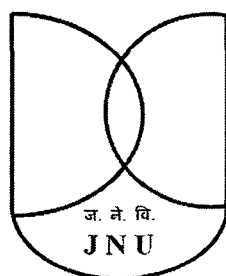


**AN ESTIMATION OF AEROSOL EXPOSURE USING PERSONAL
SAMPLER AT VARIOUS LOCATIONS OF DELHI**

**Dissertation submitted to the Jawaharlal Nehru University
in partial fulfilment of the requirements
for the award of degree of**

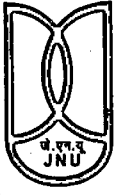
MASTER OF PHILOSOPHY

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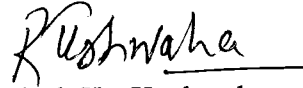
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CERTIFICATE

The research work embodied in this dissertation entitled “An Estimation of Aerosol Exposure Using Personal Sampler at various locations of Delhi”, has been carried out at the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. The work is original and has not been submitted in part or in full, for any other degree or diploma of the university



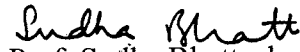
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CHAPTER 1: INTRODUCTION

Chapter 1

INTRODUCTION

Urbanization and industrialization has led to huge pollution such as air pollution, water pollution and noise pollution etc. Air pollution is one of the major causes of concern for deterioration of environmental condition, particularly in developing countries such as India, Bangladesh, China etc. It includes gaseous constituents, volatile chemicals, aerosols and their atmospheric reaction products. Industrial revolution, play an important role in air pollution as well as climate changes by global warming. Apart from GHGs, aerosols also have the potential to impact the climate, even though the nature of its impact has not yet been clearly established (Charlson et al., 1992). Scientists have much to learn about the way aerosol (directly & indirectly) affect climate. Most of the scientists believe that aerosol are offsetting 20 to 50 percent of expected global warming that is attributed to increases in the amount of carbon dioxide from anthropogenic activities (Charlson et al., 1992; IPCC, 2001). But it does not mean that the aerosol forcing will always counterbalance the greenhouse gases forcing. Meinrat et al. 2005 have pointed out that aerosol forcing will decline relative to GHGs forcing in future because aerosol have shorter life time (5-7 days) in air. In reality, we are still unaware of the sign of aerosol forcing because this information requires the understanding of chemical composition, size and shape of aerosols worldwide. The process that can disturb the overall energy balance can cause climate change or perturbation (Kaufman et al., 1997; Seinfeld and Pandis., 1998). A process that alters the radiative balances of the climate system is known as radiative forcing (Charlson et al., 1991, 1992; Hansen et al., 1997, 1998; Russell et al., 1999; Bates, 1999; Raes et al., 2000). Radiative forcing can be internal or external. External forcing operates from outside the Earth's climates system and includes orbital variation and changes in incident solar flux. Volcanic activity is an example of an internal forcing mechanism (Hoffmann et al., 1987; Moorthy et al., 1996). Similarly, changes in the composition of the atmosphere constitute another major internal forcing mechanism, and the

best examples are the greenhouse gases and aerosols (Crutzen and Andreae., 1990; Charlson et al., 1992; Clarke, 1993; Kaufman et al., 1997; Bates, 1999 Bates et al., 2000; Rode, 2000; Prospero et al., 2002). Changes in the greenhouse gas or aerosol content of the atmosphere affects the radiative balance of the climate system (Haywood and Ramaswamy, 1998). The earth climate is strongly influenced by the manner in which solar radiation is absorbed and reflected in the atmosphere (Schwartz et al., 1995). During the past 100 years the amount of carbon dioxide in the atmosphere has increased, out of which about 25% on account of the human activities (fossil fuel/ biomass burning) (Le Treut et al., 1998; IPCC., 2001). This has caused the surface temperature of the earth to increase globally by about one Kelvin (Le Treut et al., 1998). In recent years, there has been a substantial increase in interest in the influence of anthropogenic aerosols on the climate through both direct and indirect radiative effects. As the characteristics and effects of atmospheric aerosols on climate are still poorly understood, the results of aerosol research are of extreme relevance for contemporary era.

Atmospheric aerosol consists of particle of both natural and anthropogenic origins. It is now well established that the element from natural sources are generally found in the coarse particle whereas element emitted from anthropogenic activities are associated with fine particles (Seinfeld, 1986). On an average, global aerosols, due to human activities, account for about 10 percent. Most of the 10 percent is concentrated in the Northern Hemisphere, especially downwind of industrial sites, slash-and-burn agricultural regions, and overgrazed grasslands (www.earthobservatory.nasa.gov). Atmospheric aerosols can be divided into two groups, continental and marine aerosols, on the basis of their genesis. Continental aerosols prominently comprise of wind-blown mineral dust, and carbonaceous and sulphate particles produced by forest fire, land use and industrial activities (Penner, et al., 1994). On the other hand, marine aerosols are mainly sea-salt particles produced by wave-breaking, and sulphate particles formed by the oxidation of dimethyl sulphide released by phytoplankton (Charlson, et al., 1987). Continental aerosols can be of both, scattering and absorbing type, whereas marine aerosols are mostly of the scattering type.

Atmospheric aerosols are of importance because of their impact on human health (Dockery et al., 2003), ability to scatter light; thereby affecting visibility, and their role in global climate change (Scienfeld et al., 1986). These aerosol particles, consisting of complex inorganic and organic compounds, affect the radiation budget, both directly and indirectly. They directly scatter and absorb incoming solar radiation and outgoing terrestrial radiation, and indirectly have the ability to modify cloud microphysics and albedo (Charlson et al., 1987). Most importantly, the particle size distribution of aerosols is vital for an accurate and reliable assessment of their impact on human health (Fernandez et al., 1994). The US Environmental Protection Agency (EPA) has defined four terms for categorizing particles of different sizes according their diameter ultrafine $<0.1 \mu\text{m}$, fine $0.1 -2.5 \mu\text{m}$, coarse $2.5 -10 \mu\text{m}$ and supercoarse $> 10 \mu\text{m}$ (EPA 2002). The shape and density of the particle affect its aerodynamic diameter and thus the aerodynamic diameter characterizes the filtration, respiratory deposition and separation of the particle (Hinds 1999). Instead of using the terms “fine” and “coarse” particles, the terms “inhalable”, “thoracic” and “respiratory” particles are used in occupational hygiene. Particles deposit in different parts of the respiratory system, with the particle size serving as a principal factor in determining the deposition location. Relative to deposition concerns, ISO [1995] uses the following particle size classifications:

- (1) Inhalable fraction – the mass fraction of total airborne particles that is inhaled through the nose and mouth.
- (2) Thoracic fraction – the mass fraction of inhaled particles penetrating beyond the larynx.
- (3) Respirable fraction – the mass fraction of inhaled particles that reach the gas exchange region of the lung.

The 50% cut-off diameter for the thoracic fraction is $10 \mu\text{m}$ and for the respirable fraction it is $4 \mu\text{m}$ (CEN 1993). The inhalable fraction of total airborne mass fraction consists of particles that are inhaled through the nose and mouth. Particles greater than approximately $50 \mu\text{m}$ in diameter can enter the nose and mouth,

and particles $>10\ \mu\text{m}$ are deposited on the ventilation pathway surfaces above the trachea. Fine particles gain entry to the alveolar region of the lungs (Rodes and Wiener 2001). The concentrations and size distribution of trace metals are governed by the nature of emission to the atmosphere, as well as by rates of wet and dry deposition, cloud processing exchange of air between the boundary layer and free troposphere, and chemical transformations (Allen et al., 2001). The distribution of trace metals within atmospheric particles over continental Europe has been studied by many investigators (Allen et al., 2001). Particles size distribution is also an important input in models dealing with climate change studies, as radiative forcing of short wave and long wave radiation critically depends on size distribution (Bryson et al., 1967). An addition, particles size characteristic of aerosol also effect cloud physics (Hayhood et al., 1997). The existence of modalities in the distribution may also help in the identification of aerosol source (Infante et al., 1991). Size distribution of atmospheric particles within which heavy metals are associated is important since this not only influence the toxicity of a metal when inhaled, but also controls the extent to which metals may be dispersed via atmospheric transportation. Different sizes of particulate matters may cause different environmental effects for example; acid rain formation is affected by the high content of chemical aerosols contained in man-made pollutants with particles sizes in the range from 0.001 to $2\ \mu\text{m}$. As aerosol size decreases, the pH value and the content of Ca decreases, but the contents of sulphate and ammonium increase. The size distribution of aerosols is one of the important factors for acid rain formation (Zhao and Lin., 1987). The extent of the impact of dust on air quality, public health and climate depends on particles size and chemical composition (Murry et al., 2001). Nutrient such as Fe (iron) in aerosol have also been found to influence marine ecosystem when aeolian particles are deposited and disssolved (Kaufman, Tanre, Kolber, and Falkowski, 2001; Zhuang, Yi, Duce, and Brown, 1992). Heavy metal such as Zn, Pb, Cu, Sb, and Cd present health hazards due to their toxicity (Hsu et al., 2004). Coarse PM originates from crushing and grinding operations, from re-suspended dust due to high density traffic on paved roads, from vegetative detritus, and from PM generated by industrial sources, and construction (Register, 2006). These facts make

coarse PM a potential health concern because they are inhaled and can then accumulate in the upper airways of the respiratory track of human being also some biological materials are deposited which trigger , triggers asthma ,bronchitis etc. This was shown in recent panel study of NCAAES (North Carolina Association of Agricultural Extension Secretaries), which reported stronger associations in asthmatics between coarse PM level and pulmonary and vascular responses, than between fine PM and those responses (Yeatts et al., 2007). In addition, a recent epidemiological study suggested a strong causal relationship between coarse PM and hospitalization for respiratory infections in children (Lin et al., 2005). Studies have also reported that coarse PM deposited in the upper airways caused significantly more lung inflammation resulting in the release of pro-inflammatory cytokines by lung cells, through various mechanisms than other size fractions of PM (Lin et al., 2005). Changes in circulating physiological health effects have also been noted (Yeatts et al., 2007). The contact may take place between the substance in an environmental medium (such as air, water, soil, food) and the surface of the human body such as skin or respiratory tract. The chain of events starts from the source of a pollutant and ends as the dose causing health effect.

Personal exposure to pollutant is defined as the event when a person comes in contact with the pollutant at a particulate instant of time (Ott, 1982). According to this definition, exposure has units of concentration and time. After uptake of a substance into the body, it is referred to as the dose. Dose and dose-response are outcomes of an exposure, because there is no dose without exposure (Ott 1982).

Exposure assessment has been described as one of the main component of environmental health risk assessment of conjunction with hazard identification and dose response assessment (NRC, 1983). A flow chart describing the exposure to air pollutants has been shown in Fig.1

