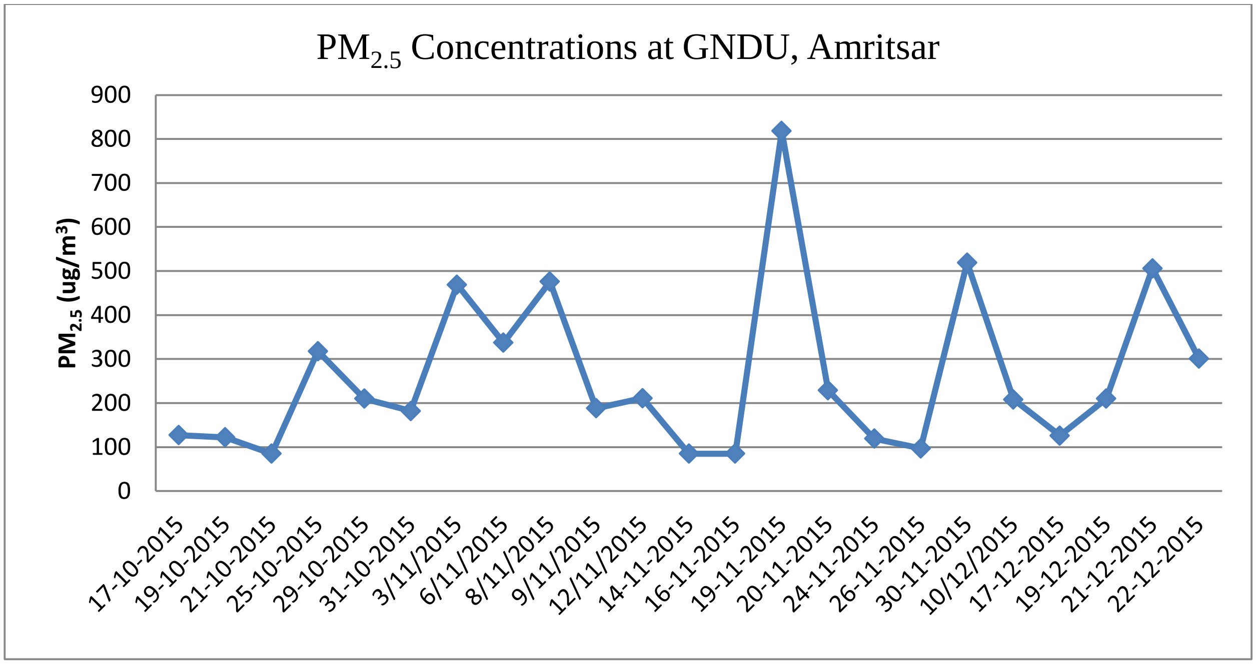


Fig.5.14: $PM_{2.5}$ concentrations at GNDU, Amritsar

During the monitoring period, the average concentration of $PM_{2.5}$ was 265ug/m^3 at GNDU, Amritsar. Maximum concentration was observed as 820ug/m^3. Pollution levels in Amritsar were found to be much greater than Delhi, Patiala as well as Chandigarh. Infact the maximum concentration observed was almost 13 times that of NAAQS $PM_{2.5}$ standards.

E. NAINITAL

➢ Aryabhatta Research Institute of Observational Sciences (ARIES), Nainital

Fig. 5.15: Location map of ARIES, Nainital
(Downloaded from Google Earth Software)

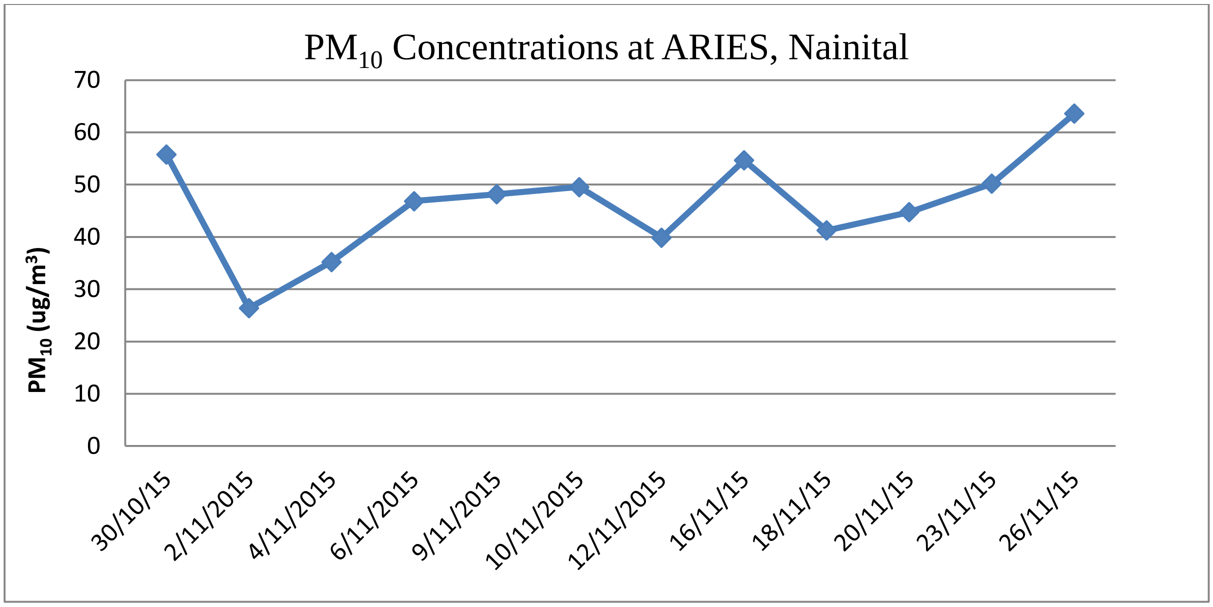


Fig.5.16: PM_{10} concentrations at ARIES, Nainital

In Nainital instead of $PM_{2.5}$, PM_{10} concentrations were measured using High Volume sampler and 24 hours monitoring was done. During the monitoring period the average concentration of PM_{10} was 46.5ug/m^3 at ARIES, Nainital. Maximum concentration was observed as 62ug/m^3. PM_{10} Concentrations remained below NAAQS standards i.e. 100ug/m^3 throughout the monitoring period.

F. KULLU

- **G.B. Pant Institute of Himalayan Environment, Kullu**

Fig. 5.17: Location map of G.B. Pant Institute of Himalayan Environment, Kullu (Downloaded from Google Earth Software)

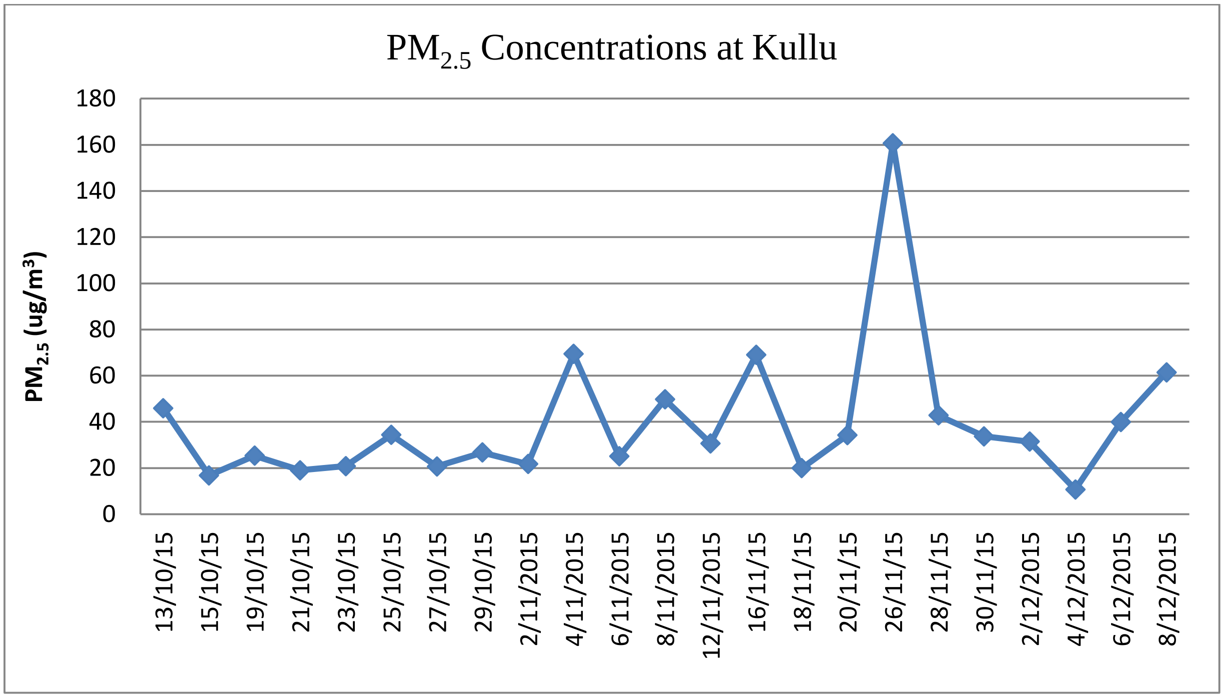


Fig.5.18: $PM_{2.5}$ concentrations at Kullu

During the monitoring period, the average concentration of $PM_{2.5}$ was 40ug/m^3 at Kullu. Maximum concentration was observed as 162ug/m^3 but most of the times $PM_{2.5}$ concentrations remained below prescribed NAAQS standards.

