6.1 ANALYSIS OF ROAD-DEPOSITED SEDIMENTS (RDS)

6.1.1 Characteristics of road dust

RDS are sediments that are deposited or accumulated on the either side of road, pavement and on the edges of divider or road medians where both natural and anthropogenic materials are present. Road dust also act as source as well as sink for various metals and contaminants formed in the urban environment (Adachi and Tainosho 2005; Qiao et al 2011). Particles present in road sediment are the by-product of combustion, suspension of soil particles and due to chemical reactivity in atmosphere (Pipal et al 2011). The study of RDS has been carried out since they are valuable and direct media which provide the measure of pollution load in a given location. Generally the dust particles preserve the traces of particles which were once present in dynamic atmosphere and now have been deposited in the sampling location (Jancsek-Turóczi et al 2013). The surface of street often acts as runoff pollutants from urban area and path for the transportation of pollutants. The road-deposited sediment does not reside in a place and can get easily mixed with the present atmospheric aerosol (Maxwell and Nelson 1978). The climatic factors like wind pattern and wind direction also play a vital role in dust characteristic by the atmospheric suspension and reshuffling of various fraction of dust.

A variety of analytical techniques can be used to delineate the characteristics of the road dust. The analytical methods equipped and discussed are the microscopic characterization (BSE-SEM) of RDS based on the shape and morphology of individual dust particles, XRD technique has been employed for the mineralogical and phase characteristics, EPMA technique was used to distinguish geochemical and mineralogical variation within the RDS, grain size analysis helps to determine particulate size and mobility indicating pollution index, magnetic study of RDS act as signal to know the load of magnetic particles in anthropogenic pollution. The detailed study has been described in the sub-chapters.

The RDS samples are variably heterogeneous and therefore the major constituents of road dust can be categorized into inorganic and organic sources. The inorganic components can be further divided be into natural (minerals like quartz, feldspar, flakes of mica and gypsum) and anthropogenic (vehicle and industrial exhaust, tire and brake wear, exhaust emissions from vehicles, emissions from power operators, broken glass pieces, plastic and metallic fragments). The organic sources can similarly be differentiated into natural (dried leaves,
bone fragments, sugarcane husks, seeds, straw, bagasse, pollen grains, hairs, human and animal wastes) and anthropogenic (paper, mills and textile wastes, mineral wools).

RDS contain toxic elements and organic matter that are derived from natural and anthropogenic sources. The main causal of pollutant and toxicity in urban areas depends on different size fraction of road-deposited sediments (Adachi and Tainosho, 2005). It has been observed that as the size of the particle in dust decreases, the concentration of elements increases (Fergusson and Ryan 1984). Studies have been conducted showing road dust lead to environmental pollution causing harmful effect to atmosphere (Manoli et al 2002; Funasaka et al 2003; Samara et al 2003). The PM$_{2.5}$ and PM$_{10}$ derived from the roadways emissions can be associated with high rate of respiratory illnesses and detrimental human health (Apeagyei et al 2011). Thus road dust can be categorized into three types- Toxic dust, Aggressive dust and Inert dust. Toxic dust forms noxious components which can lead to the physiological changes when it goes inside the body. The mechanical effect causing physiological changes leading to certain disease is called Aggressive dust. Inert dust are those dust which although remains in contact with the body for long time but itself is not the precursor of any disease (Cvetković et al 2012).

The presence of spherules is a major indicator in anthropogenic dust (Goddu et al 2004; LeGalley and Krekeler 2013). The spherical, sharp-edged particles with high brightness are mainly found in the finer fractions of road sediments. The study of road-deposited sediment directly provides us the relationship between environmental pollution and human activities through the investigation of source and distribution of road dust (Kelly and Thornton 1996; Peng et al 2010). The natural dust is posing a great threat during the whole year, whereas the natural dust is the main contributor in summer (Yisa 2010). The overall distribution of dust particles depends upon local climate, topography, location/area, road surface, traffic density etc. (Jancsek-Turóczy et al 2013; Gautam et al 2008 ) and leads gas to particle conversion which leads to the emission of suspension of road dust (Han et al 2007). There are few cost-effective and fast techniques for identification of environmental pollution of soils, sediments and dusts (Goddu et al 2004). Thus, in the present study has been carried out to understand the sources, characteristics and distributions of street dust. The spatial distribution of dust pattern is related to the topography and dominant wind direction (Kim et al 2006, 2007 and 2009). The road dusts were mainly composed of spherule, plate, irregularly shaped and agglomerate, which contains variable sizes and amounts of particles. The various particulate emissions from road-derived sediments and other sources can be related with the
environmental problems (Chaparro et al 2010). The observation clearly identifies spherules present in fly ash similar to those spherules obtained from the road-deposited sediments. The detailed study of RDS of Allahabad city, in terms of its magnetic measurement, XRD, grain size analysis and BSE-SEM study can be used as an important tool for assessing various problem related with urban pollution which can help to know the origin and spatio-temporal distribution of anthropogenic particulates.
6.2 BSE-SEM STUDY OF ROAD-DEPOSITED SEDIMENTS

6.2.1 Introduction
BSE-SEM investigation shows the presence of particular shape, size and structures of particles present within RDS including organic and inorganic particles (anthropogenic spherule).