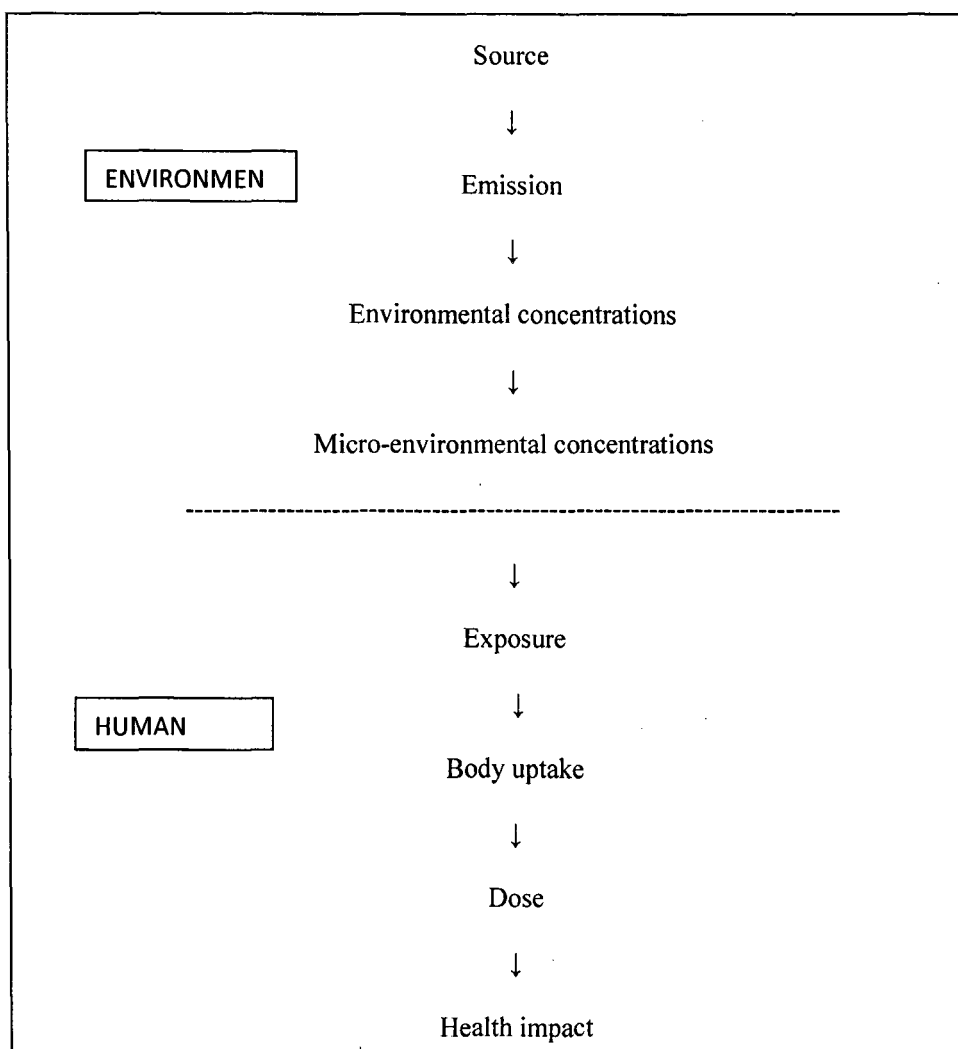


Fig 1 Dose-response assessment

There are three general types of measurements aiming at exposure assessment; direct (personal), Indirect (micro environment and questionnaires) and biological monitoring (Liroy, 1990). Microenvironments are well-defined surroundings *e.g.* home, office, automobile that can be treated as homogenous or well characterized with respect to the concentration of some pollutant or other agent (EPA, 1992). Personal

exposure to particulates has been proved to have a major impact on human health. Human exposure to particulates has been associated with increased mortality among those with cardiopulmonary disease, with symptoms for asthma, bronchitis and pneumonia, with decreased lung function, and retarded lung developments (Pope et al., 1991). Personal exposure assessment study that examined the particulate matters (PMs) and health effects with chronic obstructive pulmonary disease, heart disease and asthma were based on the mass concentration measurements of the Total Suspended Particles (TSP) (EPA, 2004). Keeping in mind the importance of above mentioned, many works on aerosols have been carried out across the world and India. Few significant are as follows;

The fine particles measured in the Helsinki area consist mainly of sulphate (21%), nitrate (12%), ammonium (9%) and other material (43%). Coarse particles mainly originate from crustal matter (59%) (Pakkanen et al., 2001). In USA it was observed that the Black Smoke mainly consists of carbon or soot particles generated during combustion processes, such as energy production and from car engines (Gray and Cass, 1998) and it is a marker component for local traffic (Pakkanen et al., 2000). A very good correlation between coarse and fine fraction of TSPM was observed. It has been observed that the elements associated with natural resources, such as soil and oceans, usually occur in coarse aerosols, while the elements emitted from anthropogenic sources are associated with fine aerosols (Sceinfeld, 1986). Air particulate matter around the Cathedral of Burgos (Spain) was studied by Esbert et al in 2000. He collected and analyzed particulate matter using SEM-EDX and found fine particles present the highest concentration. A study conducted of Seville, Spain by Fernandez et al., in 1997 showed the soil aerosol as the largest contribution in the atmospheric pollution with Fe and Al as the most abundant metals in the source. They also found that Fe and Al were mainly in carbonate or oxide fraction (40 %) and residual fraction (40 %), while Pb and Cu mainly appear as oxide and carbonate form i.e. 50 % and 40 % respectively. Cd prevails in soluble or exchangeable form. A study was conducted in UK in 1998 by Pacyna on trace metals released into environment during combustion of fossils fuels, high temperature industrial processes as well as waste

incineration. He observed that natural emissions like crustal minerals, volcanism, erosion and surface wind, as well as forest fires and ocean are mainly responsible for the high atmospheric concentration of SPM. He also concluded that the estimates for natural sources are uncertain on a global scale, re-suspended surface dusts make a large contribution to the total natural emission of trace metals to the atmosphere. The metallic contribution to the atmosphere from the natural sources for various metals were as follows; Cr, Mn, and V > 50% and Cu, Ni, Pb, Zn, Mo, and Sb > 20%. While volcanic activities probably generate 20 % of atmospheric Cd, Hg, As. Cr, Cu, Ni, Pb and Sb. Srivastava and Jain, (2009) studied size distribution and source apportionment of total suspended particulate matter (TSPM) and associated Metals concentration at Delhi. They established fine concentration is more dominant as compare to coarse, they also found most of the heavy metals were present in fine fraction of TSPM. Shandilya et al., (2007) compared pollution level of Delhi and Satna for PM_{2.5}, PM₁₀, and total suspended particulate (TSP). They found that Delhi was more polluted with the concentration of PM_{2.5}, PM₁₀ and TSP as 126.7±28, 268.6±39 and 687.7±117 µg/m³ than that of Satna where the concentration of the same pollutants were 20.5±6, 102±41 and 387.6±222 µg/m³ respectively.

In addition to this studies on personal exposure have also been carried out at various parts of world some prominent are as follows; in North Carolina (USA) a study was conducted at in 2008 by Williams et al. They observed a high variation of personal PM_{10-2.5} mass concentration between 7.6 to 40.2 µg/m³. Another study was conducted by Vallejo et al in 2004 on personal exposure, in indoor and outdoor environment, to PM_{2.5} in permanent residence of Maxico city. They found that PM_{2.5} concentration in outdoor environment was higher (89.50µg/m³) than that of indoor environment (67.55µg/m³).

In yet another study, conducted on personal exposure assessment of outdoor workers in a metropolitan city, Mumbai, India by Kulkarni and Patil in 1999, has resulted a variable exposure concentration of 66- 1026 µg/m³. Singh et al., (2008) worked at five locations of Renukoot (an industrial area of Eastern Utter Pradesh), and found that exposure concentration of PM₁₀ in the range of 69.3 to

118.9 $\mu\text{g}/\text{m}^3$. He also analyzed PM10 for some heavy metals (Fe, Zn, Cu, Cr, Cd, Mn and Pb) and found that Fe is most abundant while Cd is lowest. He also checked the correlation between different metals and PM10, and found a significant correlation between Zn, Cu Pb and Ni, and PM₁₀. Kulkarni (2006) investigated the exposure on lower Income Group (LIG) and Middle Income Group (MIG) of Mumbai, India. He found LIG to be more exposed to aerosol (186 $\mu\text{g}/\text{m}^3$) than MIG (73 $\mu\text{g}/\text{m}^3$). Kulkarni and Patil (2002), conducted the toxic metals exposure study among the citizen of Mumbai. He found the presence of Pb, Ni, Cd, Cu, Cr, K, Fe and Mn in the personal exposure. Alarmingly Pb (4.2 $\mu\text{g}/\text{m}^3$) exceeded the Indian standards (NAAQS i.e.1 $\mu\text{g}/\text{m}^3$) norms.

The above mentioned suggests the importance of particle size distribution, to better understand the personal exposure. However, many works have been carried out at various parts of world using different techniques, but for Delhi, so far, no work has been conducted on personal exposure, keeping in mind the different sizes of the particles and associated metals. This is why we have undertaken this personal exposure study at Delhi with the following objectives;

1. To determine the concentration of various sizes of aerosols during personal exposure.
2. To estimate aerosol exposure using personal sampler at various location of Delhi.
3. To assess the human exposure to toxic/nontoxic metals associated to aerosol.
4. To check the correlation between various metals and particulate matter.
5. To check the regression of various size aerosols with each other.
6. To do source apportionment of particulate matter at Delhi.

CHAPTER 2: MATERIALS AND METHODS

Chapter2

2.1 Study area

Study area Delhi is the capital city of India. It is situated 160 km south of the Himalaya. Its geographical position is $28^{\circ} 2' 17''$ N to $28^{\circ} 53'$ N Latitude and $76^{\circ} 20' 37''$ E to $77^{\circ} 20' 37''$ E Longitude, and an altitude of 213.3 - 305.4 m above the mean sea level. It is about 1,100 km away from the nearest coast of the North Arabian Sea. The Delhi region is located in the border zone lying between the rich rains washed Gangetic planes to the east and semi arid tracts to the West and South West.

The climate of Delhi is mainly influenced by the prevalence of continental air during the major part of the year. Extreme dryness with an intense hot summer and cold winters is the main characteristics of the climate of the Delhi. The normal annual rainfall is 611mm. Winds are predominantly westerly and tend to be more northerly in the afternoons. Easterly and south easterly winds are more common in the monsoon months (Srinivas, 2005). January is the coldest month with the mean maximum temperature at 21.3° C and the mean minimum temperature at 7.3° C. May and June are the hottest months of the year where the temperature touches $46-47^{\circ}$ C.

Generally low wind speed and temperature inversion conditions, which restrict the mixing height to low levels, lead to an accumulation of air borne pollutants over the city particularly in winter months. In summer, the situation is exacerbated by frequent dust storm. Westerly winds from the Great Indian Desert, Thar Desert of Rajasthan, bring a large amount of Suspended Particulate Matter (SPM), as high as 500-800 tons/ sq. miles.

It is estimated that over 3000 metric tons of air pollutants are emitted in Delhi every day. The sources of air pollution in Delhi are; emission from vehicles 67%, coal based thermal power plants 13%, industrial units 12% and domestics 8 % (MoEF, 2002).

2.2 Sampling Sites

Sampling was conducted at five different sites of National Capital Region of Delhi (NCR). The locations have been illustrated in Fig. 2 and described below

2.2.1 Jawaharlal Nehru University (JNU)

JNU campus, far from any industrial activity, is situated in the southern outskirts of Delhi. Even though it has low vehicular traffic, ongoing construction work for new school buildings and hostels during the period of sampling, has contributed to the rise in aerosol concentration. Apart from residential and academic areas for students and faculties, it also has many *dhabas* (canteens) and hostel messes which also contribute aerosols, especially carbonaceous.

2.2.2 Dhaura Kuan (DK)

DK is a major traffic junction with very heavy traffic density. The traffic density increases sharply during morning and evening rush hours.

2.2.3 Hauz Khas (HK)

HK is a residential as well as commercial area of South Delhi. Hauz Khase has a population of about 1 million. This area is surrounded by some major road networks, which could be responsible for the high pollution level in HK.