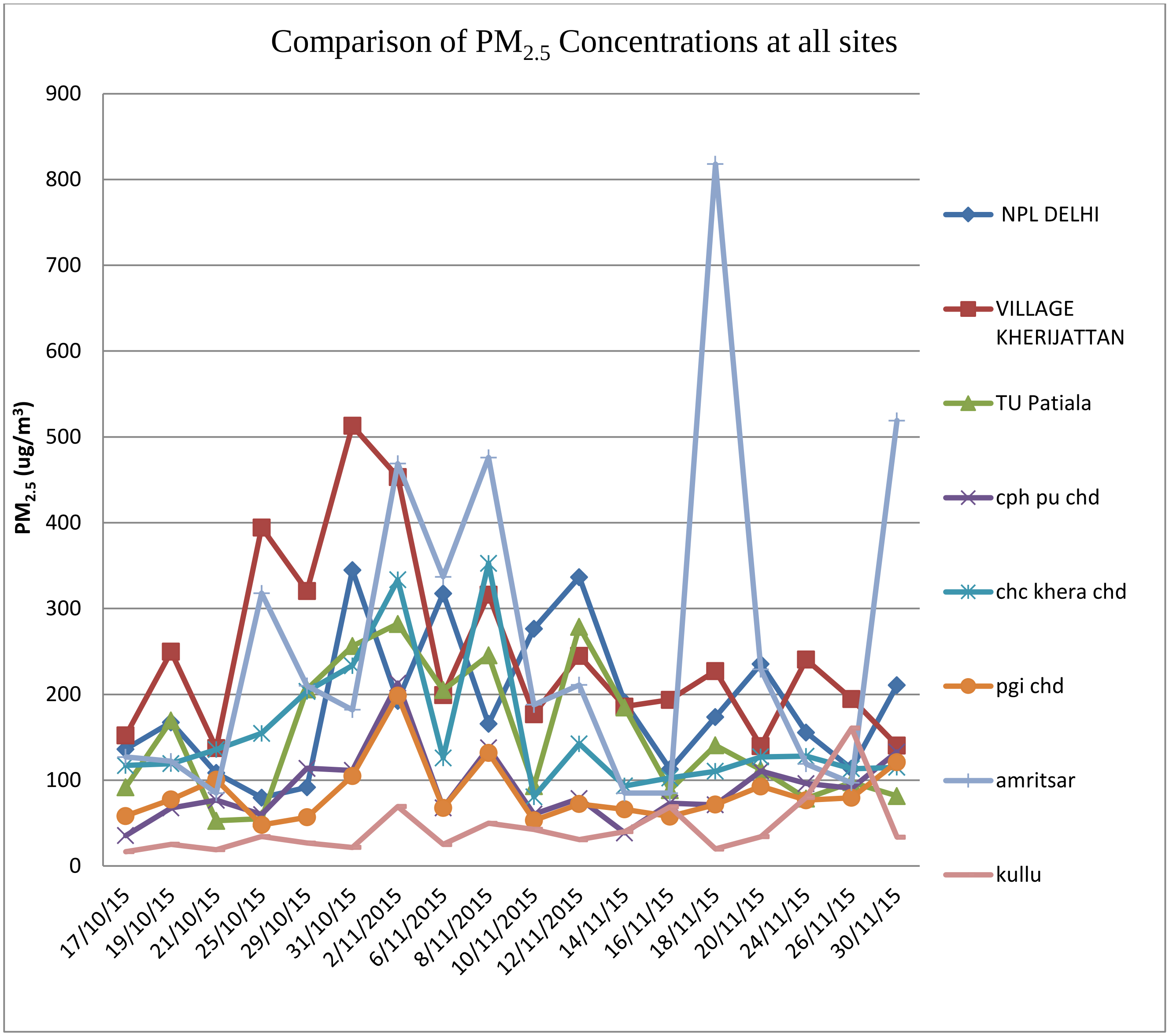


Fig.5.19: Comparison of $PM_{2.5}$ Concentrations at all the sites

Figure 5.19 indicates that Kullu was the least polluted city during crop residue burning episodes. Even most of the times $PM_{2.5}$ concentrations remained below prescribed NAAQS standards which shows kullu was not impacted much during crop residue burning episodes. On the other hand, highest $PM_{2.5}$ Concentrations were observed at Village Kherijattan, Patiala being purely agricultural site. Before stubble burning, higher $PM_{2.5}$ concentration was observed in Patiala, Delhi and Chandigarh when compared to agricultural field which may be because of the impact of vehicular emissions and industrial pollution in these cities. But concentrations in Amritsar were also comparable to agricultural site showing Amritsar is the most polluted city among all the monitored cities. Infact the highest $PM_{2.5}$ Concentration was also measured in Amritsar which was almost 13 times that of NAAQS $PM_{2.5}$ Standards and the average concentration of $PM_{2.5}$ during monitoring period was also highest in Amritsar. In Chandigarh $PM_{2.5}$ Concentrations at Location 1 and 3 i.e. PGIMER and PU were much lesser than $PM_{2.5}$ Concentrations at location 2 i.e. CHC Khera Institute. $PM_{2.5}$ in Patiala were also lesser than location 2 of Chandigarh. Also the Particulate matter concentration levels during Diwali were found much greater when compared to normal burning days at all the sites. It is also observed that Delhi has much higher concentrations of $PM_{2.5}$ as compared to Patiala and Chandigarh which indicates more vehicular pollution in Delhi. Hence increased concentrations of $PM_{2.5}$ were observed at all the monitored sites during crop residue burning episodes showing the impact of crop residue burning on North Indian cities. Figure 5.20 shows the average concentrations of $PM_{2.5}$ before, during and after crop residue burning in all the cities.

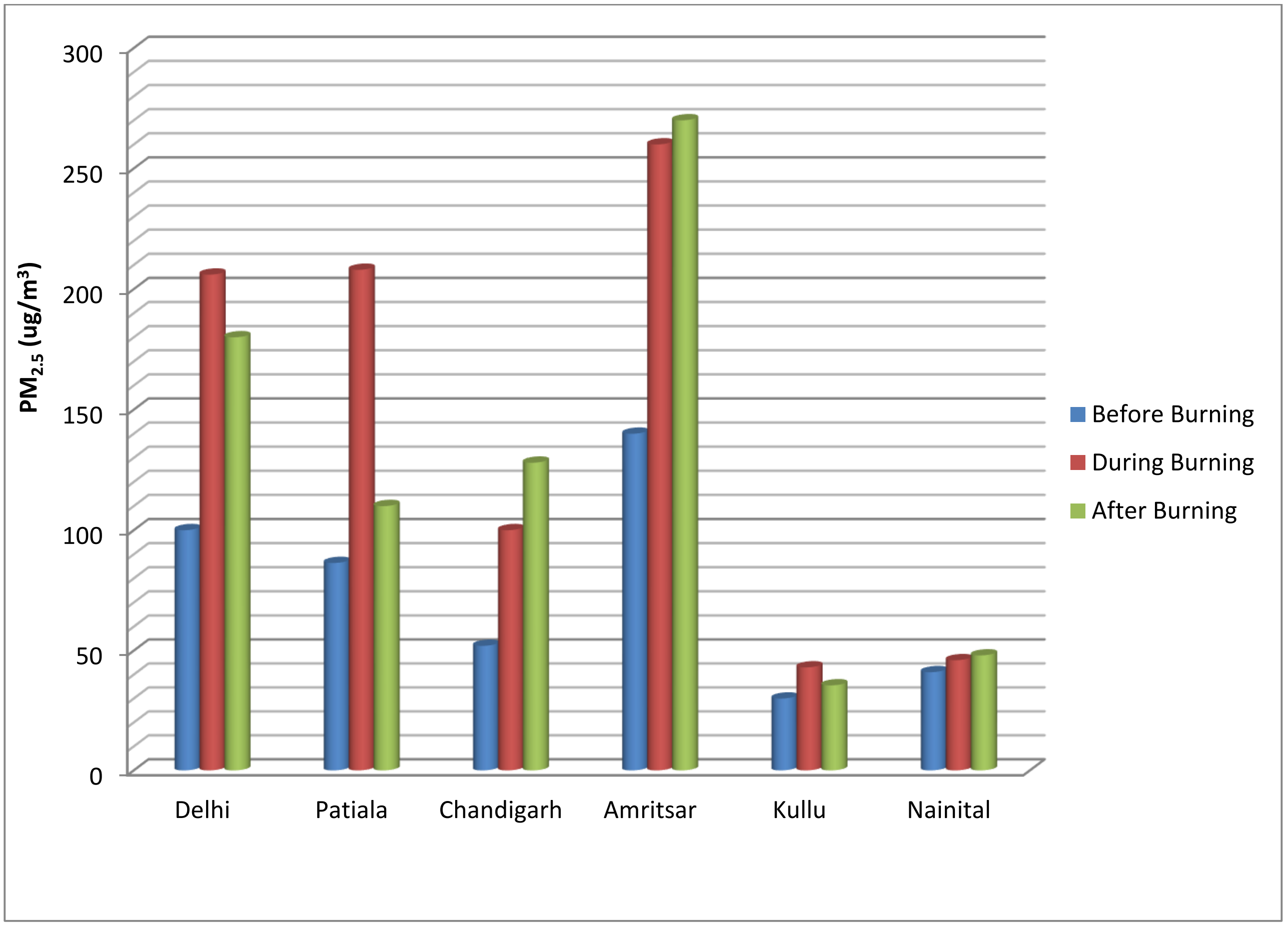


Fig.5.20: Average Concentrations of $PM_{2.5}$ before, during & after burning in all the cities

Figure 5.20 shows that just before the start of crop residue burning average concentrations in the cities were much lesser as compared to during and after burning episodes. Even after the burning stopped, its influence remained in the atmosphere leading to higher concentrations of $PM_{2.5}$. $PM_{2.5}$ and PM_{10} concentrations in Kullu and Nainital remained below prescribed standards before, during and even after burning showing that these sites were least affected during biomass burning episodes. Amritsar, Patiala and Delhi were equally affected due to crop residue burning. These three sites showed almost 100ug/m^3 increase in average $PM_{2.5}$ concentrations during burning as compared to before burning. In Chandigarh also around, 50ug/m^3 increase in average concentration of $PM_{2.5}$ was observed during burning when compared to before burning. After burning period, average $PM_{2.5}$ concentration decreased in Patiala as compared to during burning period but much difference was not observed in Delhi, Chandigarh and Amritsar which shows the impact of crop residue burning remained in the atmosphere even after burning stopped.