6.2.2 Methodology
The methodology has already been discussed in chapter 4, section 4.5. BSE-SEM analyses were performed using Cameca SX-100, PLANEX, Physical Research Laboratory, Ahmadabad. Although in the case of RDS the samples were sprinkled on the smear of Araldite® and then polished for a smooth surface for BSE-SEM study.

6.2.3 Results and inferences
It can be identified that the particles present in RDS are angular-shaped particles, aggregate compounds and spherules including biogenic particles as well. According to degree of roundness the diverse shaped particles observed in RDS were divided into angular, sub-angular, rounded, well-rounded, subrounded, acicular particles. The varied shaped particles form separate entity and are separated from each other. The lithogenic and pedogenic sources results the formation of angular to subrounded shaped particle. Hitherto, angular particles are concerned it results due to work mechanism carried out within industries and traffic-related outputs. However, the acicular particles generated mainly from wear and tear of tyres and discarded material from industries. About 94-95% of the particles observed are separated well-shaped particles. The aggregates formed as a result of mutual attraction between the particles. These proportions of particles are unknown amorphous fraction. Generally 3-4% of the particles forms aggregates which is observed in RDS. The spherules were observed in majority of samples except few. 1-2% of spherules were observed in the samples. The SEM and BSE study of different types of spherules acquired from RDS have been discussed below. The size range of the angular dust particles lies from 1 to 180µm while the spherule range lie from 100-3000 µm (Fig. 6.1). However, many microspherules were also present within the dust particles but can only be observed with through BSE-SEM study. The grain consisting of high iron content having acicular shaped structure is goethite while sub-angular particle is quartz grain.
Fig 6.1 showing the BSE and SEM image of RDS from industrial area, Naini showing angular to well-rounded shaped-particles with chemical variation. A 60µm size metallic microspherule can also be seen within the sample. The size of the particles varies from 1-180 µm. Red spot shows goethite (acicular) and quartz grain.

The presence of goethite in RDS delineates its derivation from traffic or industrial activities. The SEM aided with the elemental analysis shows the RDS having enrichment in heavy metals content. It can be inferred that anthropogenic activities from industrial sites in conjunction with traffic-related activities increases the load of dust with heavy metals. The occurrence of Fe, Al and Si within dust shows its geogenic origin while the presences of heavy metals like Cr, Ni and Zn associated with FeO and CaSO\textsubscript{4} are anthropogenic-derived particles.

The chemical composition of dust from industrial area, Naini show high percentage of iron oxide. The heterogeneous distribution of particles within the RDS is due to different sorts of activities taking place in urban environment.
6.3 MAGNETIC MEASUREMENT STUDY OF ROAD-DEPOSITED SEDIMENTS

6.3.1 Introduction

The magnetic studies of RDS have been carried out to examine various associated magnetic particles. Although various other analytical methods have been employed to study RDS but it was too difficult to sort out the magnetic particles on the basis of its intensity. Whereas the magnetic measurement is a quick, simple, non-destructive and economical method to characterize different magnetic particles and can easily quantify the atmospheric pollution. The magnetic study of road sediment can be useful for the spatio-temporal monitoring of pollution in urban areas (Yang et al 2010a; Sarangese et al 2011).

A variety of particulate matters and toxic gases are constantly released into the atmosphere from different sources such as thermal power plants, smelters and other industries, combustion of fossil fuels, abrasion of tyres, brake linings as well as road surface, and dispersion of construction materials are the important source of anthropogenic magnetic pollution in the urban zone. In industrial area major pollution is caused by industrial effluents which gets deposited in proximity and thus increases the magnetic properties of nearby sediments (Goddu et al 2004). The iron-oxides releasing from fly ash industries and factories contribute to the increase magnetic content within the sediments (Hay et al 1997). The study of soil sample and dust sample shows that the dust sample contain higher magnetic susceptibility than soil sample which predict that dust sample contain high magnetic materials than soil samples.

Magnetic susceptibility measures the degree to which a substance can be magnetized, and this can be used to identify minerals within material and used as an indicator for processes like, erosion. Therefore, magnetic susceptibility has been widely used to investigate dust related research as the values obtained correspond with the types of magnetic minerals in the soil, mainly the iron oxides such as magnetite and maghemite (higher MS, Magnetic Susceptibility), and hematite and goethite (lower MS). Thus MS acts as a signature for different types of dust allowing them to be categorized. The ferrimagnetic and ferromagnetic minerals can be derived from weathering or erosion of soil through natural process (Thompson and Oldfield 1986) and from metal extraction, fuel combustion through anthropogenic process (Goddu et al 2004). Magnetic materials are main pollutants present in urban environment since they are associated with heavy metal which get derived from
anthropogenic sources and imparts its adverse effect on the human health (Kim et al 2007). The amount of magnetic minerals present in the dust is largely dependent on the processes by which it is formed. Nearly all dusts contain magnetic particles which can be differentiated on the basis of their type, grain size and magnetic properties. The anthropogenic dust generally gets originated from the combustion process giving rise to mineral phase like magnetite. The magnetic minerals within RDS not only reflect the magnetogenic pollutants but also notify the presence of toxic metals like Pb, Cu, Cr and Zn (Reyes et al 2013 and references therein). While studying these dusts further we can observe small spherical-like particles termed as spherules. It can be silica or dark coloured metallic spherules in origin. Therefore, the origin of anthropogenic and geogenic dust can be easily marked on the basis of their origin. The aim of the present investigation is to delineate the relative degree of road dust pollution using magnetic methods and to detect and characterize the anthropogenic magnetic particles present in road-deposited sediments.