2.2.4 Okhala Industrial Area (OIA)

Okhala is Delhi's industrial area. Industries over there are involved in manufacturing mainly agricultural products, automobile spare parts, electronic and electrical parts, furniture, pharmaceuticals, chemicals,

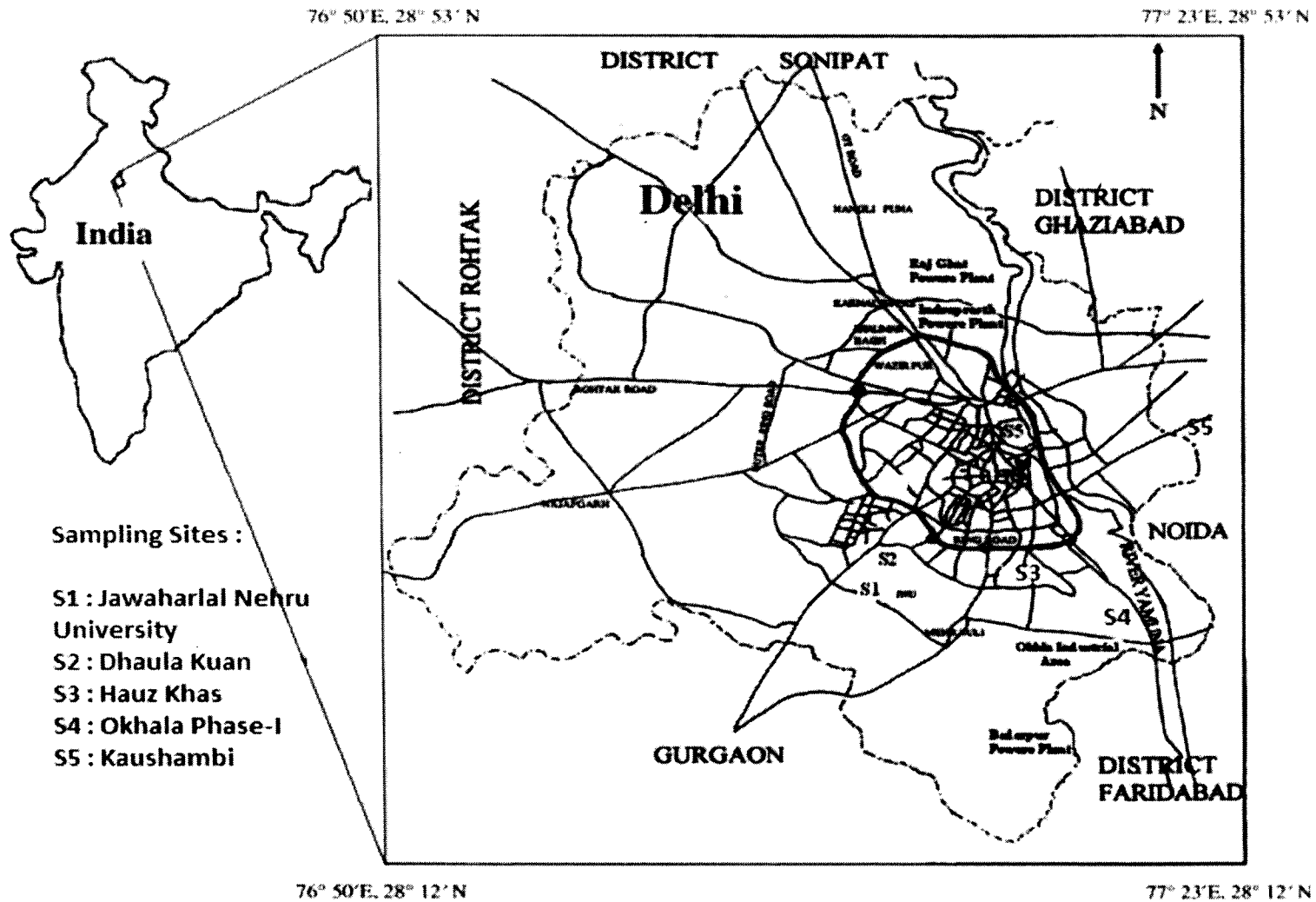


Fig. 2: location of sampling site (not in scale)

transportation accessories, scientific, printing equipments etc. this site is close vicinity to the Badarpur thermal power plant (BTPP).

2.2.5 Kaushambi (KSB)

Kaushambi is a residential area of Ghaziabad (adjacent to Delhi). Around 5000 people reside in this colony. Kaushambi is just 200 meters away from the national highway (NH2) leading to U.P.

2.3 Sampling Device

Equipment used was an eight stages personal cascade sampler, (model: NS-298) manufactured by Tisch Environmental, OH, USA. The sampler operates at an average flow rate of 2.5 LPM. The filters used were 34 mm Glass Fibre (GF-A) Grade A filters. The size range of particles which may be collected at each stage together with 50% cutoff diameter has been given in Table 1. The photo graph of the equipment (Marple Cascade Impactor) has been shown in Fig. 3.

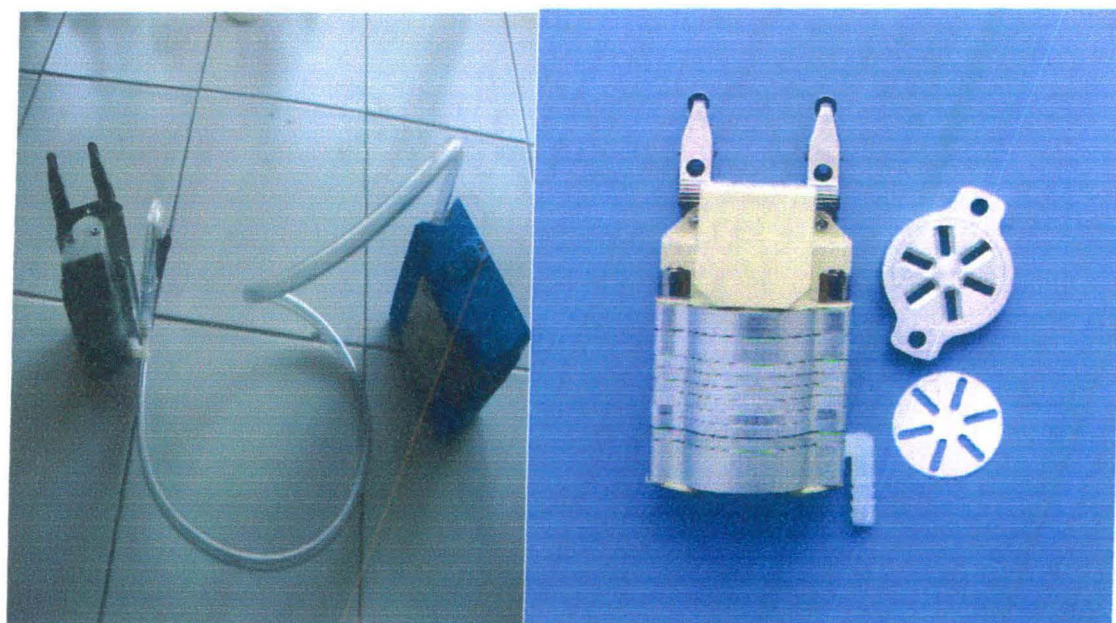


Fig. 3: Sampling instrument

Table-1 Cut-off diameter

Impactor stage number	Size ranges of particles (μm)	50 % Cutoff Diameter(μm)
1	Max-18.1	21.3
2	18.1-12.3	14.8
3	12.3-7.9	9.8
4	7.9-4.8	6.0
5	4.8-2.5	3.5
6	2.5-1.2	1.55
7	1.2-0.7	0.93
8	0.7-0.5	0.52
Back-up filter	0.5-Minimum	0.25

2.4 Sampling procedure

Samples were taken from five different sites. The samples were collecting on pre-weight Whatman GF/A filter papers. The filter were kept in a vacuum desiccator for 24 hours before sampling to removing any moisture content, before mounting on the air sampler. After sampling, filter papers are immediately transferred to vacuum desiccators to again de-moisturise them in the same manner.

2.5 Estimation of Particulate matter (Gravimetric analysis)

The concentration of various sizes of aerosols (corresponding to each filter) can be determined using the following formula.

$$C = W/V$$

Where, C = concentration in $\mu\text{g}/\text{m}^3$, $W = (W_2 - W_1)$ in grams (g),

W_2 = post sampling weight (g) W_1 = pre sampling weight (g)

Therefore, $W = (W_2 - W_1) \times 10^6 \mu\text{g}$

V = volume of the air, in cubic meter, went through the sampler can be represented as

Therefore, $V = Q \times T$

Where Q = average flow rate (cubic meter per minute), T = total sampling duration in minute.

TSPM was calculated by adding all the stages i.e. Stage 1 + Stage 2 + Stage 3 + Stage 4 + Stage 5 + Stage 6 + Stage 7 + Stage 8 + Back up filter.

2.6 Chemical Analysis

Metals present in particulate matter were detected using number of instruments like Atomic Absorption Spectrometry (AAS), Energy Dispersive X-ray Fluoresces (ED-XRF), Inductive Couple Plasma Mass Spectrometry (ICP-MS) etc. In the present work the determination of metals (Pb, Ca, Mg, Ni, Fe, Cd, Cr, Zn) were carried out using an AAS made by thermo Scientific (Model No: GF 95Z).

2.7 Metal Estimation

For estimation of metals following procedures were adapted

2.7.1 Acid Digestion of samples

Acid digestion was carried out in Teflon bombs adopting following procedures:

1. Filters were kept in Teflon bombs.
2. 1.5 ml of HF, 3 ml of HNO₃ and 0.75 ml of HCl were added in to it.
3. The closed bombs were kept at 180 °C in to hot air oven for 1 hour.
4. Afterwards the bombs were cooled and opened, to check if any residue is left or not.
5. To digest the residue, if left, 5 ml of 5M HCl was added and evaporated to dryness.

Process No. 5 was repeated till the sample was completely digested and converted in to a transparent solution. After the digestion is complete the sample was diluted to 15 ml with distilled water and stored. The entire process was repeated for all the samples.

2.7.2 Preparation of standards

The standards for various metals to be used in AAS, were prepared as follows.

2.7.2.1 Nickel: - 4.9530 gm of nickel nitrate was dissolved in 100 ml of distilled water, and diluted upto 1 litre in a volumetric flask.

2.7.2.2 Lead: - 1.598 gm lead nitrate was dissolved in 50 ml of 2M HNO₃ and diluted upto 1 litre with distilled water.

2.7.2.3 Cobalt: - 4.038 gm of cobalt chloride was dissolved in 200 ml of distilled water and further diluted upto 1 litre in a volumetric flask with distilled water.

2.7.2.4 Copper: - 1.00 gm of copper metal was dissolved in a minimum volume of 6N HCl and 2 % (V/V) of HNO₃, solution was further diluted upto 1 litre by distilled water in a volumetric flask.

2.7.2.5 Cadmium: - 1.00 gm of cadmium metal was dissolved in 20 ml of 4M HCl and two drops of HNO₃. It was further diluted upto 1 litre in volumetric flask with distilled water.

2.7.2.6 Calcium: - 2.7693 gm of calcium chloride was dissolved in 100 ml of distilled water. It was further diluted upto 1 litre in a volumetric flask with distilled water.

2.7.2.7 Magnesium: - 1.00 gm of magnesium was dissolved in 6N HCl and diluted upto 1 liter in volumetric flask with distilled water.

2.7.2.8 Manganese: - 1.00 gm of manganese metal was dissolved in 50 ml of HCl (S.G.1.18). It was further diluted upto 1 litre in a volumetric flask with distilled water.

2.7.2.9 Iron: - 1.00 gm of iron powder was dissolved in 20 ml of 5M HCl and 5 ml of HNO₃ (S.G.1.42). It was further diluted up to 1 litre in a volumetric flask with distilled water.

2.7.2.10 Potassium: -2.86 gm of potassium chloride was dissolved in 100 ml of distilled water. It was further diluted up to 1 litre in a volumetric flask with distilled water.

2.8 Analysis of samples by AAS

First the instrument was calibrated by aspirating different concentration of standards. Then concentrations against absorbance of various metals were noted by fixing their specific wavelength. The metals content X_1 is expressed in $\mu\text{g/ml}$ and X_2 is blank solution in same unit and subtracted from X_1 to get the corrected concentration of metals. Multiplication with dilution factor gave the total quantity of the metal in samples.

$$T = (X_2 - X_1) \times f \times 15 / V$$

T = Metal concentration ($\mu\text{g} / \text{m}^3$), V = volume of air sample (m^3), X_1 = concentration of unknown test solution, X_2 = concentration of blank test solution, 15 = sample dilution (ml), F = dilution factor.

CHAPTER 3: RESULTS AND DISCUSSIONS

Chapter 3

To understand the aerosol exposure, size fractionated aerosol concentrations were measured in the collected samples at various locations following the procedures given in the section 2.4. The total aerosol concentration was obtained after summing up the concentration of all stages including back-up filter. The sum total of stages 5, 6, 7, 8 and back-up filter were considered as fine. Similarly sum total of stages 3, 4 and 5 considered as coarse. While the sum total of the stages 1 and 2 were assumed as super coarse.