5.2 TOTAL SUSPENDED PARTICULATE MATTER (TSPM)

Total suspended particulate matter was measured at three different proper agricultural sites which are within 15 Km distance from Patiala. Various sites which were monitored for TSPM included Village Rakhra, Village Bishanpur and Sirhind road. Total suspended particulate matter concentration was monitored during the peak time of burning for two hours with flow rate of 0.5 LPM. TSPM were monitored using handy air dust sampler and were also calculated gravimetrically by measuring initial and final weights of the filter papers and by using formula described in section 4.5.2. Location maps of three sites which were monitored for TSPM are shown in figures 5.21, 5.22 and 5.23. Specifications of these sites are also described in Table 5.1. Graphical bar diagram for the concentration of Total Suspended Particulate Matter at different sites is shown in figure 5.24.

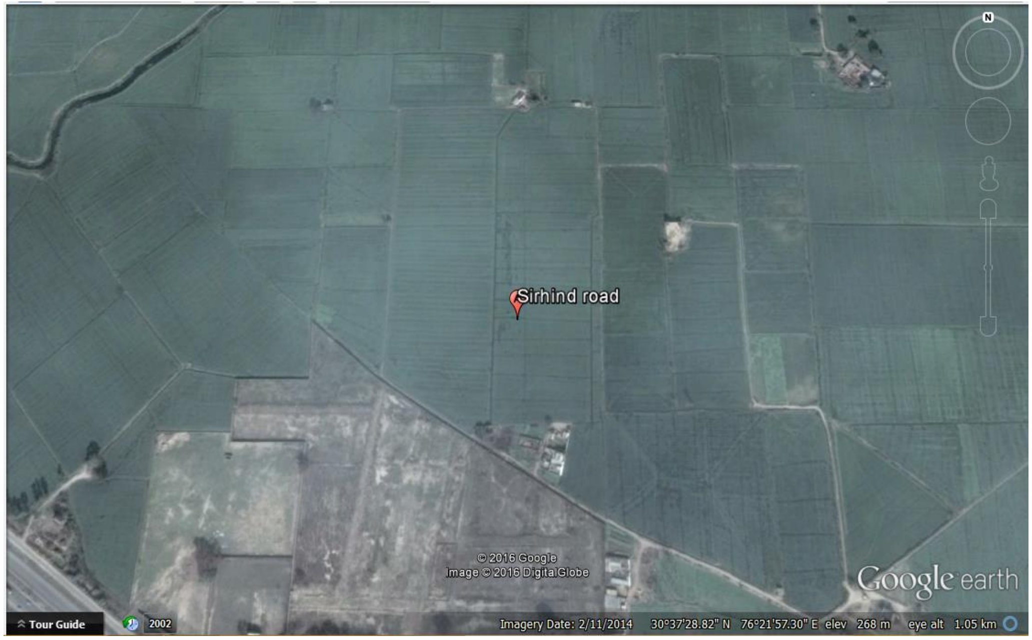


Fig. 5.21: Location map of Sirhind road, Patiala
(Downloaded from Google Earth Software)

Fig. 5.22: Location map of Village Rakhra, Patiala

(Downloaded from Google Earth Software)

Fig. 5.23: Location map of Village Bishanpur, Patiala
(Downloaded from Google Earth Software)

Table 5.1: Specifications of all TSPM monitoring sites

S.No	Date	Site specifications
1	06/11/15	Village Rakhra; 30º21’17.09”N; 76º17’52.40”E
2	07/11/15	Village Rakhra; 30º21’17.09”N; 76º17’52.40”E
3	09/11/15	Sirhind road; 30º26’10.88”N; 76º24’18.62”E
4	13/11/15	Village Bishanpur ; 30º32’84.38”N; 76º30’19.98”E
5	14/11/15	Village Bishanpur ; 30º32’84.38”N; 76º30’19.98”E
6	16/11/15	Village Bishanpur ; 30º32’84.38”N; 76º30’19.98”E
7	17/11/15	Village Bishanpur ; 30º32’84.38”N; 76º30’19.98”E
8	19/11/15	Village Bishanpur ; 30º32’84.38”N; 76º30’19.98”E
9	20/11/15	Village Bishanpur ; 30º32’84.38”N; 76º30’19.98”E
10	21/11/15	Village Bishanpur ; 30º32’84.38”N; 76º30’19.98”E

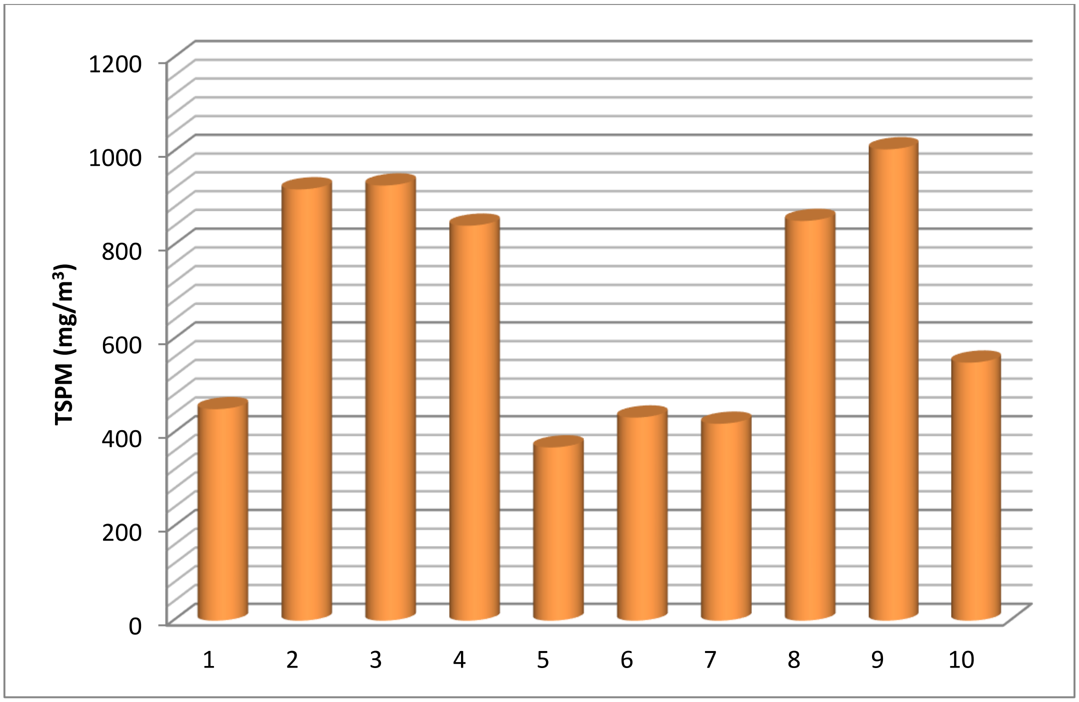
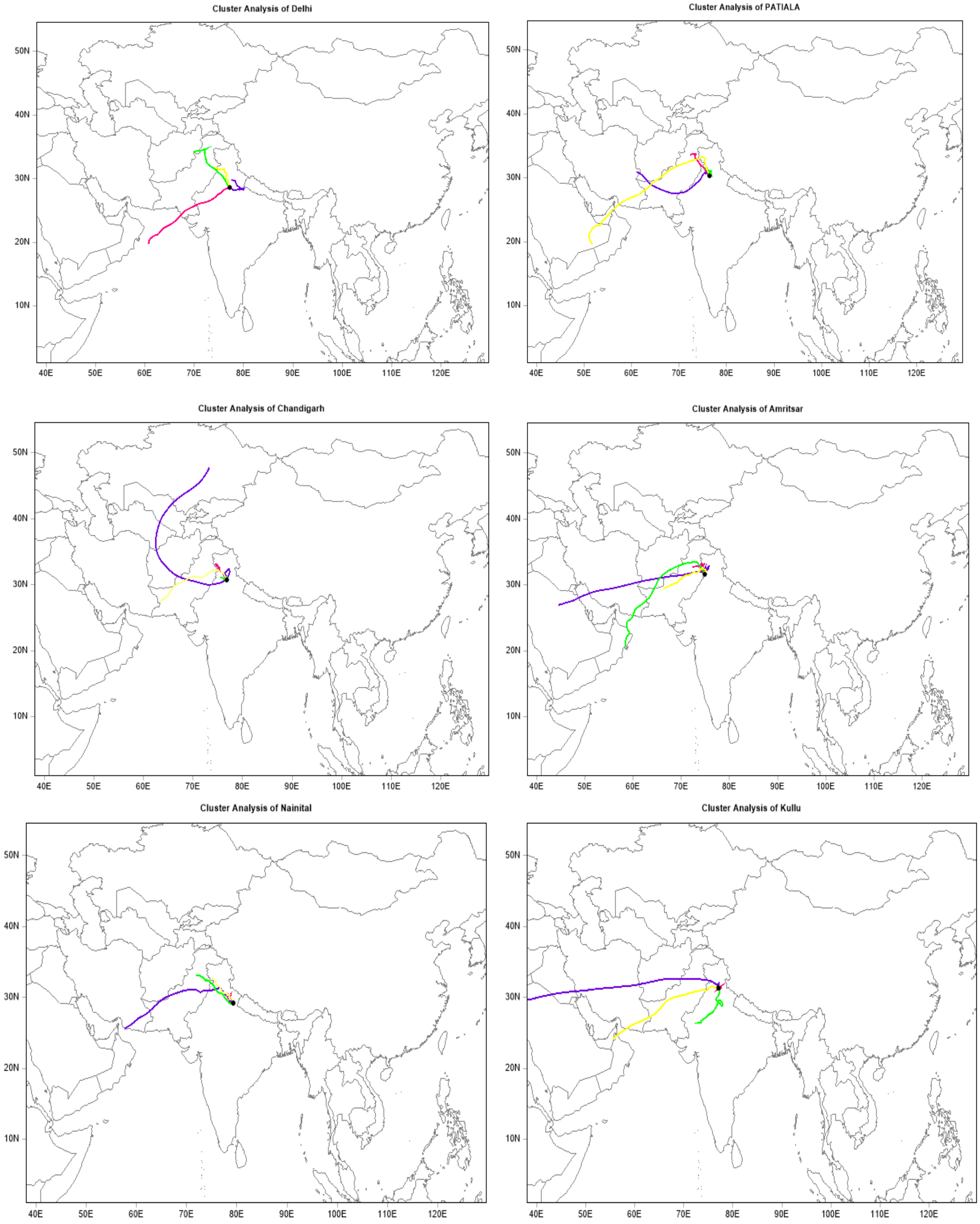


Fig.5.24: TSPM Concentrations at different sites

TSPM released from crop burning were much higher. Although as compared to $PM_{2.5}$ monitoring, total volume sampled is much lesser but the concentration of TSPM came out to be in milligrams which is very large. As we can see from figure 5.24, TSPM Concentrations varied from 420 to 1005 mg/m^3 at the peak time of burning. This shows that crop residue burning leads to release of very high concentrations of Total suspended particulate matters.