6.3.2 Methodology

A total of 442 samples are studied for volume and mass magnetic susceptibility measurements of road-deposited sediment samples are collected during pre monsoon, 2009; fog, 2010 and fog, 2011. The dust samples are weighed in Mettler (Germany) electronic balance and the low- and high-field magnetic susceptibility (χ_{LF} and χ_{HF} x 10^{-8} m^3 kg^{-1}) of road sediment samples (in SI unit) is measured using a dual frequency (0.47 and 4.7 KHz) magnetic susceptibility meter (MS2B; Bartington, U.K.). The frequency dependent magnetic susceptibility (χ_{FD}%) is also calculated. About 20 samples are selected from each period of sampling pre monsoon, 2009; fog, 2010 and fog, 2011 for further magnetic study. All magnetic measurements except the magnetic susceptibility are made using the facilities available in Dr. K.S. Krishnan Geomagnetic Research Laboratory (Government of India), Allahabad. Anhysteretic remanent magnetisation (ARM x 10^{-5} m^3 kg^{-1}) is measured when the sample is introduced to a DC bias field in the presence of a decreasing alternating magnetic field. The remanence is measured in Molspin spinner magnetometer with χ_{ARM} x 10^{-8} m^3 kg^{-1}. Isothermal remanent magnetisation (IRM x 10^{-5} Am^2 kg^{-1}) is measured when the sample is introduced to a strong DC magnetic field and after that measured in Molspin spinner magnetometer and then introduced for magnetisation in Pulse magnetiser in fields of 20, 100, 300 mT, 1T and is again re-introduced for demagnetisation in -20, -30, -40, -50, -100 and -300 mT. The other magnetic parameters calculated are SIRM (10^{-5} Am^2 kg^{-1}), χ_{ARM}/SIRM (10^3 mA^{-1}), SIRM/χ_{LF} (10^3 mA^{-1}), χ_{ARM}/χ_{LF}, HIRM ([SIRM-IRM_{20mT}]/2 x 10^{-5} Am^2 kg^{-1}), HARD% (100*[HIRM/SIRM]), SIRM/ARM, SOFT ([SIRM-IRM_{-20mT}]/mass) x 10^{-5} Am^2
kg\(^{-1}\)) and S-ratio% \((\text{IRM}_{300\text{mT}}/\text{SIRM})\). The \(\chi_{\text{LF}}\) interpret the total ferrimagnetic concentration and for the determination of coarser magnetic fraction, pseudo- single domain (PSD) and multi domain (MD) grains within the sample \((\text{Shu et al 2001})\). ARM is used for the determination of the single domain (SD) and fine PSD grains present in sample. \(\chi_{\text{FD}}\)% shows the concentration of superparamagnetic (SP) ferromagnetic grains. SOFT % and HARD % can be used for the relative proportion of ferromagnetic and canted anti-ferromagnetic components within the sample, respectively \((\text{Shu et al 2001})\). SIRM is known to provide a rough measure in terms of concentration of all minerals having high magnetic remanence. The fine-grain \((\text{diameter} < 1.4 \, \mu\text{m})\), high ferrimagnetic minerals SD can be determined by SIRM/\(\chi_{\text{LF}}\) \((\text{Dunlop 1973})\).

### 6.3.3 Results and inferences

The high concentration of magnetic minerals within the samples corresponds to the high susceptibility \((\chi)\), ARM, SIRM values which are concentration dependent parameters whereas \(\chi_{\text{FD}}\)%, \(\chi_{\text{ARM}}/\chi_{\text{LF}}, \chi_{\text{ARM}}/\text{SIRM}, \text{SIRM}/\chi\), S-ratio% indicates grain size and type of magnetic materials of the sample. The high value of magnetic parameters is due to increase in pollution level caused by anthropogenic human activity. The parameters have been described briefly below.

The respective plots shown in (Fig. 6.2, a-c) are associated with three periods of sampling \((\text{pre monsoon, 2009; fog, 2010 and 2011})\) which includes industrial area, high traffic areas, commercial places and residential areas.