3. 1 Total Suspended Particulate Matter (TSPM)

Fig.4 shows total aerosol concentration at all the different sites. The maximum concentration of $2118.45\mu\text{g}/\text{m}^3$ was observed at OKI followed by DK ($1271.05\mu\text{g}/\text{m}^3$), HK ($1059.21\mu\text{g}/\text{m}^3$), KSB ($776.74\mu\text{g}/\text{m}^3$) and JNU ($490.17\mu\text{g}/\text{M}^3$). Total aerosol concentration is well above the standards by CPCB (Table 2) for ambient environment. While that, it is within the limit, if we compare with the standards provided by OSHA (Table 2)

Table 2: Standards for ambient air and personal exposure (www.osha.gov)

Pollutants($\mu\text{g}/\text{m}^3$)	CPCB Standards For Ambient	OSHA Standards for Personal Exposure
Aerosol Exposure	200 (residential) 500 (Industrial)	5 (mg/m^3) 8 hours
PM _{2.5}	60($\mu\text{g}/\text{m}^3$) 24 hours
PM ₁₀	100($\mu\text{g}/\text{m}^3$) 24 hours
Lead	1($\mu\text{g}/\text{m}^3$) 24 hours	50 ($\mu\text{g}/\text{m}^3$) 8 hours
Nickel	20(ng/m^3) 24 hours	1 ($\mu\text{g}/\text{m}^3$) 8 hours
Chromium	2.5 ($\mu\text{g}/\text{m}^3$) 8 hours
Cadmium	2.5 ($\mu\text{g}/\text{m}^3$) 8 hours
calcium	5 (mg/m^3) 8 hours
Manganese	1 (mg/m^3) 8 hours
Iron	1 (mg/m^3) 8 hours

The concentration of fine fraction at all sites is given in Fig 5. It can be inferred that the fine concentration again exceeds the limits provided by CPCB at all the sites. The maximum fine concentration is found at HK and minimum concentration at JNU. The concentration of coarse and super coarse fractions is depicted in Figs 6 and 7 respectively. It can be observed that the maximum concentration is at OIA, while that lowest is at JNU

From the Figs 4, 6 and 7, it is evident that OIA is most polluted of all the sites. It has maximum concentration of Total aerosol concentration, coarse and super coarse among all the sites. The reason of this type observation could be due to the fact that OIA is an industrial belt of

Delhi, having number of industries. The roads over there are also poorly maintained. Therefore, those industries and roads are the potential sources of total aerosol, coarse and super coarse.

HK has the maximum concentration of fine fraction of total aerosol concentration. The only possible reason for this could be due to a huge number of surrounding roads. These roads are full of vehicles from morning and evening. Therefore contribution from this huge number of vehicles amounts to the maximum concentration of fine particulate matters at HK.

3.2 Size distribution of TSPM

TH-19/33

The percentage contribution of different size fraction (viz. Fine, coarse and super coarse) with the TSPM have been plotted in Fig 8. It shown that at all the sites fine fraction contribution to TSPM is maximum except OIA. Where maximum contribution is due to super coarse ($\approx 50\%$) then coarse (30 %) and lowest is due to fine (23.3 %). It can be due to the fact that roads over there are in very poor condition and are a potential source of larger particles. The traffic flow is also not smooth. Apart from all these, metal, concrete plastic and wood cutting practices continuously go on, which also contributes to the coarser fractions. Contrary to this maximum contribution of fine fraction at all the remaining sites again confirms that the vehicles are the main source of SPM in Delhi (Srivastava and Jain, 2007). Figs 9-13 show the concentration of particulate matter against each size at five different sites. We can conclude that as such no definite pattern of size distribution of particulate matter at various sites is observed.



3.3 Regression analysis of Particulate Matter

Regression analyses were carried out between different size fraction viz. fine and coarse, fine and super coarse and coarse and super coarse. The regression results together with coefficient of regression and equation have been plotted in Figs 14a, b and c. It can be inferred that a very bad regression of fine over super coarse is observed ($R^2 = 0.0226$). It shows that there is no much bearing of fine over super coarse. Similarly a bad regression of fine over coarse is also observed meaning not much explanation of coarse by fine. But a good regression of coarse over super coarse ($R^2 = 0.5923$) depicts that the variation in super coarse can very well be defined by variation in coarse particles.

3.4 Metals

The metal concentrations of all the sites are given in Figs 15, 16 and 17. It can be inferred from these figure that potassium (K) is dominant metal at all the sites, followed by Ca, Mg and Fe. Concentration of K is extremely high at JNU and KSB, this could be due to the fact that JNU is a rocky area (situated on the Aravali ranges) and KSB is in the vicinity of farms, that is why natural soil and rock contribute to the elevated level of K. K is lowest at HK, because this area is full of pavements and surrounded by roads, that is why, due to lack of natural soil and rocks, we observed lowest concentration among the metals. Among the anthropogenically emitted metals viz. Pb, Ni, Cu, Cd, Co and Pb has maximum concentration at all the sites. The reason could be, the road side dust still contains significant amount of Pb. However leaded fuel has been banned in Delhi since 2000. Apart from this, there are many industries of paints, varnishes, pipes, storage batteries and insecticides which do lead related works.

3.5 Size distribution of metals:

The size distribution of 10 metals at different sites is given in Figs 18 a, b, 19a, b, c, d, and 20 a, b, c, d has been discussed in preceding paragraphs.

Lead (Pb): however, there is no definite pattern in the size of particles with concentration, but the dominance of fine at JNU, HK and DK can be seen. While at OKH and KSB coarse is also significant.

Iron (Fe): A very clear descending pattern from fine to Coarse to Super coarse at all sites except JNU, where Fe is totally absent.

Nickle (Ni): Similarly Fe, Ni also shows a descending pattern from fine to coarse to supercoarse at all the sites. In this case fine significantly exceed the coarse and super coarse.

Copper (Cu): Although no definite pattern is observed in this case, but it is clear that fine and coarse dominant at all sites, while the contribute from super coarse is very low.

Manganese (Mn): Here also a clear descending pattern from fine to coarse to super coarse is seen except at JNU, where Mn is very low. Whatever a little concentration of Mn at JNU is observed that is in the coarse and super coarse fraction.

Cadmium (Cd): No definite pattern is observed in the case of Cd but it is clear that fine fraction dominate the distribution at all the sites, except JNU. Alarming a very high concentration of Cd in fine size range is observed at OIA.

Calcium (Ca): However, no precise pattern is observed in case of Ca, but it is clear that fine fraction dominate the distribution. While the concentration of Ca in coarse and super coarse does not differ much at all the site.

Magnesium (Mg): Similar to Ca, Mg also has maximum concentration in fine size range. However the Mg concentration in coarse and super coarse again does not differ much.

Potassium (K): Similar to previous two metals, Ca and Mg, it also has the maximum concentration in fine size range and the concentration in coarse and super coarse is more or less equal.

Cobalt (Co): In this case also distribution is dominated by fine size fraction except HK, where the dominance of coarse is observed. Once again here is not much difference in the concentration of super coarse and coarse fraction except HK.

3.6 Correlation analysis:

Correlation analysis was carried out separately among the different fraction of particulate matter and among the 10 metals. The results (correlation coefficient r), are shown in the Table 3 and 4 respectively. It can be observed from table 2 that a very poor correlation is observed between fine and super coarse while an average correlation is observed between fine and coarse. While a good correlation is observed between coarse and super coarse. It means that there are successive correlation i.e. fine to coarse and then coarse to super coarse.

In case of metals it is found that, a very good correlation ($r > 0.8$) exists between 8 pairs of metals i.e. Cu-Ni, Cd-Ni, Cd-Cu, Mg-Cd, Mg-Ca, K-Mn, K-Ca and K- Mg. While good

correlation ($r = 5-7$) among 10 pairs of metals i.e. Fe-Pb, Mn-Fe, Cd-Pb, Ca-Cu, Ca-Cd, Mg-Mn, Co-Fe, Co-Ni, Co-Ca and Co-Mg was observed.

3.7 Source apportionment

We have tried to identify and estimate the possible sources of different size fractions using principle component analysis (PCA). PCA was executed by the Varimax Rotated Factor Matrix method, based on orthogonal rotation criteria which maximizes the variance of the squared elements in the column of a factor matrix, using a statistical package SPSS (version 16).

A total of 10 components were obtained out of which, three were extracted as principle components (PCs) for TSPM, whilst three PCs were extracted by considering Eigen values more than 1. The detailed results are given in Table 5. The three sources contribute over 95% of Delhi's pollution. The factor 1 (crustal re-suspension i.e. road side dust) contributes about 46%, most of the metals are associated with this because the metals generated from various sources become the part of road side dust in due course of time. The significant contributors are vehicles.

Second source (factor 2), contributes about 26%. This is possibly the industrial source. The main industries are electroplating, plastic and metal alloy industries. Third source (factor 3) is natural or trans-boundary migration, it contributes around 24% of all the sources. Trans-boundary migration brings a good amount of dust, which also elevates the metal concentration of ambient air of Delhi (Yadav and Rajamani, 2006).

Table 3: Result of Correlation Analysis for particulate matter

	fine	coarse	Super coarse
fine	1		
coarse	0.4989	1	
Super coarse	0.1502	0.7696	1

Table 4: Result of Correlation Analysis for metals

Pb	1 Pb	Fe	Ni	Cu	Mn	Cd	Ca	Mg	K	Co
Fe	0.688	1								
Ni	0.412	-0.290	1							
Cu	0.303	-0.224	0.931	1						
Mn	-0.278	-0.655	0.159	-0.125	1					
Cd	0.682	0.190	0.855	0.892	-0.338	1				
Ca	0.149	0.094	-0.349	0.575	-0.738	0.612	1			
Mg	0.292	0.150	0.069	-0.129	0.551	-0.983	-0.818	1		
K	-0.100	-0.147	-0.200	-0.439	0.790	-0.498	-0.987	0.872	1	
Co	0.058	0.584	-0.560	-0.478	-0.169	-0.360	-0.503	0.571	0.452	1

Table 5: Source apportionment of different metals

VARIABLE	FACTOR-1	FACTOR-2	FACTOR-3
Pb			.849
Fe			.637
Ni	.640	.694	
Cu	.785	.500	
Mn		.799	
Cd	.835		.501
Ca	.937		
Mg			.704
K			
Co			
Eigenvalue	4.559	2.572	2.373
% of variance	45.6	25.7	23.7
Cumulative variance	45.6	71.3	95.0
Possible source	Crustal re-suspension	Industrial	Natural/Trans boundary migration

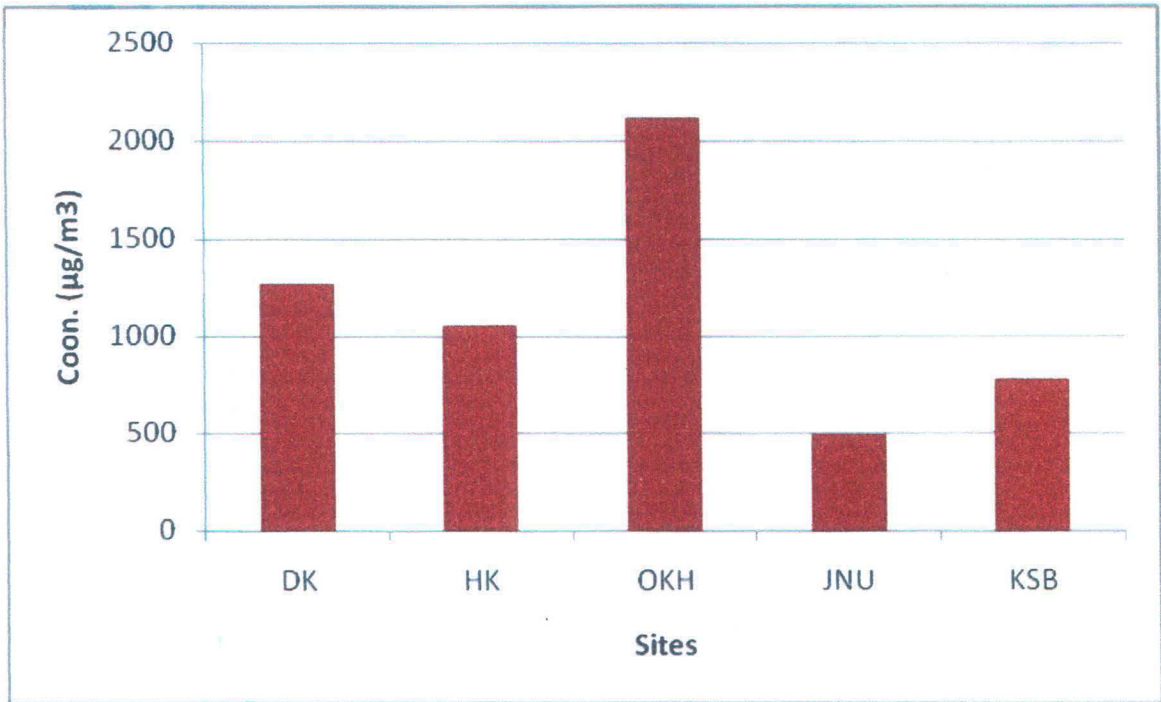


Figure 4 -Total Concentration of particulate matter at All Sites.