5.3 CLUSTER ANALYSIS AND CONCENTRATION WEIGHTED TRAJECTORY (CWT) ANALYSIS

CWT analysis was performed using HYSPLIT five days back trajectories for all the six cities. To observe the role of long range transport, 5-day isentropic airmass back trajectory arriving at all the sites were plotted at 500m agl (above ground level) and combined with $PM_{2.5}$ concentrations to perform the backward trajectory analysis and with PM_{10} concentrations in case of Nainital. Transport paths of air masses with similar history and origin were obtained by cluster analysis. Use of four clusters was attempted to provide the best representation of air mass classifications. And the mean $PM_{2.5}$ concentrations of each cluster were calculated by performing cluster statistics. Figure 5.25 show the trajectories of all cities clustered in groups.


Cluster Analysis of Delhi

Cluster Analysis of PATIALA

Cluster Analysis of Chandigarh

Cluster Analysis of Amritsar

Cluster Analysis of Nainital

Cluster Analysis of Kullu

Fig.5.25: Cluster Analysis of all the cities

Four clusters were generated from backward trajectory cluster analysis of Delhi, Patiala, Chandigarh, Amritsar, Nainital and Kullu respectively. Cluster analysis of Delhi shows arrival of air masses from West (W), Western-North (WN), North (N) and Eastern-North (EN). While cluster analysis of Patiala shows trajectories arriving from Southern-West (SW), West (W), Western-North (WN) and one arising in the place itself. At both the sites maximum concentration of $PM_{2.5}$ is contributed from Western North (WN) region. From cluster analysis of Chandigarh it is evident that air masses are arriving from West (W), Western-North (WN), North (N) and one arising in the place itself. Cluster analysis of Amritsar shows arrival of air masses from Southern-West (SW), Northern-West (NW), West (W) and Western-North (WN) with different number and concentration of Trajectories. In Nainital also four clusters arrived from West (W), Western-North (WN), North (N) and Western-North (WN). Cluster analysis of Kullu shows arrival of air masses from West (W), Southern-West (SW), Northern-West (NW) and one arising at the place itself. Hence most of the trajectories reached North Indian cities from Western-North directions.