The respective sampling period is divided according to its sampling area like Chawk, Civil lines, Alopibagh, Cantonment and Industrial area \((\text{Naini and IFFCO, Phulpur})\). As the sampling areas have been described in the previous chapter \((\text{present study})\) it can be seen that the cantonment area has lowest magnetic susceptibility in all three sampling periods. The susceptibility value varies from 39.46 to 57.41 x 10\(^{-8}\) m\(^3\) kg\(^{-1}\) in pre monsoon, 2009 while 39.31-72 and 29.42-29.84 x 10\(^{-8}\) m\(^3\) kg\(^{-1}\) during fog, 2010 and 2011, respectively. It can be seen that the susceptibility values lies in similar range and corresponds to each other in all sampling periods which delineates that the magnetic minerals lesser amounts of in sediments. Since the area does not encounters large vehicular traffic with greenery and has less human density. Therefore, the area has paucity of magnetic mineral content. The Alopibagh area can be marked as high traffic density. The susceptibility value is higher during fog period, 2010 and 2011 \((113.5-248.25 \text{ and } 72.22-718.14 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1})\) than pre monsoon period \((145.78-218.76 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1})\). The reason can be ascertained that during fog period the dust particles acts as an absorber sink and gets condensed more. Civil lines area is mainly known for its
commercial and business activities leading to heavy traffic congestion. The magnetic study conducted reveals that the mass susceptibility in pre monsoon (81.5- 187.26 x 10^{-8} \text{ m}^3 \text{ kg}^{-1}) shows wide range of variation from fog, 2010 (143.7-249.92 x 10^{-8} \text{ m}^3 \text{ kg}^{-1}) and 2011 (139.64- 244.94 x 10^{-8} \text{ m}^3 \text{ kg}^{-1}). In Chawk area, the susceptibility shows increasing trend during fog, 2010 and 2011(144.45 and 82.85-465.29 x 10^{-8} \text{ m}^3 \text{ kg}^{-1}) rather than pre-monsoon revealing that high traffic load and human congestion reflect increase anthropogenic contribution during fog condensate. The industrial area (Naini and Phulpur, IFFCO) reflects high susceptibility of all which can be interpreted by the fact that the presence of heavy industry with traffic load imparts the load of susceptibility.

The $\chi_{\text{FD}}\%$ indicates fine superparamagnetic grains within the sample. The study shows that the cantonment area has $\chi_{\text{FD}}\% > 3\%$ value in all three sampling periods. While the other sampling area like Alopibagh, Civil lines, Chawk shows low to moderate $\chi_{\text{FD}}\%$ value. The industrial zone of Naini and IFFCO, Phulpur relatively has less than 3% value, indicating that the dust sediments are contaminated due industrial activities. Hence, it can be delineated from the above study that the lesser polluted area generally has $> 3\%$ value, indicating ample superparamagnetic and finer grains generated from pedogenic processes. While the polluted area shows $< 3\%$ value implying heavy anthropogenic pollution load with abundance of ferrimagnetic minerals. Therefore, it can be concluded that since road sediments acts as a natural sink, the pollutants ultimately gets deposited and making it more visible that as susceptibility increases, $\chi_{\text{FD}}\%$ decreases and marking a threshold between low and high polluted zone.

SIRM signifies the concentration of total magnetic grains (Evans and Hellers 2003). The SIRM value measured during sampling ranges from 27.4 to 7452.63 in pre monsoon while during the value observed in fog, 2010 and 2011 were 19.09 to 5648.54 and 208.7 to 5266.38, respectively. It can be confirmed that the higher SIRM value was observed in the pre-monsoon indicating heavy vehicular traffic load than fog period.

S-ratio\% is a magnetic mineralogy dependent parameter which indicates the magnetite/hematite ratio within the sample. If the value is $>80\%$, then the sample is dominated by magnetite while $<80\%$ shows the presence of hematite and should lie within 100\%. It is a dimensionless parameter. In the road dust samples S-ratio\% vary from 53.28-96.67 (pre monsoon, 2009); 51.88-99.16 (fog, 2010) and 65.12-94.74(fog, 2011) indicates both the presence of magnetite and hematite. The high value of S-ratio\% shows the presence of ferromagnetic minerals. However, it can be seen that the city area is dominated by magnetite minerals while the industrial area depicts the presence of hematite ones. The
magnetite observed being derived from particulate emissions of vehicles while the fly ash originated from power plant confirms the presence of hematite. The S-ratio\% measured from three sampling periods show similar trend without many variations.