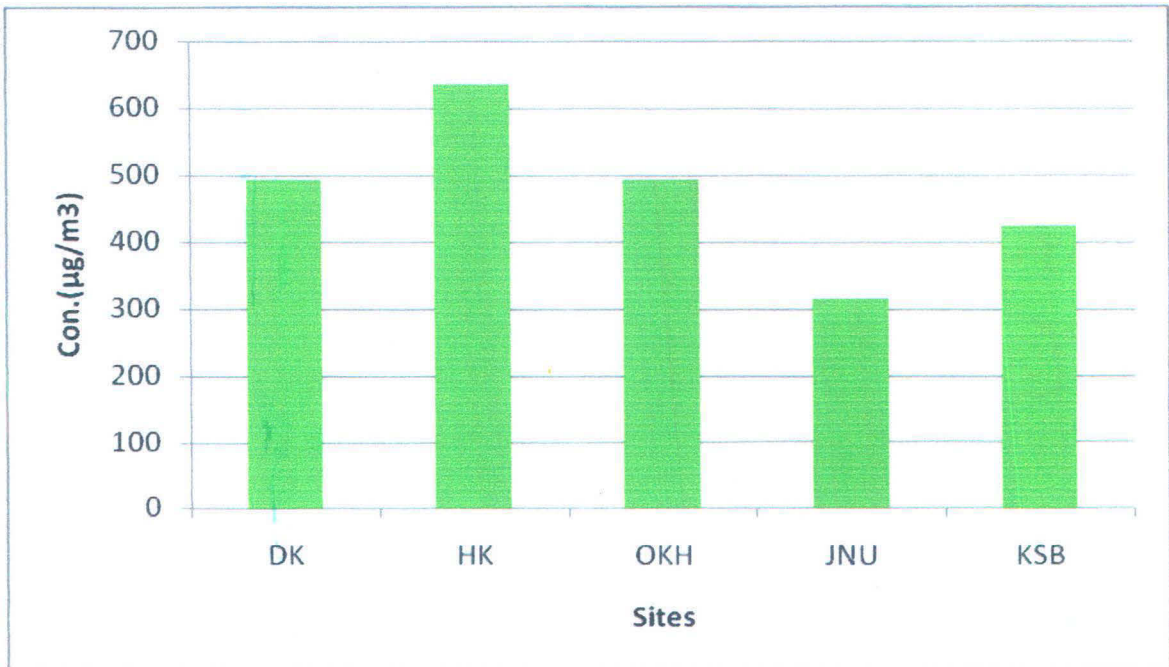


Figure 5 Fine Concentration at All Sites.

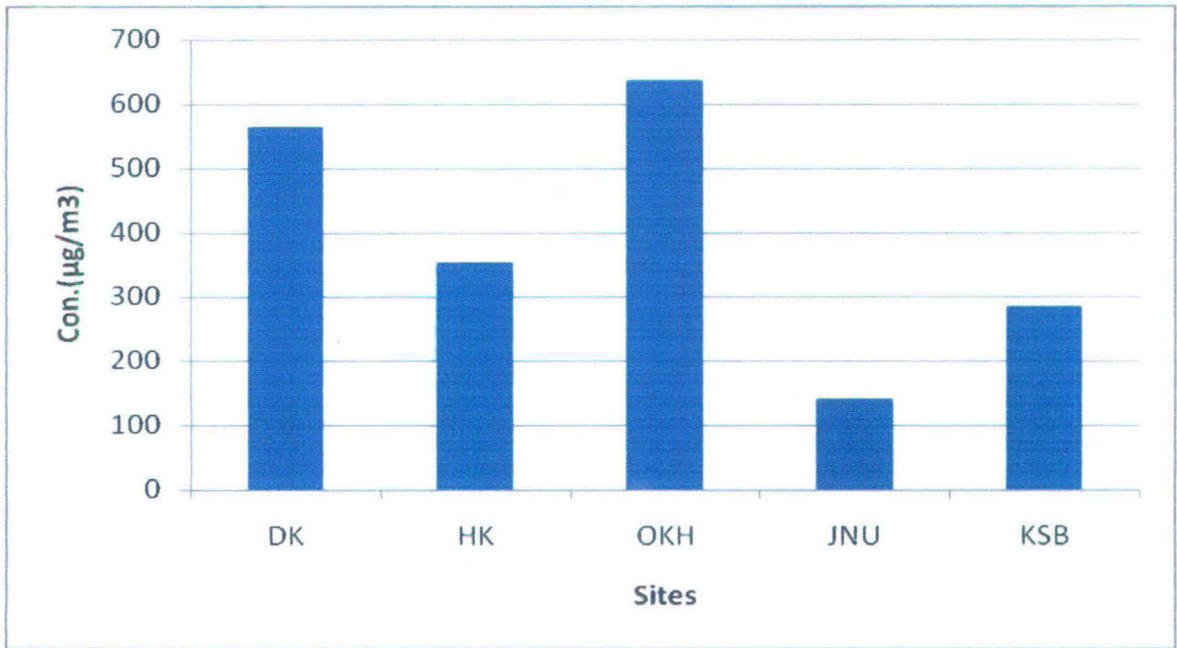


Figure 6 Coarse Concentration at all sites.

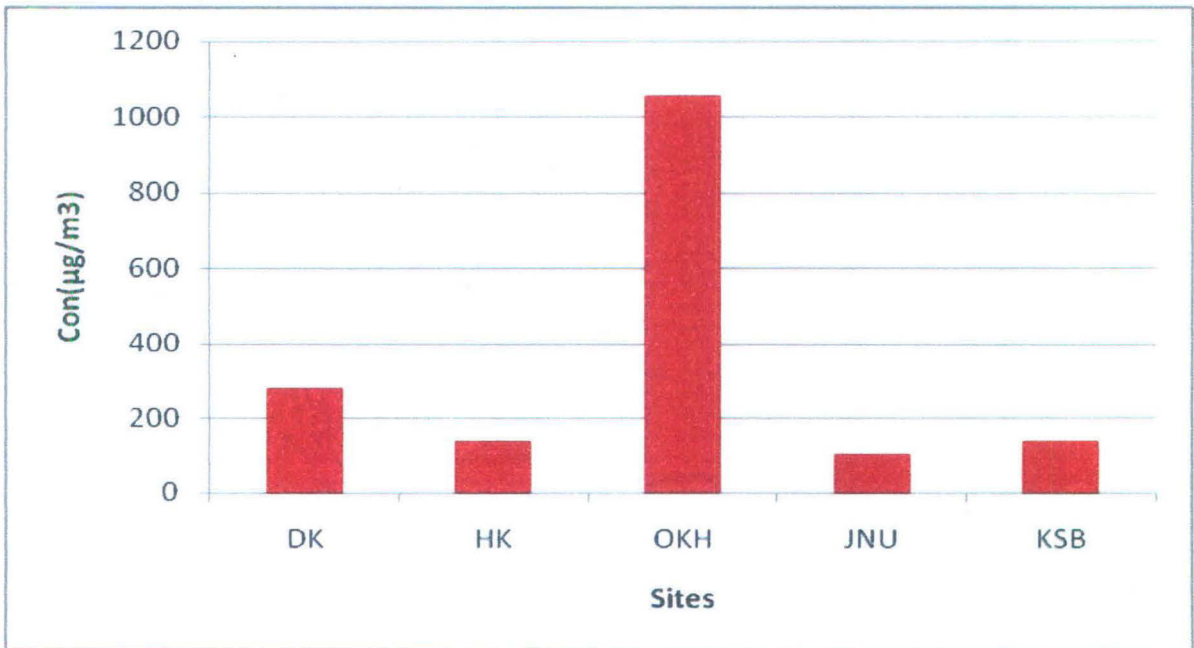


Figure 7 Super coarse Concentrations at All Sites.

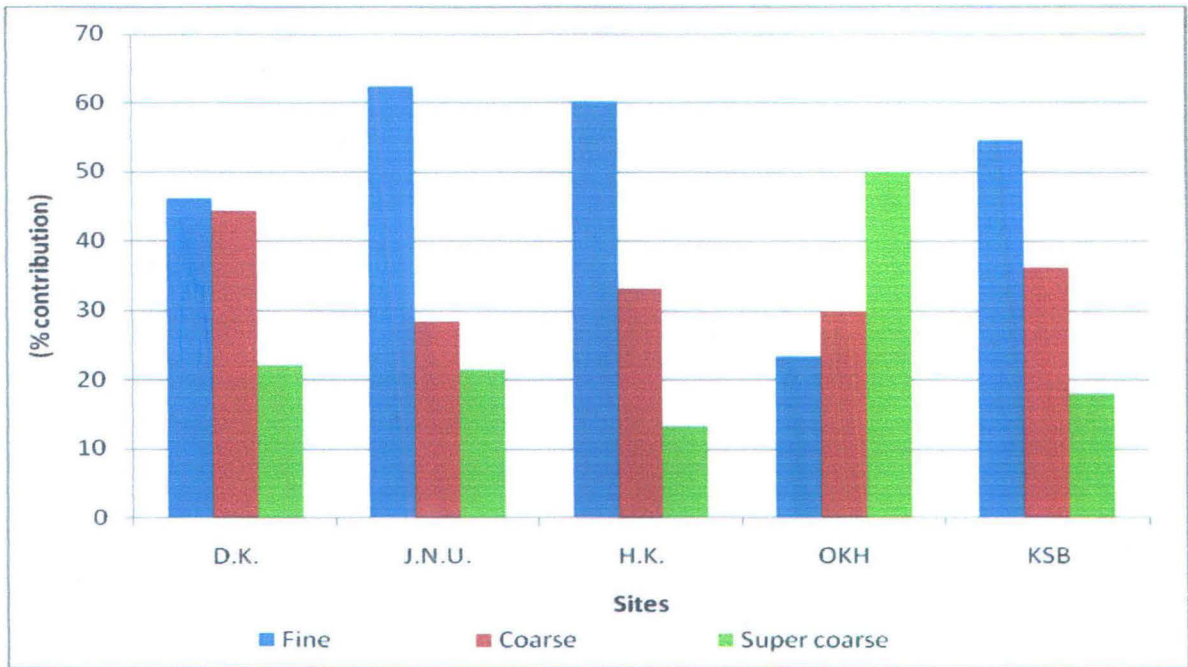


Fig-8 Percentage Contribution of Fine, Coarse and Supercoarse at All Sites.

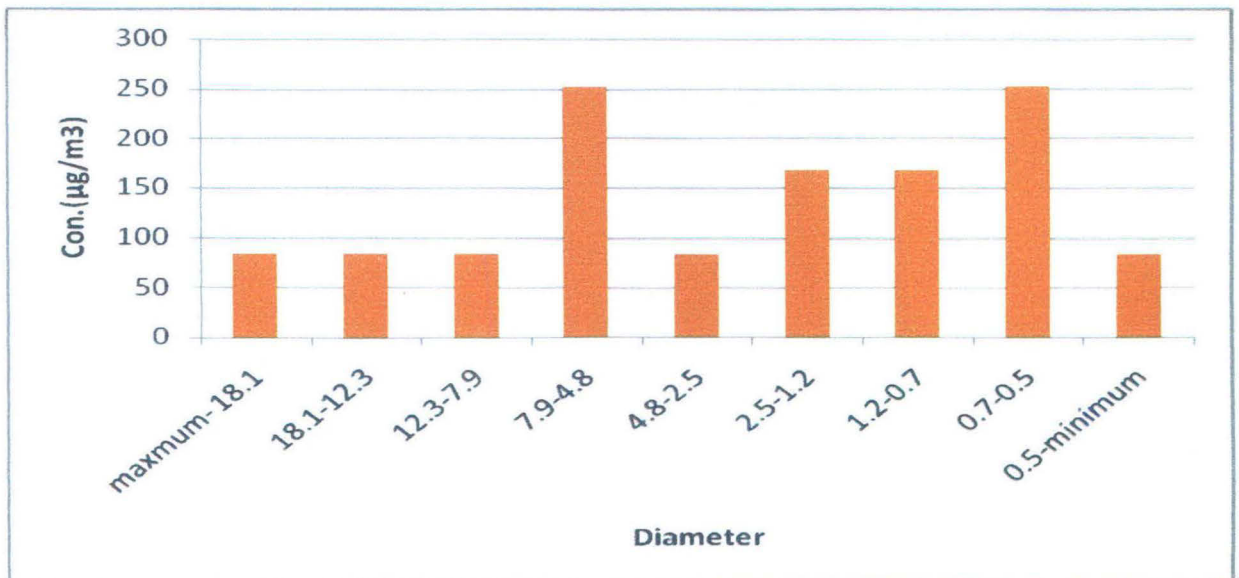


Figure-9 Fractionated Size segregated concentration (µg/m³) of aerosol at Hauz Khas.