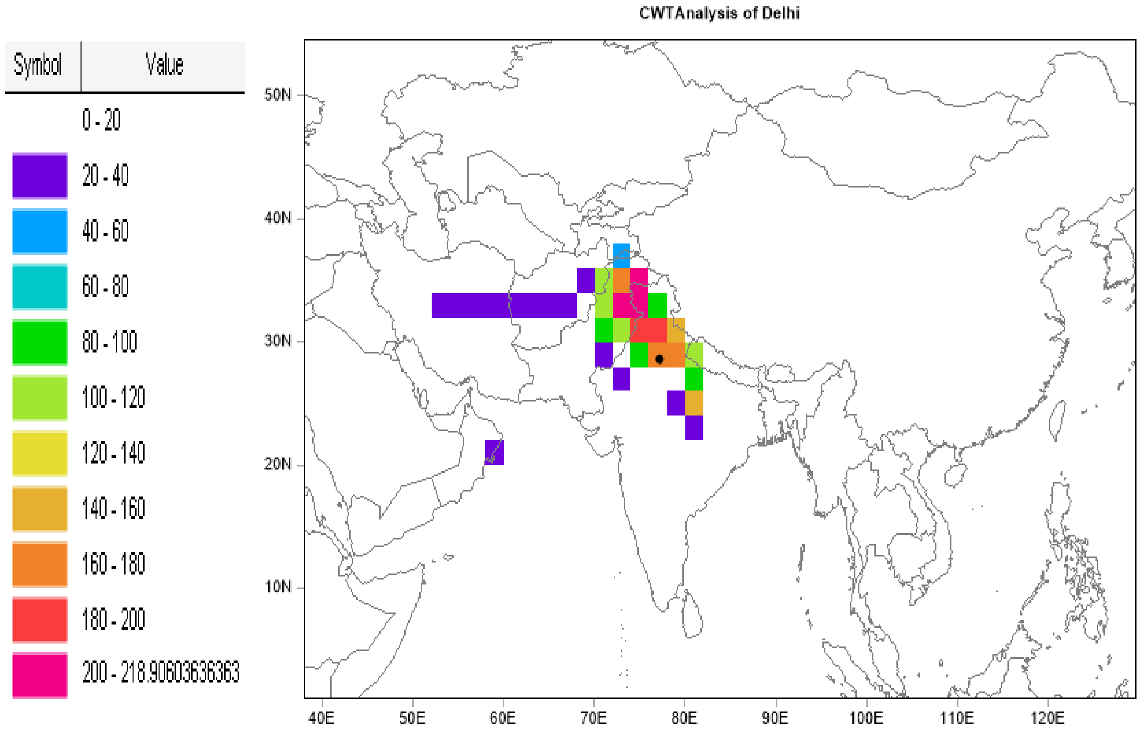


Fig.5.26: CWT Analysis of Delhi

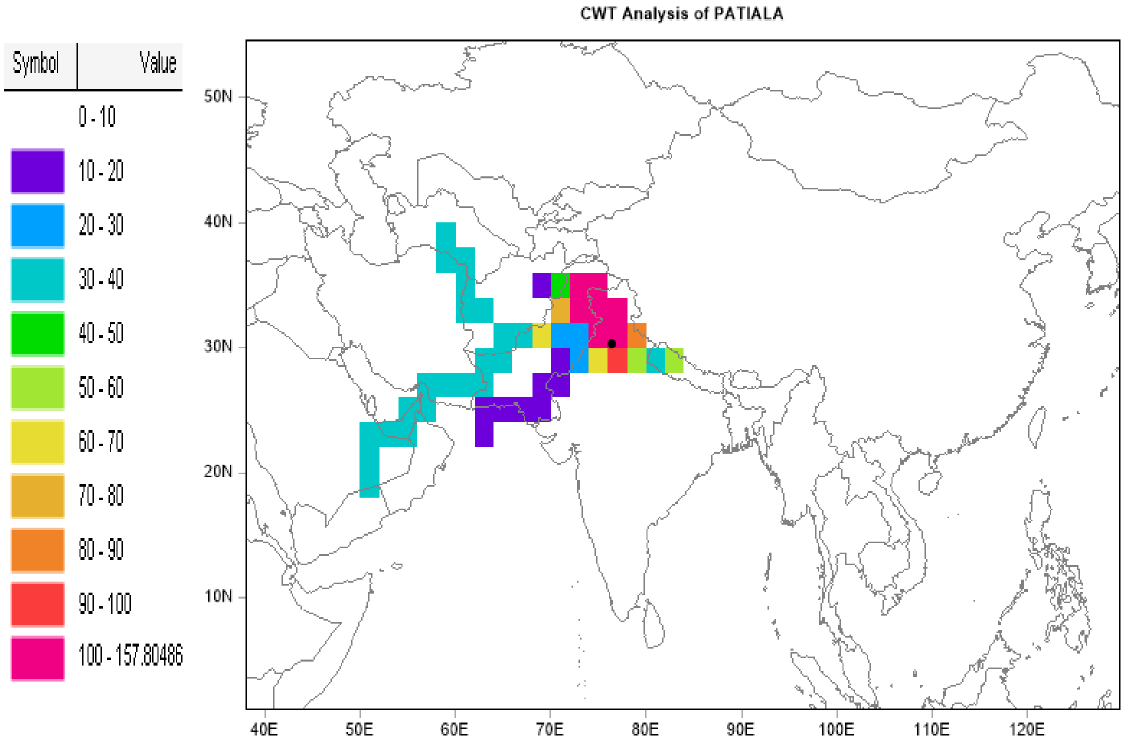


Fig.5.27: CWT Analysis of Patiala

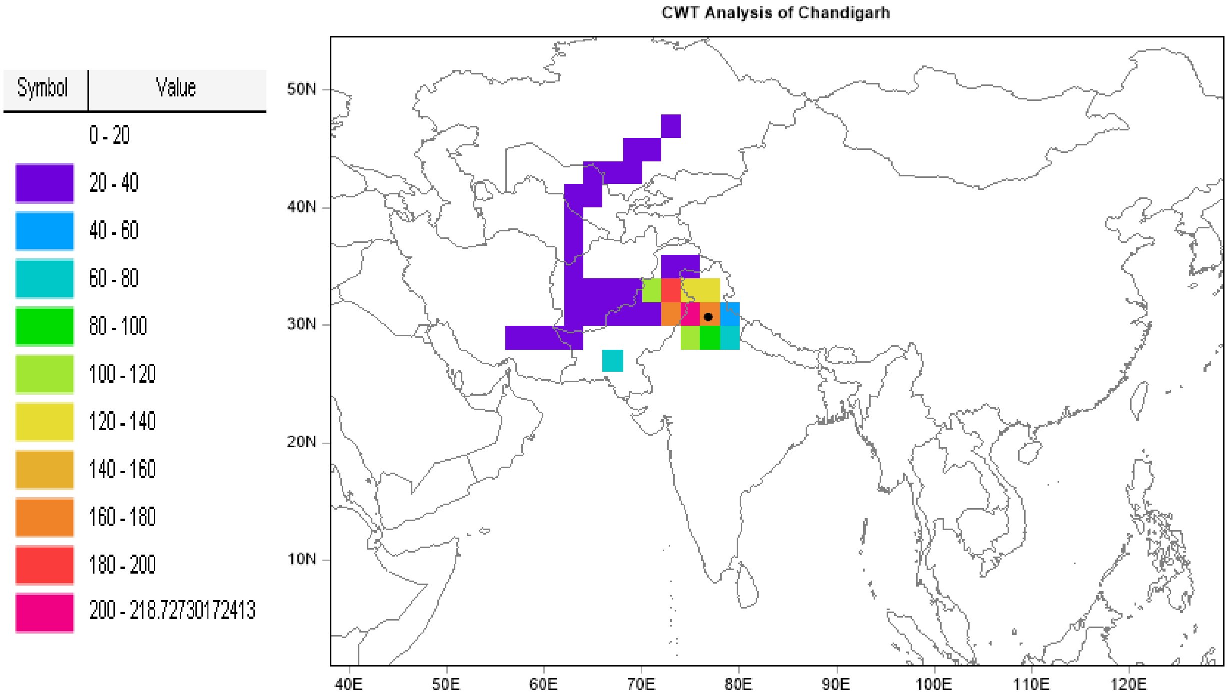


Fig.5.28: CWT Analysis of Chandigarh

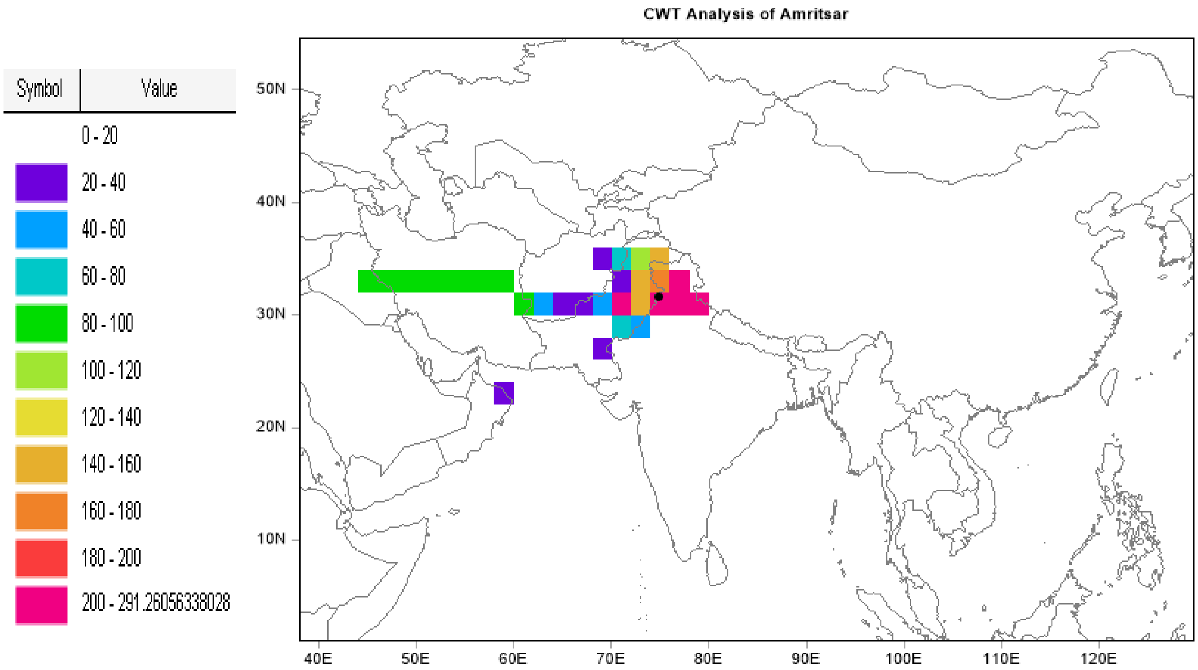


Fig.5.29: CWT Analysis of Amritsar

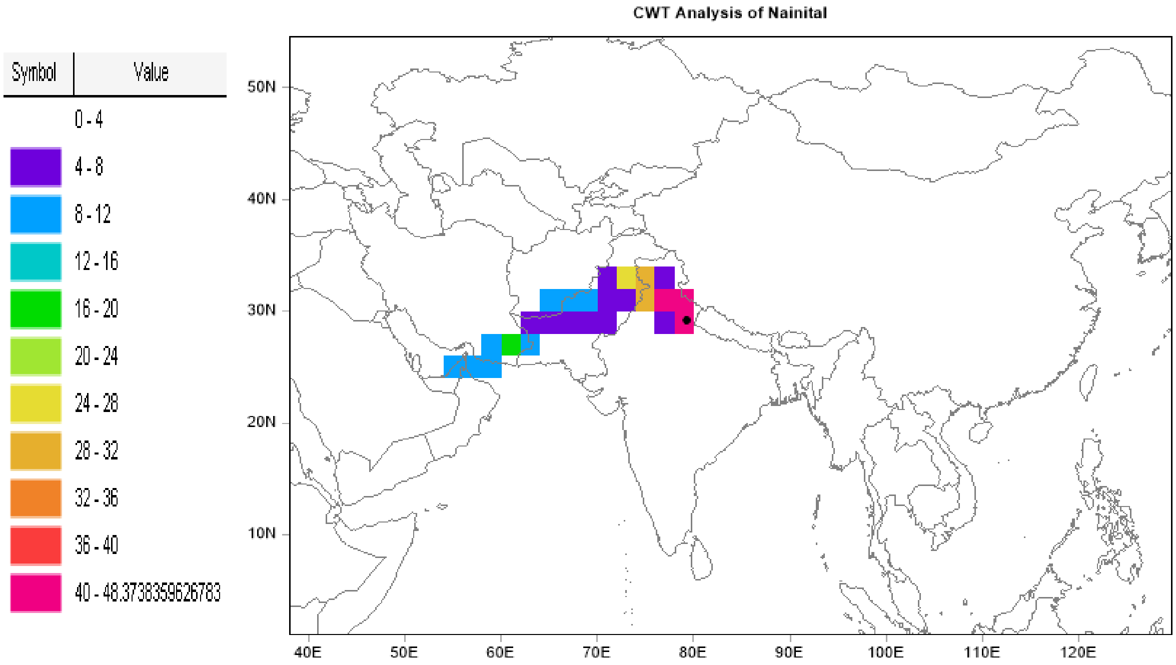


Fig.5.30: CWT Analysis of Nainital

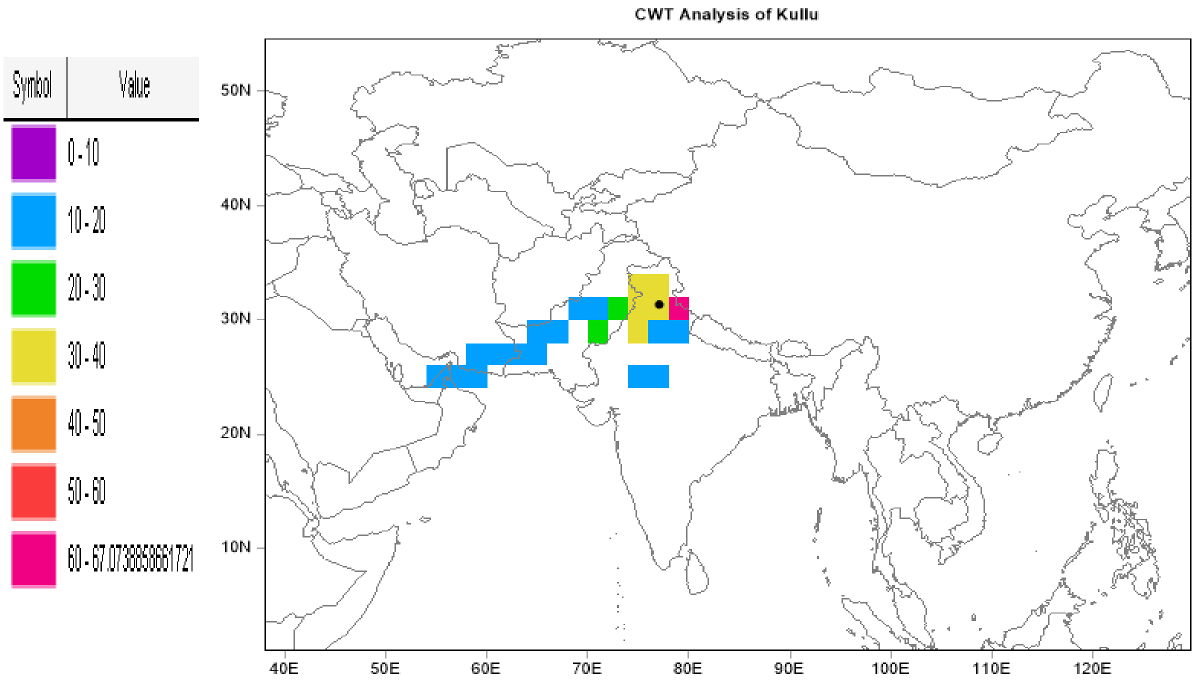


Fig.5.31: CWT Analysis of Kullu

Figures 5.26, 5.27, 5.28, 5.29, 5.30 and 5.31 show the distribution of weighted trajectory concentrations which gives the information on the relative contribution of source regions potentially affecting $PM_{2.5}$ concentrations at Delhi, Patiala, Chandigarh, Amritsar, Nainital and Kullu respectively. According to the results of the CWT analysis, potential source areas contributing to $PM_{2.5}$ concentrations in Delhi are Jammu Kashmir, Pakistan (Gujranwala, Falsalabad), Punjab and Haryana. And in Patiala also, maximum $PM_{2.5}$ concentration is contributed from North. Major source areas contributing to Patiala are Jammu Kashmir, Punjab, Himachal Pradesh, Haryana and Northern Pakistan (Gujranwala). Potential source areas contributing to $PM_{2.5}$ concentrations in Chandigarh are Amritsar, Lahore and Chandigarh itself. After these Delhi is also contributing to $PM_{2.5}$ concentrations in Chandigarh but in lesser concentrations than the potential source areas. $PM_{2.5}$ has also travelled from Himachal Pradesh but in lesser concentrations than areas in Punjab. On the other hand, in Amritsar potential source areas are Amritsar itself, Chandigarh, Himachal Pradesh and Uttar Pradesh. Lesser amounts are also contributed from Jammu & Kashmir and Gujranwala (Pakistan). Potential sources contributing to PM_{10} concentration in Nainital are Himachal Pradesh and Uttar Pradesh. Amritsar is also contributing to pollution in Nainital although in very less amounts. But PM_{10} concentrations in Nainital are below NAAQS Standards. In Kullu only Uttar Pradesh was identified as potential source contributing to $PM_{2.5}$ concentrations. Himachal Pradesh and Punjab also contributed but concentrations were very less. Hence from the results it is very clear that states undergoing crop residue burning are contributing the most in $PM_{2.5}$ Concentrations in North Indian cities.