(a) Pre Monsoon, 2009

(b) Fog, 2010
It can be seen from the above study that the high susceptibility, SIRM, S-ratio and low $\chi_{FD\%}$ denotes the RDS are dominated by ferrimagnetic minerals originated from anthropogenic sources probably derived from vehicular origin. Therefore, it can be inferred that the magnetic grains are derived both from geogenic and anthropogenic processes. Although it can be seen in the given study that lithogenic origin does not play a bigger role in magnetic susceptibility. The different magnetic particle observed in RDS includes irregular and angular shaped particles with anthropogenic phase like spherules of 200 to 1700 $\mu$m in diameter with agglomerates as well. Table 6.1 showing summarized data of various magnetic parameters which was observed in the present study. The 2-D mass susceptibility $\chi_{LF}$, are shown with the help of colour contour maps collected from each sampling periods pre monsoon, 2009; fog, 2010 and fog, 2011 has been shown in Fig. 6.3, 6.4 and 6.5, respectively. The contour maps are showing relative high susceptibility in Naini area as compared to other city areas which can be marked in all three sampling periods.
Table 6.1 Environmental magnetism parameters of Road-deposited sediment, Allahabad city, India

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<th>Sampling Period</th>
<th>χ&lt;sub&gt;LF&lt;/sub&gt; (10&lt;sup&gt;-8&lt;/sup&gt; m&lt;sup&gt;3&lt;/sup&gt; kg&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>χ&lt;sub&gt;FD&lt;/sub&gt;%</th>
<th>SIRM (10&lt;sup&gt;-5&lt;/sup&gt; Am&lt;sup&gt;2&lt;/sup&gt; kg&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>χ&lt;sub&gt;ARM&lt;/sub&gt; (10&lt;sup&gt;-8&lt;/sup&gt; m&lt;sup&gt;3&lt;/sup&gt; kg&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>χ&lt;sub&gt;ARM&lt;/sub&gt;/SIRM (10&lt;sup&gt;3&lt;/sup&gt; mA&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>SIRM/χ&lt;sub&gt;LF&lt;/sub&gt; (10&lt;sup&gt;3&lt;/sup&gt; mA&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>χ&lt;sub&gt;ARM&lt;/sub&gt;/χ&lt;sub&gt;LF&lt;/sub&gt;</th>
<th>S-ratio%</th>
<th>SOFT (10&lt;sup&gt;-5&lt;/sup&gt; Am&lt;sup&gt;2&lt;/sup&gt; kg&lt;sup&gt;-1&lt;/sup&gt;)</th>
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<tr>
<td>Pre Monsoon, 2009</td>
<td>Max. 2320.76 6.45 7452.63 3116.14 7.16 16.71 6.35 96.67 3381.51</td>
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<td>Min. 39.46 0.76 27.4 64.06 0.05 0.25 0.04 53.28 4.27</td>
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<td>Avg. 604.36 2.02 1677.73 920.73 1.73 3.42 2.86 74.16 541.21</td>
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<td>Fog, 2010</td>
<td>Max. 379.2 31.7 5648.54 1523.77 18.05 36.31 8.91 99.16 1404.49</td>
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<td>Min. 37.87 0.66 19.09 15.38 0.01 0.49 0.21 51.88 1.29</td>
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<td>Avg. 174.44 7.51 1586.30 461.64 1.94 8.96 3.38 74.27 439.32</td>
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<td>Fog, 2011</td>
<td>Max. 1415.88 28.01 5266.38 5400.28 6.71 113.88 27.27 94.74 1243</td>
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<td>Min. 29.42 0.37 208.7 80.45 0.07 0.98 1.14 65.12 41.27</td>
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<td>Avg. 298.90 7.65 2421.51 1099.68 0.77 17.54 5.87 81.30 576.36</td>
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Table 6.1 Environmental magnetism parameters of Road-deposited sediment, Allahabad city, India
Fig 6.3 2-D Mass Susceptibility contour map of pre monsoon, 2009
Fig 6.4 2-D Mass Susceptibility contour map of fog, 2010
Fig 6.5 2-D Mass Susceptibility contour map of fog, 2011
The various parameters have been described briefly with their respective interpretations.

1) The $\chi_{LF}$ versus $\chi_{ARM}$ shows the grain size of magnetic mineral within the sample (Fig. 6.6). The King-plot (Peng et al 2010 and references therein) reveals the sizes of road dust collected during sampling period from Allahabad city is dominated by 1->5µm, implies the magnetic domain is PSD, MD and SSD. The outcome therefore can be correlated from the previous work that the coarser size fraction >2µm are anthropogenic-derived magnetic particles (Hay et al 1997).