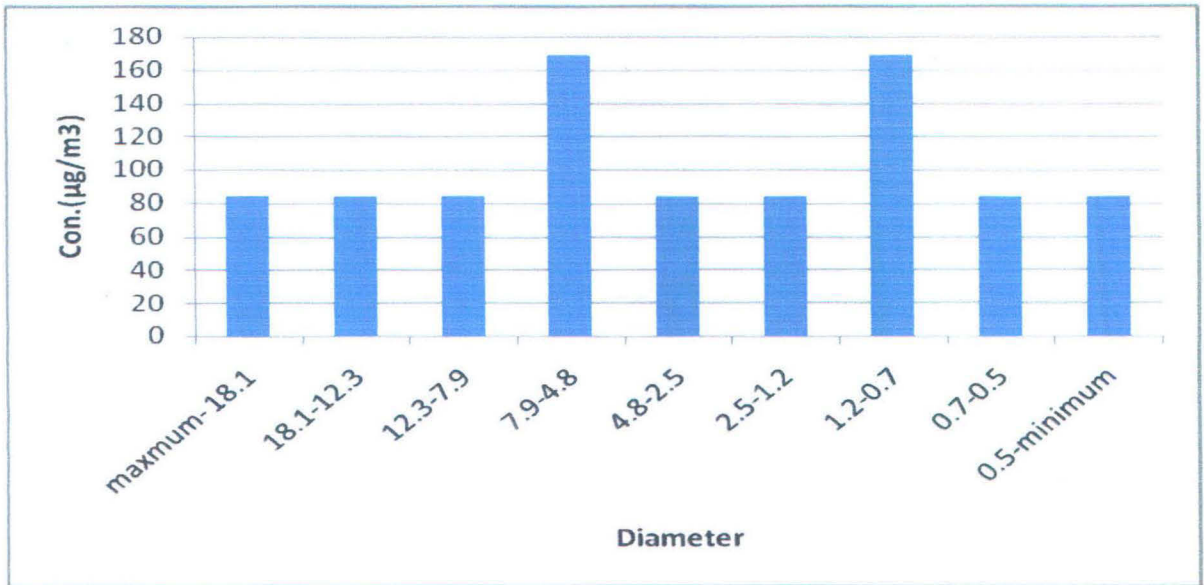


Figure- 10 Fractionated Size segregated concentration (µg/m³) of aerosol at Kaushambi.

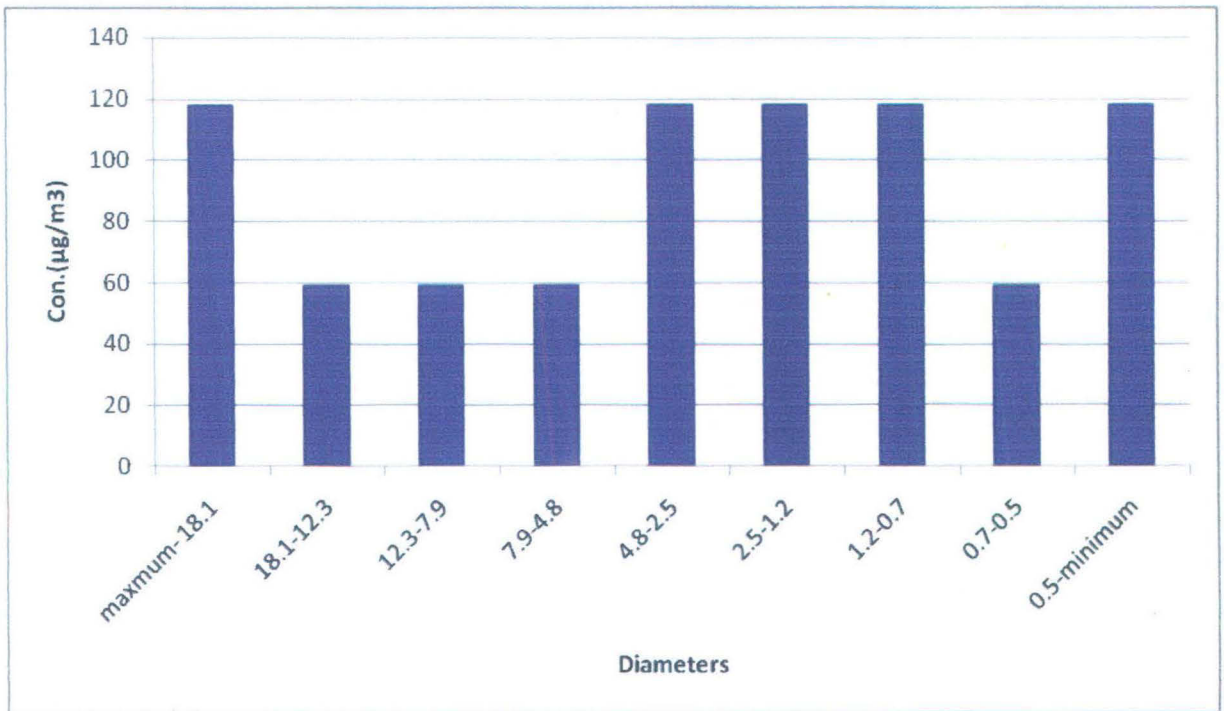


Figure- 11 Fractionated Size segregated concentration (µg/m³) of aerosol at JNU.

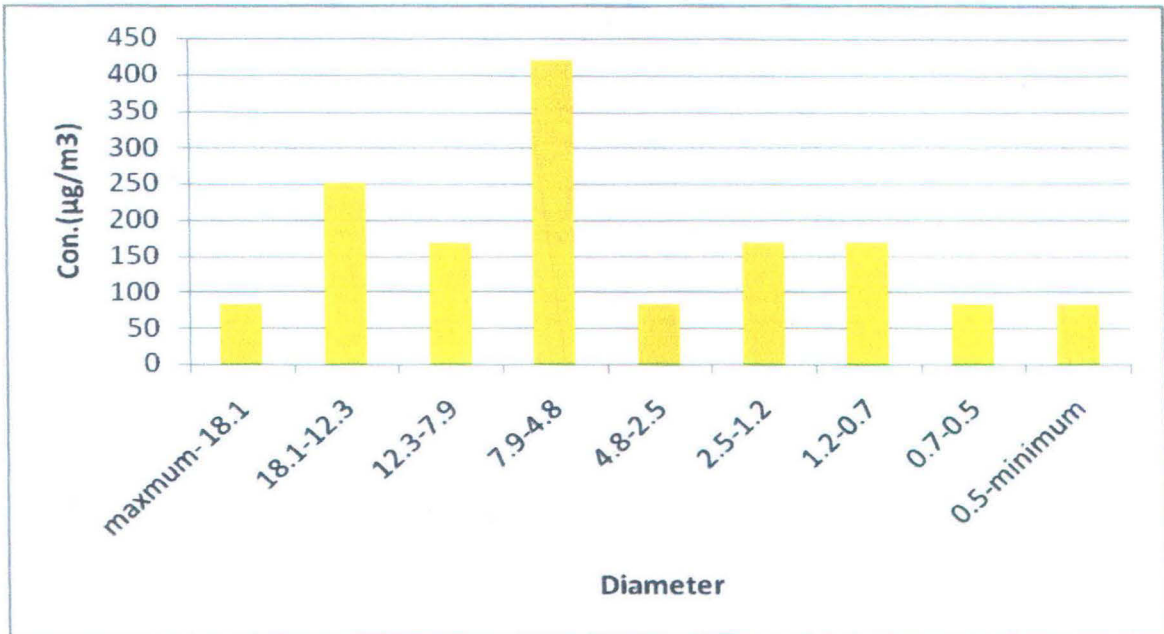


Figure -12 Fractionated Size segregated concentrations (µg/m³) of aerosol at Dhaula Kuan.

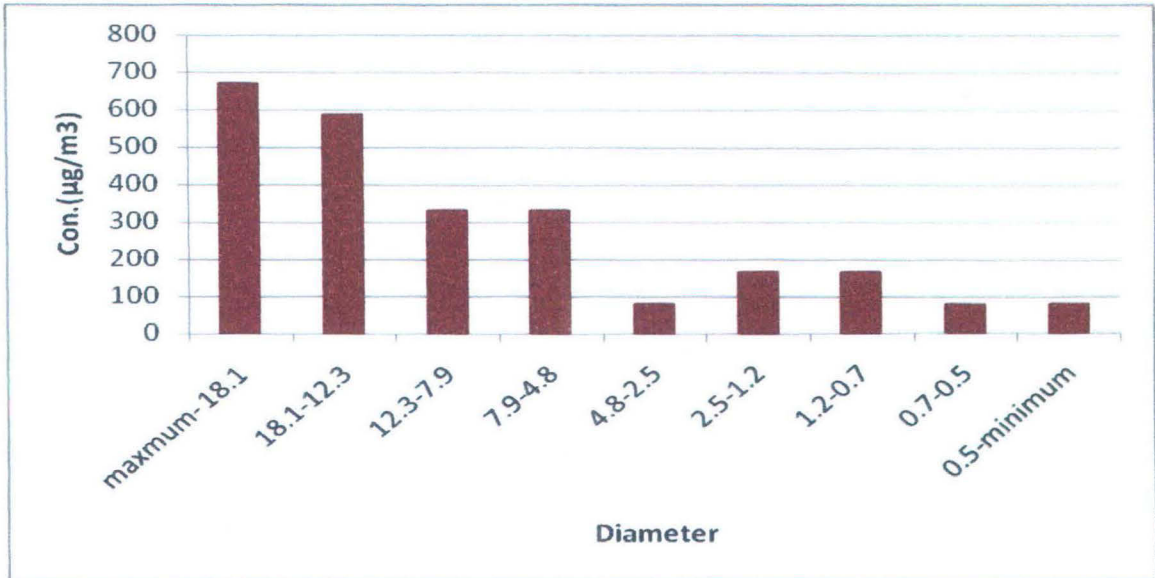
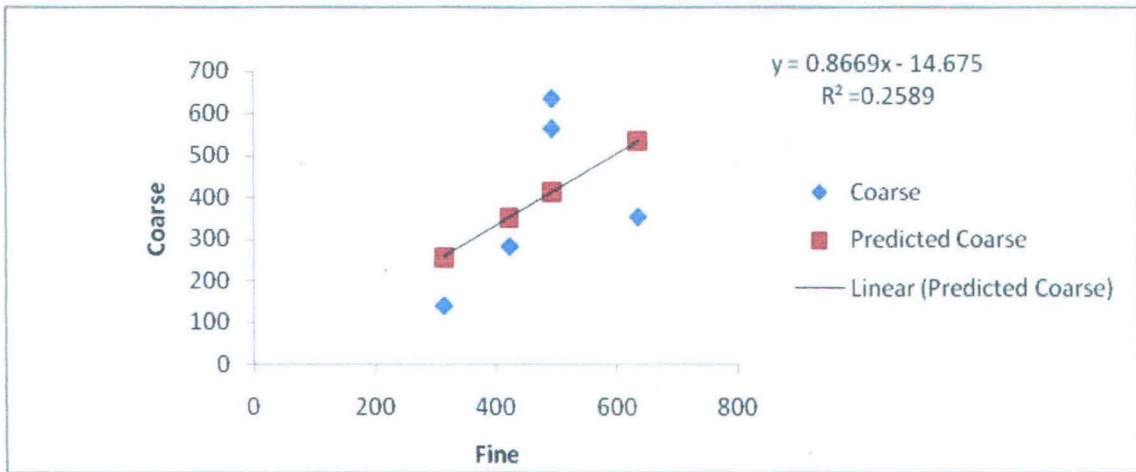
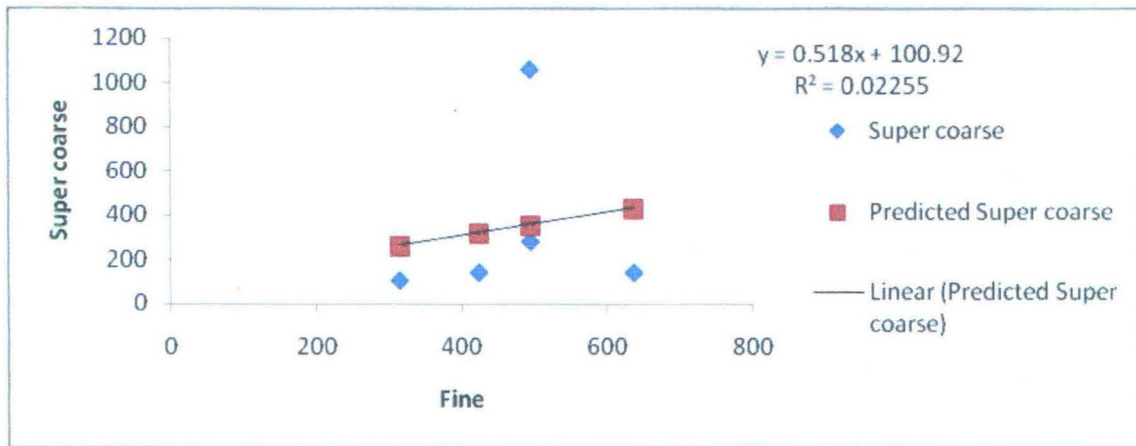


Figure-13 Fractionated Size segregated concentration (µg/m³) of aerosol at Okhala Phase-I.