5.4 CHARACTERIZATION

Quartz filters on which ambient air $PM_{2.5}$ samples were collected were analyzed for the determination of concentrations of ionic species (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) of the three sites i.e. NPL, Delhi; Village Kherijattan, Punjab and Thapar University, Patiala as well as filters on which TSPM were collected in three different agricultural sites were also analyzed. Characterization was done at NPL, Delhi. Graphical representations of all the ions at NPL, Delhi; Village Kherijattan, Punjab and Thapar University, Patiala are shown in figures 5.32, 5.33 and 5.34 respectively and that of TSPM samples are shown in figure 5.35.

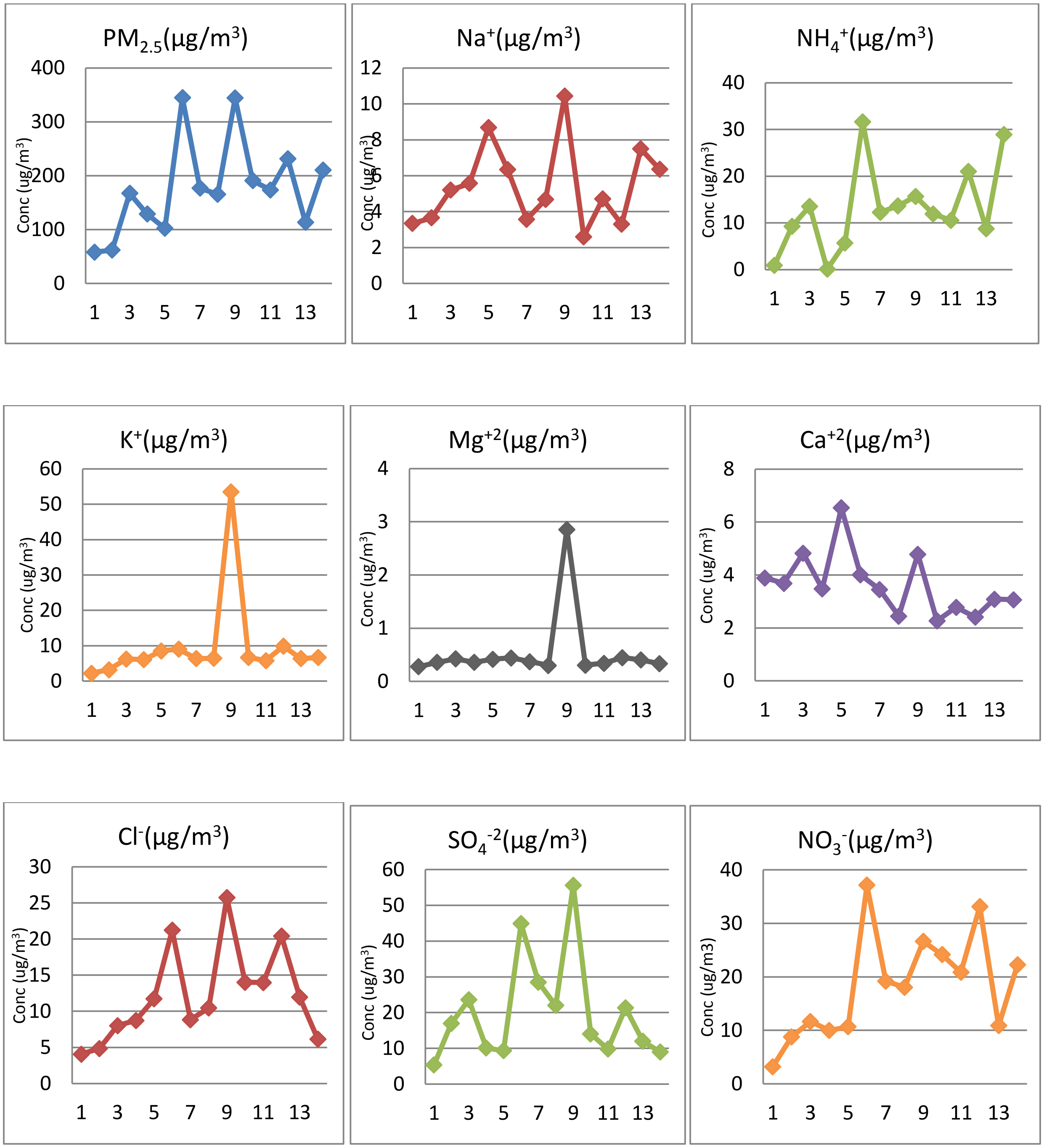


Fig.5.32: Graphs of concentration of all the ions at NPL, Delhi

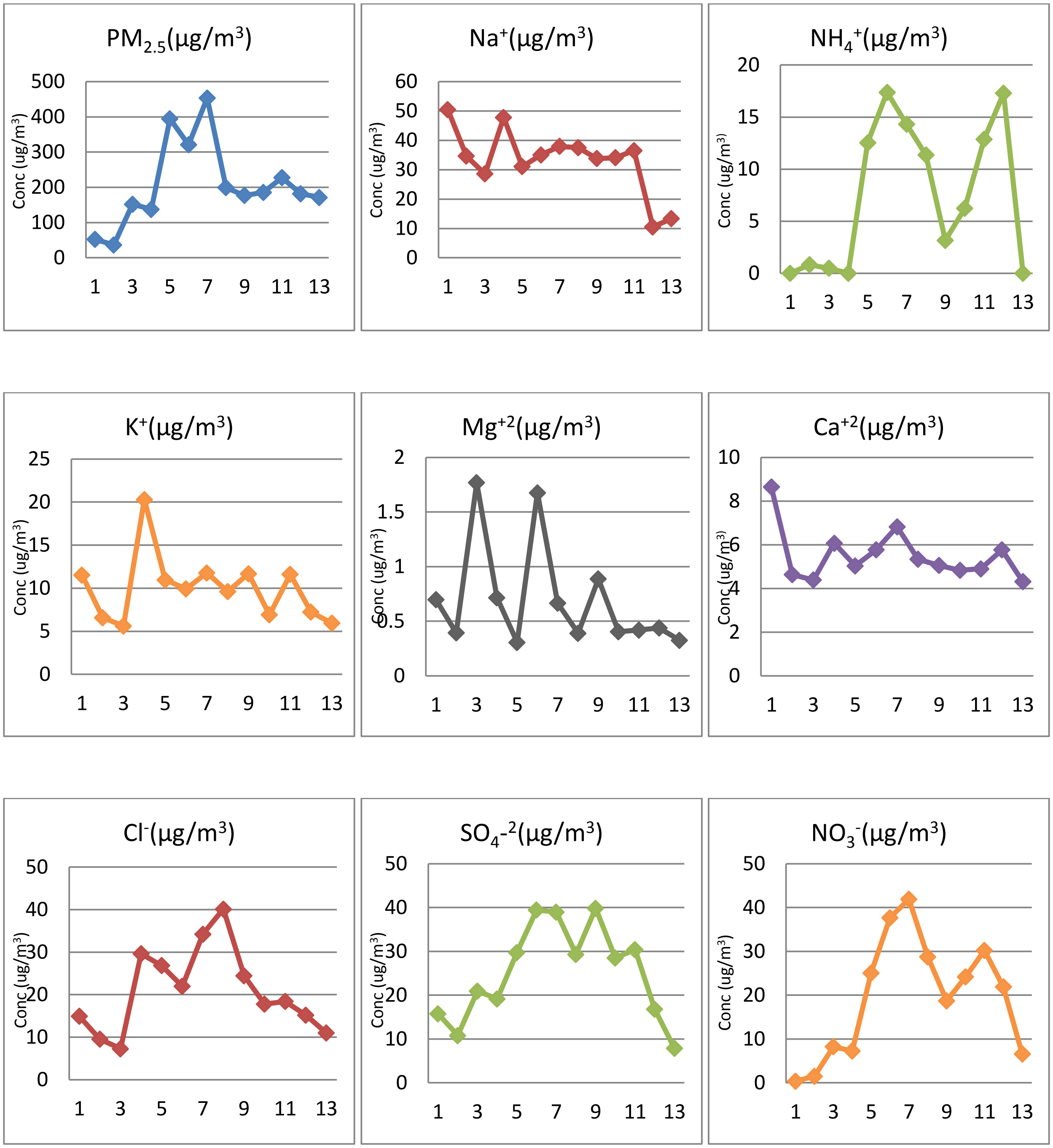


Fig.5.33: Graphs of Concentration of all the ions at Village Kherijattan, Punjab

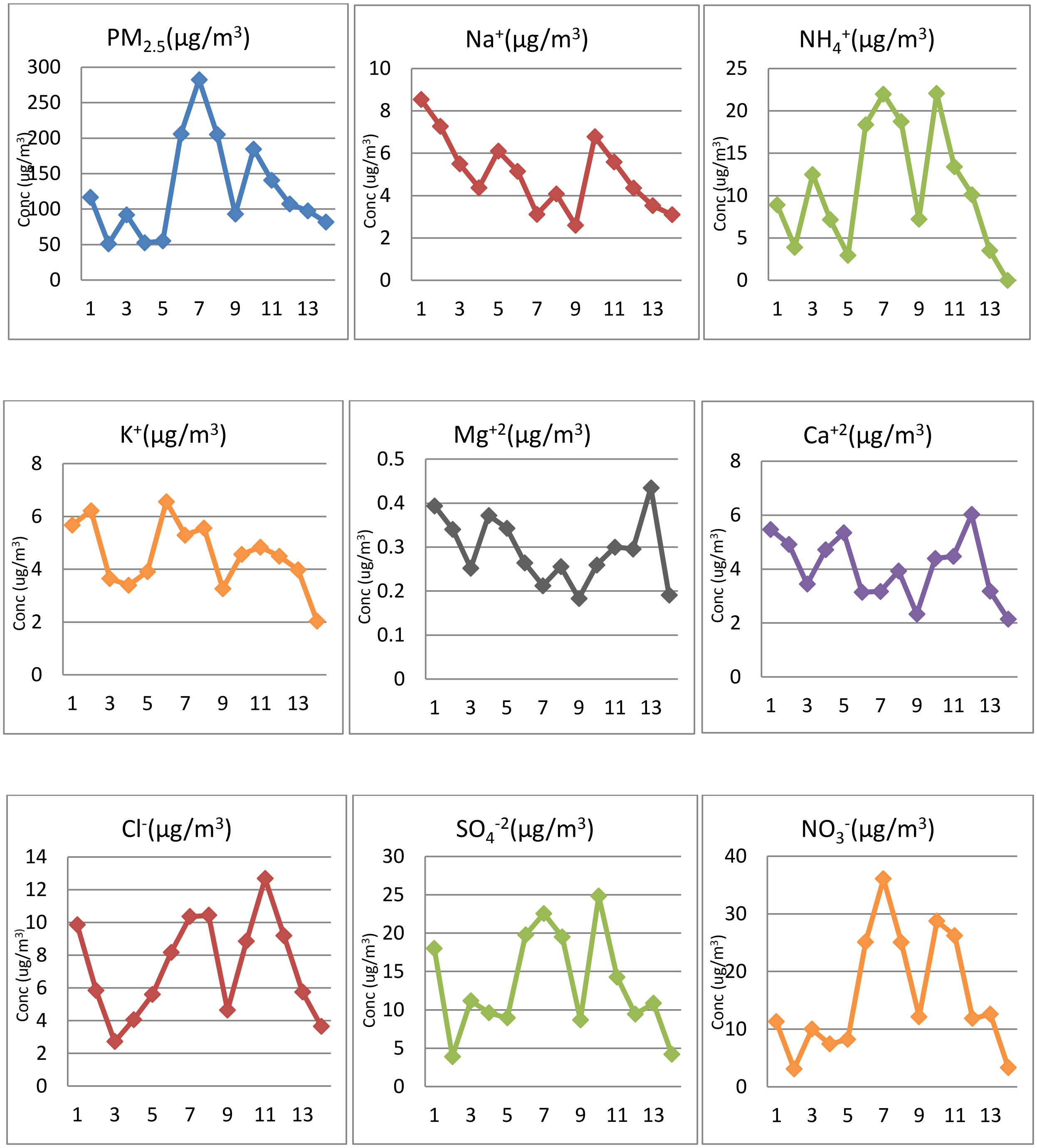


Fig.5.34: Graphs of concentration of all the ions at Thapar University, Patiala

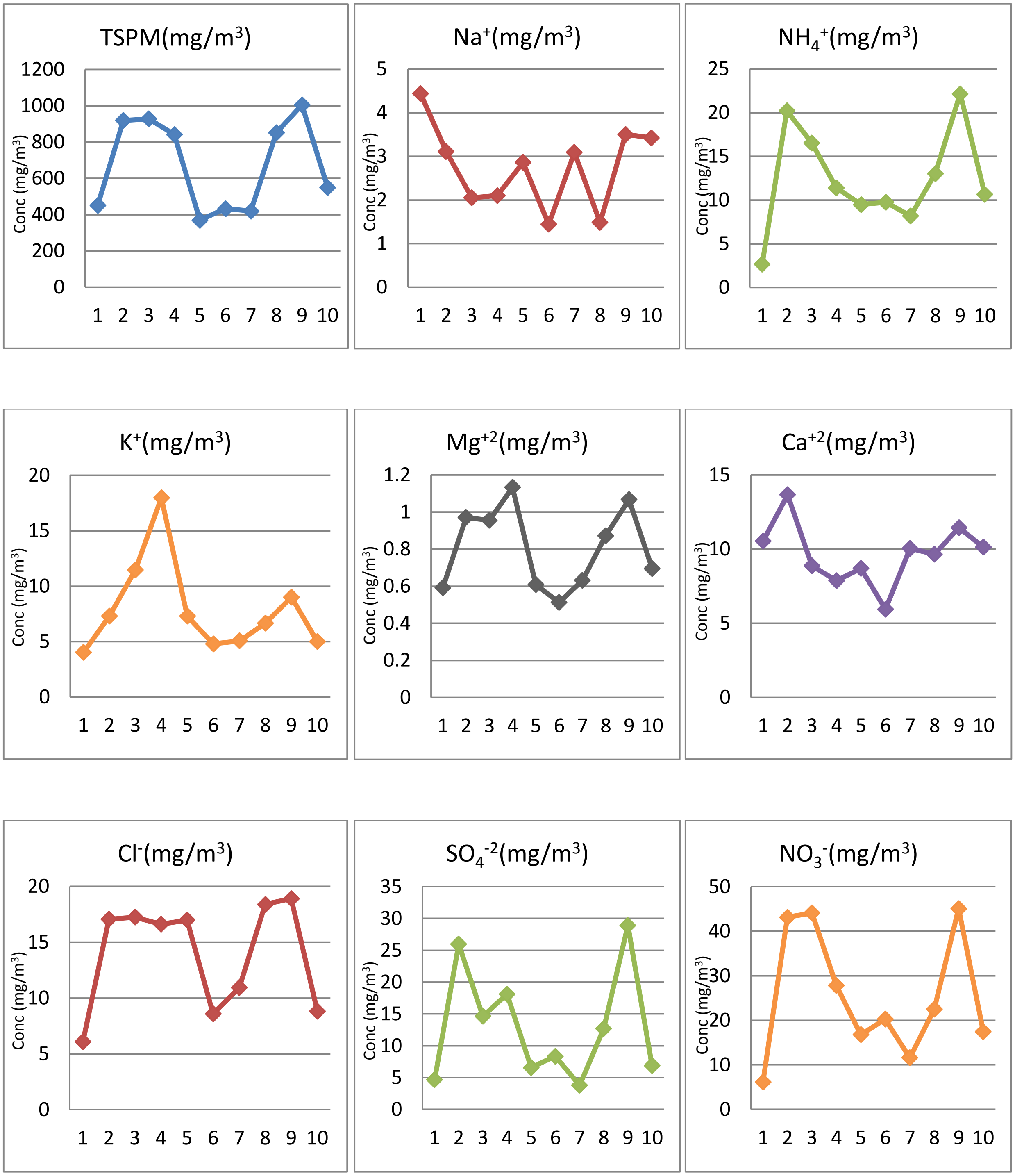


Fig.5.35: Graphs of concentration of all the ions of TSPM samples

In village Kherijattan which is purely an agricultural site Na^+, K^+, Ca^{+2} concentrations are varying in same trend so probably they are coming from the same source which is crop burning since K^+ is the marker of biomass burning *(Lynam and Keeler, 2006; Zhang et al., 2008; Tiwari et al., 2009; Chelani et al., 2010)*. Also initially NH_4^+ was much lesser and increased suddenly when the burning started at the field. Hence burning also released NH_4^+. At Thapar University, Patiala Mg^{+2} and Ca^{+2} trend are almost same so they are coming from same source probably road dust, since both are markers of road dust (*Almeida et al., 2005; Lynam and Keeler, 2006; Shridhar et al. 2010; Gajghate et al. 2012)*. From the above figures it is clear that the maximum $PM_{2.5}$ concentration at NPL, Delhi was observed on the day of Diwali i.e. 11/11/15 and the concentration of ions