2) The $\chi_{ARM}$/SIRM parameter depicts the concentration of SD and PSD, which increases according to concentration. The $\chi_{ARM}$/SIRM versus $\chi_{FD}$% show the grain size of magnetic mineral (Fig. 6.7, a). The Dearing plot (Fig. 6.7, b) similar to King-plot reflects the magnetic domains of road dust. The above plot indicates that the street dusts of Allahabad city shows the presence of PSD and MD with coarse SSD (stable single domain) as they are frequency independent showing similar susceptibility at low and high frequencies (Hay et al 1997). Therefore, if $\chi_{FD}$% is < 4 absence of SP grains with the dominance of MD and SSD grains whereas $\chi_{FD}$% >10 shows pedogenic SP grains (Dearing 1999). The $\chi_{FD}$% for majority of samples is low. However, few samples show higher concentration of SP particles (> 50%) within the sample. The PSD and MD grains show its provenance from industrial activity, fuel combustion and traffic pollution.
3) In general, the $\chi_{\text{ARM}}$/SIRM and $\chi_{\text{ARM}}$/ $\chi_{\text{LF}}$ plot (Fig. 6.8) shows the variation amongst SD ferrimagnetic grains having varied particle size (Maher 1998). The higher value of $\chi_{\text{ARM}}$/SIRM shows the presence of finer ($< 1\mu m$) ferrimagnetic grains whereas the lower value indicates their coarser ($>10\mu m$) fractions. (http://www.irm.umn.edu/hg2m/hg2m_d/hg2m_d.html, accessed on 25:01:2014). In Fig. 6.8, it can be seen that during pre-monsoon sampling period of 2009, there finer fraction of ferrimagnetic grains were dominant. However, gradually the value ($\chi_{\text{ARM}}$/SIRM) gets lower during fog, 2010 with two exception peaks indicating the conversion of particle size from finer to coarser fraction while the abundance of coarse grains increased during fog, 2011. The probable reason for finer fraction during pre-monsoon is due high wind activity leading to weathering, abrasion and attrition of particles while very low wind activity take place due to fog condensate during the prevailing period. Thus, we can conclude that the RDS of Allahabad city is dominated by SD with finer ferrimagnetic grain during pre-monsoon period and coarse grains during fog period.
4) The SIRM/\(\chi\)LF parameter is sensitive to magnetic grain size (Fig. 6.9). Peters and Dekkers (2003) stated that the SIRM/\(\chi\)LF value decreases with increasing grain size of magnetite (ferromagnetic mineral?). Therefore, the ferromagnetic grain size increases during pre monsoon, 2009 period and decreases in fog, 2010 and 2011 period. This is due to the low moisture content in pre monsoon which inhibit the process of rusting while during fog the atmosphere is moisture laden speed ups the mechanism.

5) It can be seen from \(\chi\)LF versus \(\chi_{FD}\)% plot (Fig. 6.10) that the parameters are negatively correlated to each other which indicates the susceptibility variations resulting from industrial pollution. As stated in earlier work that the negative behaviour between susceptibility and \(\chi_{FD}\)% depicts the contribution of pedogenic SP grains within the sample (Sheng-Gao and Shi-Qing 2008). However, the urban dust also contain coarse multidomain ferrimagnetic grain (Peng et al 2010 and references therein). The \(\chi\)LF value vary widely from 39.46-2320.76 x
\(10^{-8} \text{ m}^3 \text{ kg}^{-1}\) during pre monsoon, 2009; \(37.87-379.2 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}\) in Fog, 2010 and \(29.42-1415.88 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}\) during fog, 2011 while \(\chi_{FD}\%\) shows variation from 0.76-6.45; 0.66-31.7 and 0.37-28.01, respectively for the given sampling period. The low value of \(\chi_{FD}\%\) in sample is due to the concentration of paramagnetic and canted anti-ferromagnetic minerals (Hay et al 1997). Therefore, from the above study the susceptibility value indicates the presence of ferrimagnetic minerals within the sample.

![Fig 6.10 $\chi_{LF}$ versus $\chi_{FD}\%$ plot of the representative samples](image)

6) The linear correlation between the correlation between SIRM and $\chi_{LF}$ (Fig. 6.11, a) also indicate that the magnetic properties of the street dust samples are dominated by ferromagnetic minerals. While the relation between SOFT and SIRM interprets (Fig. 6.11, b) that the samples are dominated by ferromagnetic minerals.

![Fig 6.11 (a) $\chi_{LF}$ versus SIRM plot, (b) SOFT versus SIRM plot of 20 representative samples](image)

The magnetic parameters from the above study suggest high \(\chi, \chi_{ARM}, \text{SIRM}\) values implying that the iron-oxide magnetic spherules of anthropogenic origin can easily delineate the
prospect of air pollution by their higher magnetic concentration which is relatively higher in the industrialized area. Therefore, these spherules can be used as an indicator to depict the pollution rate within sediment (sink). The magnetic study of RDS having such spherules can be used for monitoring, mapping and differentiation of sources of roadside pollution.
6.4 X-RAY DIFFRACTION (XRD) STUDY OF ROAD-DEPOSITED SEDIMENTS

6.4.1 Introduction
The XRD technique is used to determine the chemical composition and intensity of mineral phases in RDS and the amorphous or glassy material, as well as crystalline phases present in fly ash (Sharma et al 2005; Sutherland 2003; Gunawardana et al 2012). The method is based on the quantitative analysis of different mineral phases within the dust sample and fly ash collected during a given time period.

6.4.2 Methodology
The RDS samples are sieved to — 200 mesh size (ASTM) then the powdered sample of RDS is transferred to a sample holder. This holder type is chosen due to the absence of low-angle X-ray scatter experienced when using metal holder. The sample is placed in an approximately 1 cm² metal holder. The sample is compressed with the help of a glass slide to evenly spread the sample and then the holder is placed inside the XRD chamber. The XRD analysis is made using Phillips Pan Analytical X’Pert High Score System, University of Allahabad with accelerating voltage of 30 kV and beam current of 25 mA using CuKα target and Ni filter. Analytical conditions for all samples scans are conducted from 10 to 60 (2θ) at a rate of 2° per minute, divergence slit= 1°, antiscatter slit= 1°, receiving slit= 0.30mm. The Silicon standard is used for calibration.