(a)



(b)

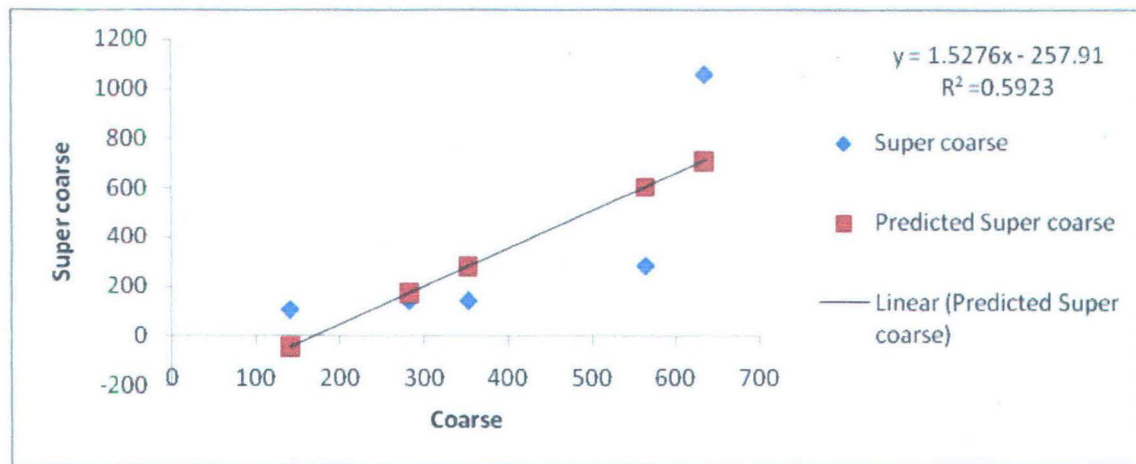


Figure 14 regression analysis of PM in different size fraction (a, b, c). (c)

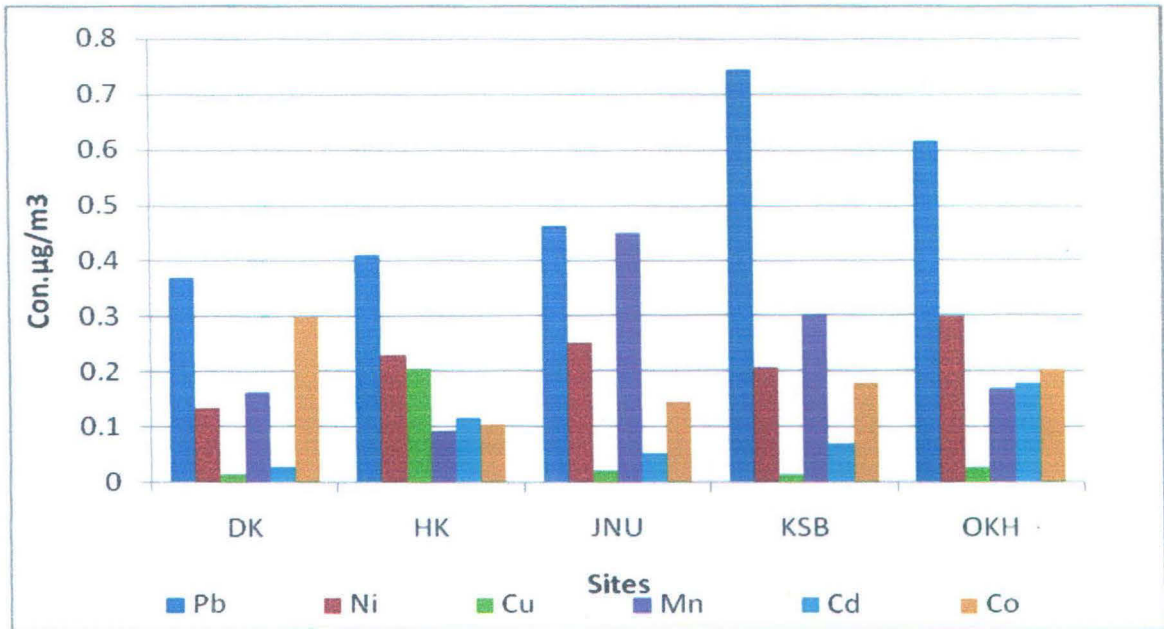


Figure 15 Metals concentrations ($\mu\text{g}/\text{m}^3$) at all sites.

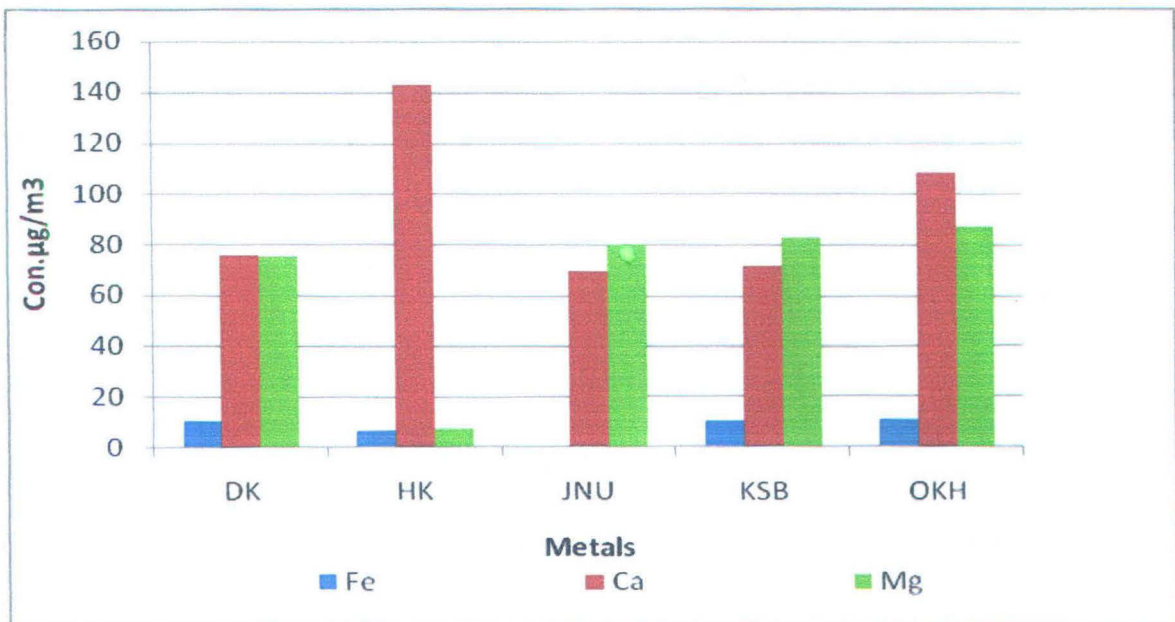


Figure 16 Metals Concentrations ($\mu\text{g}/\text{m}^3$) at all sites.

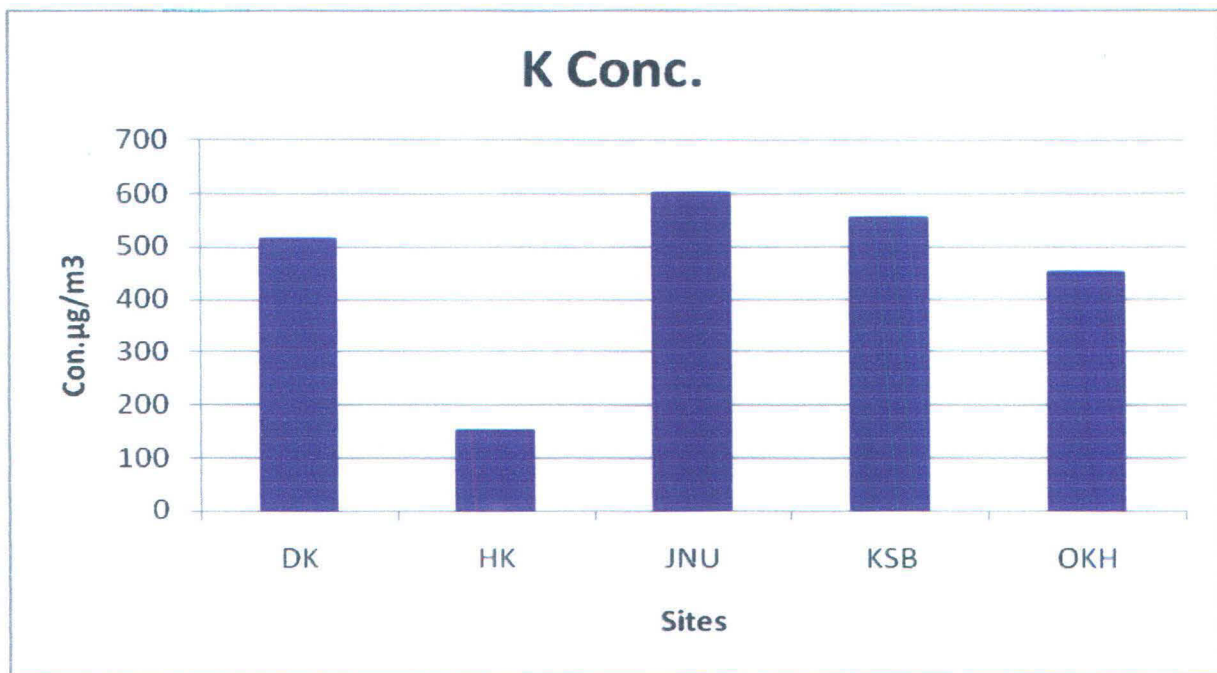


Figure-17 potassium concentration at all sites.