Na^+, K^+, Mg^{+2}, Cl^-, SO_4^{-2} showed a marked increase on that day. Average concentration of Na^+ in Village Kherijattan was 35ug/m^3, on the other hand it was only 5ug/m^3 and 5.4ug/m^3 at TU, Patiala and NPL, Delhi respectively. Similarly average concentration of K^+ in Village Kherijattan was 10ug/m^3 and at TU, Patiala and NPL, Delhi was 4ug/m^3 and 6ug/m^3 respectively. Thus it shows the more concentrations of biomass burning markers in Village Kherijattan which is the proper agricultural site. As compared to $PM_{2.5}$ samples at agricultural field TSPM samples had much lesser concentrations of Na^+ concentrations, almost 5 times lesser but K^+ concentrations were almost same for both $PM_{2.5}$ and TSPM samples. Average concentration of NH_4^+ ions in Delhi and Patiala was almost same showing the formation of secondary aerosols *(Watson et al., 2008; Shridhar et al. 2010)*. Nitrate ion concentrations were almost same at all the sites which may be coming from secondary aerosol formation or diesel vehicles (*Maykut et al., 2003; Chelani et al., 2008)*, hence showing the diesel vehicular pollution at the sites. Therefore it is clear that crop residue burning lead to release of $PM_{2.5}$ having K^+ and Na^+ ions as major components.

5.5 PRINCIPAL COMPONENT ANALYSIS

PCA was applied using IBM-SPSS Statistics software. The criteria used in selecting the optimal models in terms of source identification (PCA) was the identification of major sources with physically reasonable principal components whose eigen values were larger than 1 after Varimax rotation. Various ionic concentrations were given as an input to the model and after that the following steps were performed to run the PCA in software to get the results. Hence the tables 5.9 and 5.11 explain the total variance of components at Patiala and Delhi, respectively and the tables 5.10 and 5.12 show the rotated component matrix of Patiala and Delhi respectively. Rotated component matrix explained the dependence of each ion on particular component.