For fly ash the representative samples of fly ash are finely powdered and each powdered sample of fly ash is analyzed by XRD in a manner similar to dust samples.

6.4.3 Results and inferences

6.4.3.1 X-ray diffraction of road dust fraction
The XRD pattern of RDS samples collected during pre monsoon, 2009; fog, 2010 and 2011 for the span of three consecutive years from different sampling locations is given in (Fig. 6.12, a-d; 6.13, a-d and 6.14, a-d). The major phase identified is quartz with other phases like feldspar (plagioclase and orthoclase), calcite, gibbsite, aragonite, apatite and gypsum. The RDS comprise mineral matter which account for about 70-80% of the sample and the remaining 20 to 30% is composed of amorphous constituents. The amorphous matter can be of anthropogenic origin, being incorporated into the road dust as a result of vehicular activities.

The RDS is composed of various mineral phases with predominance of quartz followed by other tecto-silicates (feldspars) and a phosphate (apatite) suggesting their derivation from...
Upper Crustal Composition as large stretch of Allahabad (study area) is composed of alluvial sand derived from both cratonic source (Bundelkhand craton) and Himalayan Mountain chains. However, granite stone quarries in the vicinity (Bundelkhand craton) may have contributed silicates in the dust form and transported in area as well. The iron oxide minerals like goethite, magnetite and hematite possibly derived from both lithogenic (weathering of rocks) and anthropogenic processes (vehicular exhausts and other traffic-related activities). Minerals like calcite, dolomite, aragonite and anhydrite also owe their origin to lithogenic and anthropogenic sources. The gypsum within the RDS originated in the coal-fired thermal power plant, as the burning of coal generally leads to its formation. The mineralogy of the RDS samples collected is consistent with respect to its regional geology and the volume of heavy metals indicates their anthropogenic origin.

The XRD data of the dust samples of a given locations sampled in different seasons interestingly show similar patterns. This means the source remains constant and the climate has little to no effect on the minerals present in RDS and their relative abundance over the sampling period.
Fig 6.12 XRD pattern of representative samples from sampling locations with sample number (a) Chawk, (b) Big Bazar, Civil lines, (c) C.M.P Boys Wing and (d) Sail Warehouse, Naini during pre monsoon, 2009. Mineral abbreviations: Qtz-Quartz, Or-Orthoclase, Pl-Plagioclase, Gy-Gypsum, Gbs-Gibbsite, Chl-Chlorite, Ap-Apatite, Arg-Aragonite, Cal-Calcite, Dol-Dolomite and Anh-Anhydrite
Fig 6.13 XRD pattern of representative samples from sampling locations with sample number (a) Axis Bank, (b) High Court, (c) Chawk and (d) Rambagh during fog, 2010. Mineral abbreviations: Qtz-Quartz, Pl-Plagioclase, Gy-Gypsum, Gbs-Gibbsite, Ap-Apatite, Arg-Aragonite, Cal-Calcite, Dol-Dolomite and Anh-Anhydrite
Fig 6.14 XRD pattern of representative samples from sampling locations with sample number (a) Tulsi Chauraha, Civil lines, (b) Indira Bhawan, (c) Chawk and (d) Sail Warehouse, Naini during fog, 2011. Mineral abbreviations: Qtz-Quartz, Or-Orthoclase, Pl-Plagioclase, Gy-Gypsum, Gbs-Gibbsite, Ap-Apatite, Arg-Aragonite, Cal-Calcite, Dol-Dolomite and Anh-Anhydrite
6.4.3.2 X-ray diffraction of fly ash (IFFCO, Phulpur)

The X-ray diffraction analysis of fly ash shows the presence of crystalline phases like quartz, gypsum, hematite, magnetite and calcite (Fig. 6.15, a-b) etc. The fly ash sample shows that both magnetic fractions are a mixed population. The magnetite and hematite are derived from coal combustion. The magnetite generally forms in the reducing and hematite in oxidizing condition during the conversion of coal to fly ash (Ramsden and Shibaoka 1982). Therefore, the conversion of magnetite to hematite must have taken place at high temperature and high $fO_2$.