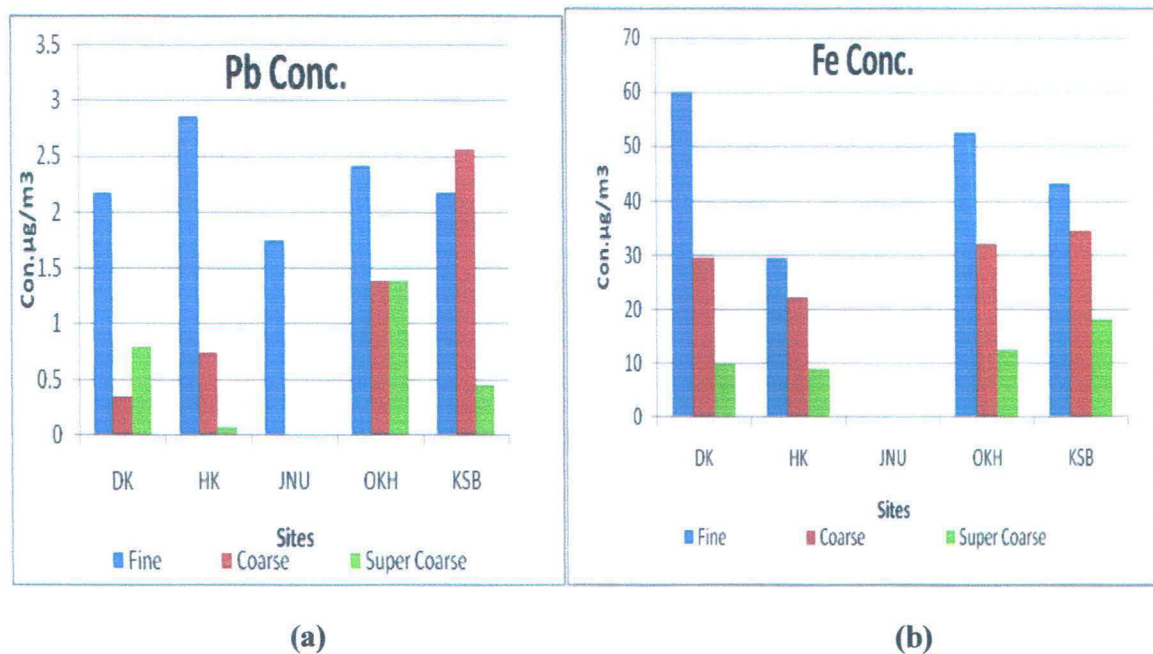
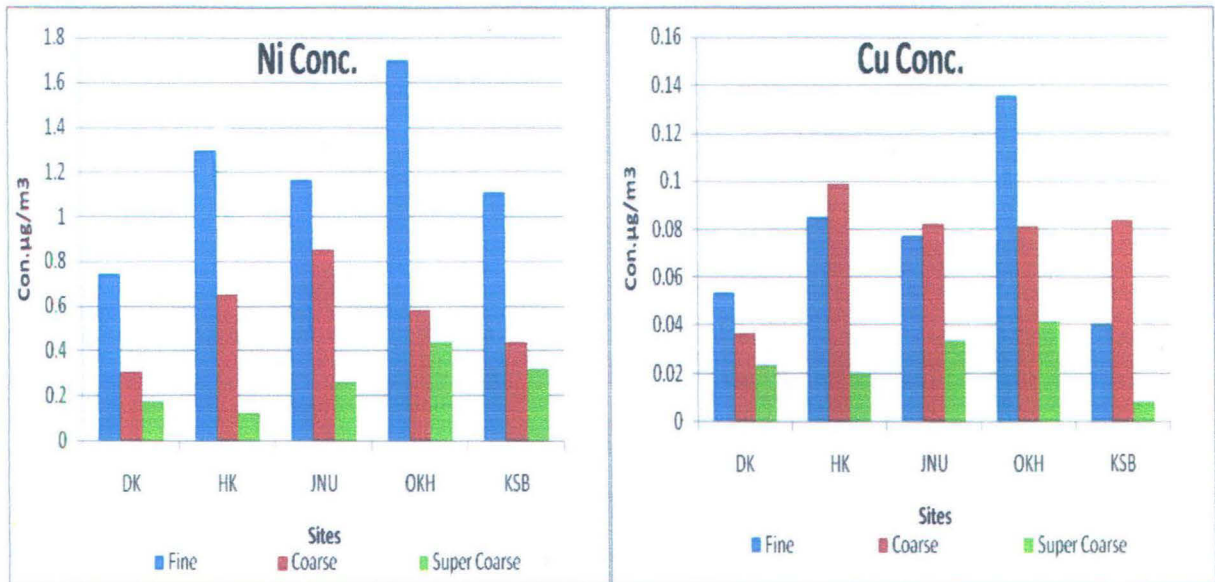
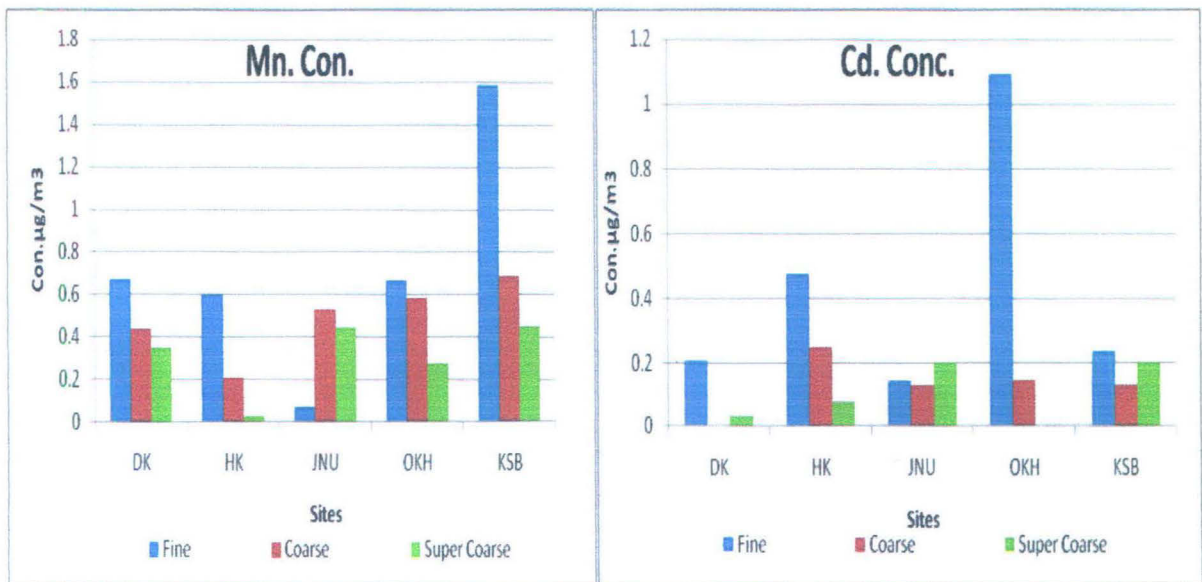


Figure-18 Lead (a) and Iron (b) Con. at all sites.



(a)

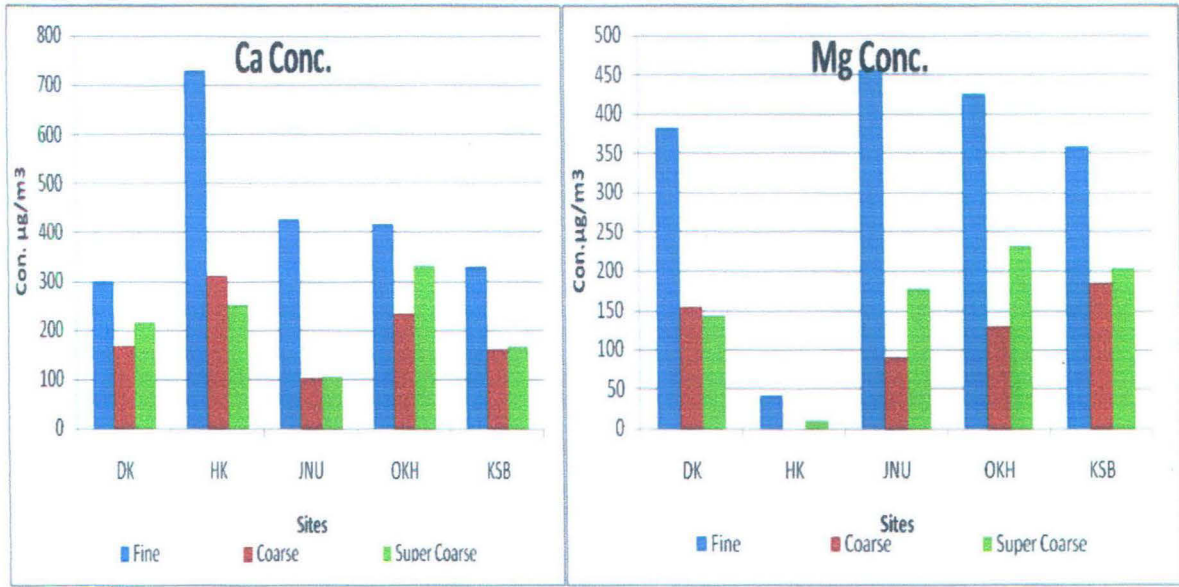
(b)



(c)

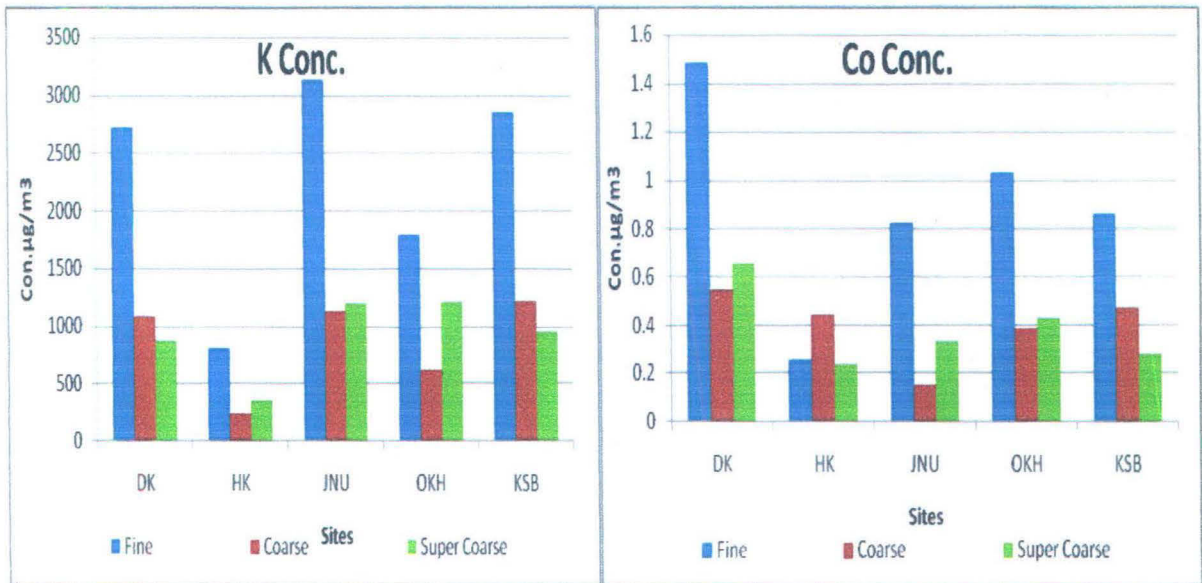
(d)

Figure-19 (Ni, Cu, Mn,Cd) Con. at all sites.



(a)

(b)



(b)

(d)

Figure -20 (Ca, Mg, K, Co) Con. at all sites.

CHAPTER 4. CONCLUSION

4: CONCLUSION

From the present study following conclusions can be drawn.

1. Total aerosol concentrations at all the sites are found to be well above the standards prescribed by Central Pollution Control Board (CPCB) for ambient environment. Whilst, it is within the limit, if we compare with the standards provided by Occupational Safety and Health Administration (OSHA) of USA. This must be noted that so far, no standards have been prescribed for air related occupational health hazards in India. Therefore, we followed the standards prescribed by OSHA.
2. The maximum concentration of TSPM is observed at Okhla Industrial Area and minimum at JNU.
3. The concentration of fine particulate matters exceed the limits prescribed by CPCB at all the sites.
4. Among the various sites fine particles concentration is maximum at Hauz Khas and minimum at JNU.
5. The concentration of coarse and super coarse fractions is found to be maximum at Okhla Industrial Area, while lowest at JNU.
6. Fine particles, contribute maximum to the TSPM followed by coarse and super coarse. The only exception is Okhla Industrial Area, where the trend is reversed, the maximum contribution comes from super coarse then coarse, and then fine.
7. A very bad regression of fine over coarse and super coarse is observed meaning no change can be observed in the concentration of coarse and super coarse if the concentration of fine fraction

changes. But a good regression of coarse over super coarse suggests that change in the concentration of coarse changes the concentration of super coarse.

8. Potassium was found to be the dominant metal at all the sites followed by Ca, Mg and Fe.
9. Among different sites, JNU and Kaushambi have the highest concentration of potassium showing significant natural contribution.
10. Pb, Ni, Cu, Cd, Co and Pb have maximum concentration at all the sites, as far as anthropogenically emitted metals are concerned.
11. Metals, associated with fine fractions, have generally dominated the distribution, but not at all the sites.
12. A very poor correlation between fine and super coarse and an average correlation between fine and coarse were observed. But a good correlation between coarse and super coarse suggest that there are successive correlations among the different sizes i.e. fine to coarse and then coarse to super coarse but not fine to coares.
13. In case of metals a very good correlation was found between 8 pairs of metals i.e. Cu-Ni, Cd-Ni, Cd-Cu, Mg-Cd, Mg-Ca, K-Mn, K-Ca and K- Mg. While good correlation among 10 pairs of metals i.e. Fe-Pb, Mn-Fe, Cd-Pb, Ca-Cu, Ca-Cd, Mg-Mn, Co-Fe, Co-Ni, Co-Ca and Co-Mg was observed.
14. Source apportionment revealed three main sources contributing to the atmospheric environment of Delhi viz. Crustal re-suspension, Industrial and Natural/Trans boundary migration.

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