A) Principal Component Analysis of Patiala

Table 5.2: Total Variance Explained at Patiala

Component	Initial Eigen values			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.681	52.012	52.012	4.681	52.012	52.012
2	2.604	28.929	80.941	2.604	28.929	80.941
3	.533	5.920	86.861			
4	.456	5.071	91.931			
5	.415	4.612	96.543			
6	.205	2.283	98.826			
7	.061	.681	99.506			
8	.028	.316	99.822			
9	.016	.178	100.000			

Table 5.3: Rotated Component Matrix of Patiala

	Component	
	1	2
NO_3^-	.956	-.180
NH_4^+	.943	
$PM_{2.5}$	.943	-.265
SO_4^{-2}	.929	
Cl^-	.800	.321
K^+	.342	.838
Ca^{+2}		.881
Na^+		.852
Mg^{+2}	-.259	.773

PCA analysis of Patiala yielded two factors with eigen values greater than 1.0 after Varimax rotation. The overall model explained 81% of the total variance. The rotated component matrix (factor loading) is presented in table. However, interpretation of the extracted principal components was not straightforward. The first factor component accounted for 52% of the total variance, and showed high loadings of NO_3^-(0.956) which is indicative of diesel vehicular pollution as well as higher concentration of SO_4^{-2}(0.929) and Cl^-(0.8) which indicate industrial pollution from coal fire powered plants and cement kilns *(Saolapurkar and Sharma, 2006; Wan et al., 2009; Shridhar et al. 2010; Majewski et al., 2013; Xu et al., 2015)*. Hence source 1 extracted is combination of vehicular pollution as well as industrial pollution. Source 2 highly loaded with elements K^+ (0.83) and Na^+ (0.85) can be interpreted as biomass burning *(Harrison et al., 1997; Watson and Chow, 2001; Zheng et al., 2005; Duan et al., 2006; Song et al., 2006; Tiwari et al., 2009; Chelani et al., 2010; Dall'Osto et al., 2013)*. Source 2 was validated using the K/Na ratio for different biomass burning reported in literature. The K/Na ratio varies 0.6 to 2.92 for various type of biomass burned *(Zheng et al., 2007; Ke et al., 2008; Kong et al., 2010; Pant and Harrison, 2012)*. The ratio estimated in this study also lies in this range which clearly indicates that the second component which accounts for 28% of the total variance is biomass burning.

B) Principal Component Analysis of Delhi

Table 5.4: Total Variance Explained at Delhi

Component	Initial Eigenvalues			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.113	56.812	56.812	3.986	44.290	44.290
2	2.244	24.930	81.742	3.371	37.453	81.742
3	.767	8.525	90.267			
4	.365	4.058	94.325			
5	.325	3.611	97.936			
6	.118	1.316	99.252			
7	.053	.586	99.838			
8	.013	.146	99.984			
9	.001	.016	100.000			

Table 5.5: Rotated Component Matrix of Delhi

	Component	
	1	2
NO_3^-	.977	
$PM_{2.5}$	.920	.335
NH_4^+	.840	-.105
Cl^-	.470	.463
SO_4^{-2}	.589	.368
Mg^{+2}	.342	.864
Na^+		.861
K^+	.410	.847
Ca^{+2}	-.349	.711

It is seen that two components have eigen values greater than one, therefore two source categories were identified in Delhi. The first identified principal component which accounts for 57% of total variance was clearly interpreted as vehicular emissions because of higher loadings of NO_3^-(0.977) *(Keeler et al., 2006; Lee and Hopke, 2006; Watson et al., 2008; Zhang et al., 2008; Owoade et al. 2015).* The second identified principal component was highly loaded with elements K (0.84) and Na (0.86) which can be interpreted as biomass burning *(Harrison et al., 1997; Watson and Chow, 2001; Zheng et al., 2005; Duan et al., 2006; Song et al., 2006; Tiwari et al., 2009; Chelani et al., 2010; Dall'Osto et al., 2013).* The evidence of open agricultural field burning and biomass fuel burning been reported in literature *(Parmer et al., 2001; Nair et al., 2006, Chowdhury et al., 2007)* for Delhi region. Source 2 was also validated using the K/Na ratio for different biomass burning reported in literature. The K/Na ratio varies 0.6 to 2.92 for various type of biomass burned. The ratio estimated in this study also varied from 0.98 to 1.86 lies in the range of values reported in literature indicting the strong influence of paddy biomass burning during winter in Delhi region *(Zheng et al., 2007; Ke et al., 2008; Kong et al., 2010; Pant and Harrison, 2012).*

CHAPTER 6

CONCLUSION

This study was conducted to analyze the contribution of wheat and rice stubble burning practices on concentration levels of $PM_{2.5}$ over North India. $PM_{2.5}$ was monitored in the ambient air at several sites of northern India viz. Patiala, Chandigarh, Amritsar, Delhi, Nainital and Kullu. Aerosol samples were collected on Quartz filter papers of 47mm of Whattman brand using dual channel dust sampler and fine dust sampler units for a 24 h period during rice harvesting season (October,2015-November,2015). Total Suspended Particulate Matter (TSPM) was also measured at three different agricultural sites near Patiala during the peak time of burning for two hours.

The concentration weighted trajectory (CWT) receptor model was used to identify spatial source distribution and contribution of regional-scale transported aerosols. Three-dimensional 5-day backward trajectories arriving at all the sites, 500m above ground level were calculated using HYSPLIT-4 trajectory model during burning episodes. $PM_{2.5}$ samples of Delhi and Patiala were further analyzed for ionic composition using ion analyzer. PCA Model source apportionment was made to understand the depth of effect of agricultural residue burning. Principal component analysis with varimax rotation was used to qualify the source contributions to $PM_{2.5}$. Most striking features are given below:

- Distinct increase in concentrations of $PM_{2.5}$ was observed at all the monitored sites during crop residue burning episodes showing the impact of crop residue burning on North Indian cities. The impact of crop residue burning remained in the atmosphere even after burning stopped which indicates large residence time of particulate matter (PM) in the atmosphere. It was also seen that Delhi had much higher concentrations of $PM_{2.5}$ as compared to Patiala and Chandigarh which indicates more vehicular pollution in Delhi. Amritsar was found to be the most polluted city among all the monitored cities showing the impact of Industries and agricultural fields in its vicinity.
- CWT results indicated that states undergoing crop residue burning were potential contributors of $PM_{2.5}$ concentrations in North Indian cities. Hence, aerosols released from crop residue burning travelled long distances causing local as well as regional air pollution.

- Crop residue burning led to release of $PM_{2.5}$ having K^+ and Na^+ ions as major components. Although, increase in K levels was observed at all the sites but strong association between K levels and Crop Residue Burning was obtained at Village Kherijattan (Agricultural site) as compared to other monitoring sites. This indicated that Crop Residue Burning was a dominating source at agricultural site as compared to the other sources in the increment of $PM_{2.5}$ load. Since K^+ 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 $PM_{2.5}$ pollution in North India.
- Using PCA, in Delhi the first identified principal component which accounted for 57% of total variance was clearly interpreted as vehicular emissions. The second identified principal component was highly loaded with elements K (0.84) and Na (0.86) which was interpreted as biomass burning.
- Over Patiala first component extracted from Principal Component Analysis was interpreted as combination of vehicular pollution as well as industrial pollution and second component in this case also was interpreted as biomass burning. Hence, it is evident that biomass burning was one of the principal sources of pollution in Delhi as well as Patiala.

FUTUTRE RECOMMENDATIONS

The present study covers the impact of crop residue burning with respect to $PM_{2.5}$. Therefore, further refinement in the study can be carried out by considering the effect on gaseous pollutants i.e. NO_x, SO_x and CO_2.

In present study chemical characterization of samples included only ion analysis, hence analysis of $PM_{2.5}$ samples targeting large number of metals, Organic carbon/Elemental carbon and organic compounds would better improve understanding of the state of particulate pollution due to biomass burning and its associated impacts on human health.

The present study involved the chemical characterization of two cities only and thus source apportionment of only Patiala and Delhi was done using characterization results. Therefore in future samples of all the cities can be analyzed and source apportionment of all the cities that were monitored can be done to find out the contribution of crop residue burning to air pollution.

In this study Principal Component Analysis was used for source apportionment which qualifies the sources thus to refine the source apportionment results quantification of sources can also be done by using Positive Matrix Factorization or Chemical Mass Balance receptor models.

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ANNEXURE I

Revised national Ambient Air Quality Standards (NAAQS) - 2009

S. No	Pollutant	Time Weighted Average	Concentration in Ambient Air		
			Industrial, Residential, Rural and Other Area	**Ecologically Sensitive Area (notified by Central Govt.**	**Methods of Measurement**
1.	Sulphur Dioxide (SO_2), µg/m^3	Annual* 24 hours**	50 80	20 80	- Improved West and Gaeke -Ultraviolet fluorescence
2.	Nitrogen Dioxide (NO_2), µg/m^3	Annual* 24 hours**	40 80	30 80	- Modified Jacob & Hochheiser (Na-Arsenite) -Chemiluminescence
3.	Particulate Matter (<10µ), µg/m^3	Annual* 24 hours**	60 100	60 100	- Gravimetric -TOEM - Beta attenuation
4.	Particulate Matter (<2.5µ), µg/m^3	Annual* 24 hours**	40 60	40 60	- Gravimetric - TOEM - Beta attenuation
5.	Ozone (O_3), µg/m^3	8 hours** 1 hour**	100 180	100 180	- UV photometric - Chemilminescence - Chemical Method
6.	Lead (Pb), µg/m^3	Annual* 24 hours**	0.50 1.0	0.50 1.0	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper - ED-XRF using Teflon filter

7.	Carbon Monoxide (CO), mg/m^3	8 hours** 1 hour**	02 04	02 04	- Non Dispersive Infra Red (NDIR) spectroscopy
8.	Ammonia (NH3), µg/m^3	Annual* 24 hours**	100 400	100 400	- Chemiluminescence - Indophenol blue Method
9.	Benzene (C6H6), µg/m^3	Annual*	05	05	- Gas chromatography based continuous analyzer -Adsorption and Desorption followed by GC analysis
10.	Benzo(a)Pyrene(BaP)- particulate phase only, ng/m^3	Annual*	01	01	- Solvent extraction followed by HPLC/GC analysis
11.	Arsenic (As), ng/m^3	Annual*	06	06	- AAS /ICP method after sampling on EPM 2000 or equivalent filter Paper
12.	Nickel (Ni), ng/m^3	Annual*	20	20	- AAS /ICP method after sampling on EPM 2000 or equivalent filter Paper

* Annual arithmetic mean of minimum 104 measurements in a year at a particular site taken twice a week 24 hourly at uniform intervals.

** 24 hourly or 08 hourly or 01 hourly monitored values, as applicable, shall be complied with 98% of the time in a year. 2% of the time, they may exceed the limits but not on two consecutive days of monitoring.

Note: Whenever and wherever monitoring results on two consecutive days of monitoring exceed the limits specified above for the respective category, it shall be considered adequate reason to institute regular or continuous monitoring and further investigation.