Fig 6.15 (a)-(b) XRD pattern of representative samples of fly ash from IFFCO plant, Phulpur, Allahabad showing quartz (Qtz), dolomite (Dol), hematite (Hem), magnetite (Mag), calcite (Cal), plagioclase (Pl), gibbsite (Gbs), gypsum (Gy)
6.5 PARTICLE SIZE ANALYSIS OF ROAD-DEPOSITED SEDIMENTS

6.5.1 Introduction
The particle size analysis of RDS shows the percentage of different size fractions of particulate matter (PM) present and their respective dominance in varied size range. It is recommended that the size classification should be used in any new study dealing with dust analysis, due to its potential value in tracing pollutant sources; furthermore, it would help to identify particular particle sizes, especially those of concern to human health (Al-Rajhi et al 1996). The particle size of road dust deposited on road sides varies from coarser to finer particles. It has been shown that the finer fraction of road-deposited sediments are more toxic than the coarser ones (Adachi and Tainosho 2005; Al-Rajhi et al 1996). Therefore, finer sediments can be used to assess the particulate pollution and of metal fraction, in particular. On the basis of size and toxicity, the particle distribution of the collected sample from different locations can be classified as: PM: >10µm, PM: 10-2.5 µm and PM: <2.5 µm (Cvetković et al 2012; Kisku et al 2012). The PM having aerodynamic diameter less than 10 µm (PM₁₀) is known as one of the most toxic air pollutants on human health as it falls within the range of respirable particles (Jancsek-Turóczi et al 2013). In the case of fly ash, the fine particulates released are not trapped by any devices and mainly comprise PM₂.₅. Thus, particle size distribution is an important physical parameter to analyze the PM and to determine the particle behaviour (Bian and Zhu 2009).

The long distance transport of particulate matter is also reported across the continents. PM₀.₁-PM₅ derived from Asian dust storms has been reported from Greenland (Biscaye et al 1997; Svensson et al 2000) and in ice cores from Canada (Zdanowicz et al 2006). The particle size range for long distance transport may vary and in regional scale. The aerosol particles from Korea ranging in diameter from 12 to 13 µm are observed in Beijing (Yang et al 2007 a).

6.5.2 Methodology
The dust samples and fly ash are sieved to 200 mesh (ASTM). The sieved portion is analyzed using Malvern Mastersizer 2000 (Ver. 5.60) laser-granulometer with a detection range from 0.3 to 300 µm with an accuracy of ± 3% in the beam wavelength range between 633 and 435nm. About 10-20 gm of the sample is used to ascertain grain size distribution. Each sample is run three times and then the average is taken for the particle size measurement.
6.5.3 Results and Inferences

6.5.3.1 Particle Size Distribution of Road Dust Fraction

The RDS are sorted according to their eight grain size fractions of <45, 45-63, 63-106, 106-150, 150-250, 250-500, 500-1000, and 1000-2500 µm. In sedimentology, the size fraction of sediments are classified (Sutherland 2003) as: <63 µm (silt and clay), 63–125 µm (very fine sand), 125–250 µm (fine sand), 250–500 µm (medium sand), 500–1000 µm (coarse sand), and 1000–2000 µm (very coarse sand).
Fig 6.16 (a)-(f) showing grain size versus mass% variation sampled from different locations showing polymodal distribution

The cumulative grain size fraction distributions observed during the present study from different sampling locations show polymodal size distribution (Fig. 6.16, a-f) with three prominent modes (63-106, 150-250 and 1000-2500 μm). It can be seen that <63 μm grain size fraction constitutes about 10-18% from the bulk RDS. The fractions of 45-63, 106-150, 250-500, 500-1000 μm constitutes of 25-30% within the sample. RDS particles with grain size of 63-106, 150-250 and 1000-2500 μm are the most abundant among all the eight size fractions comprising 55-60% of the whole sediment samples. The finer fraction of sediments <10 μm are present (<1%) in RDS. The grain size distribution is seen to be uniform except in the Industrial area, Naini where <45 μm size fraction is more than 11% showing the presence of relatively finer grains. The samples are collected from major traffic junctions (Johnstonganj, In front of Chandralok Talkies, Rambagh) (Fig. 6.16, a-c), college area (In front of Ewing Christian College) (Fig. 6.16, d), commercial area (Axis Bank) (Fig. 6.16, e) and industrial area (In front of Sail Warehouse, Naini) (Fig. 6.16, f).

From the above data it can be inferred that Naini area has maximum RDS in terms of absolute mass and the cause can be attributed to low removal efficiency of finer dust fractions from the roadsides. It is also noticed that broken road surface with larger cracks leading to the formation of pot holes on the surface have resulted in the deposition of finer dust fractions. The particle size analyses of RDS samples from the three sampling periods (pre monsoon, 2009; fog, 2010 and 2011) show similar grain size patterns irrespective of temporal variations with respect to different locations.
6.5.3.2 Particle Size Distribution of fly ash (IFFCO, Phulpur)

The particle size distribution of bulk fly ash fraction refers to volume fraction in a particular size range. The grain size distribution of fly ash sample includes spherules, composite/aggregates and large agglomerates whereas PM$_{2.5}$ and PM$_{10}$ fractions of fly ash consist of individual microspherules. The grain size of fly ash ranges from 10 to 1000µm and about 47.3% of the total volume of the given sample lies within 10 to 100µm size as presented in Fig. 6.17 The silica spherules observed in fly ash, in general, occur in size range between 0.1 and 1000 µm.

![Particle size distribution of fly ash](image)

Coal-fired power plants along with traffic activities are the major contributors of PM$_{2.5}$ in any urban area (Grobéty et al 2010). The fine-grained fly ash lying within the “respirable” size range (<10 µm) and suspended particulate matter size range >10 µm.