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Pollution-Related Magnetic Signature of Atmospheric Fine Particulate Suspended Dust Collected By Cloth Samplers in Visakhapatnam City, India: A New Tool for Detecting and Monitoring Sources of Air Pollution

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ABSTRACT:
Using rock and environmental magnetism techniques, magnetic analysis is done on 118 cloth (textile) samplers loaded with fine particulate atmospheric dust suspended on them to identify the sources of air pollution and to delineate the pollution signatures of the various zones in the Visakhapatnam city affected by industrial pollution and road traffic. A new method to collect suspended particles in air using cloth samplers as atmospheric fine dust catchers for monitoring air pollution was introduced known as "Textile sampling method" in contrast to the traditional bio-monitoring techniques of identifying sources of pollution by means of magnetic susceptibility signatures of dust-loaded leaves in the fast growing industrial cities in India like Visakhapatnam. The weight of accumulated dust (in milligrams) on these cloth samplers in a period of two months collected at various industrial and traffic zones of the city clearly point out the presence of the emissions of fine magnetic suspended particles (SP) from various sources. The variations of magnetic susceptibility (k) distinguish pollution source within the city and is mainly controlled by the local pollution effects. The percentage frequency dependence susceptibility (kfd%) variations indicating high ultrafine percentage of magnetic grains in the Particulate Matter (PM) at various sampling sites. Higher kfd% values are found at heavy traffic areas pointing out that vehicular emissions contain a higher percentage of ultrafine SP grains than the SP in industrial zones. The variation of kfd% is interpreted as the relative degree of human health hazardous zones.

Keywords:
Textile sampling, bio-monitoring, suspended fine magnetic matter, magnetic susceptibility, particulates.

1. INTRODUCTION:
Air pollution is a serious problem in developing countries with fast growing industrialisation and poor governmental regulation on environmental issues. These 'Fine Suspended Particles' (FSP) vary in size, composition and origin. They originate mainly from combustion processes in vehicles, power plants and industries. FSP between 2,5 µm to 10 µm contain both natural dust materials and transient dust from roads and industries. FSP ranging from 100 nm to 2.5 µm mainly stem from gas to particle conversion, combustion and re-condensed organic and metal vapours. (WHO report 2003). FSP are considered as a threat for human health due to their chemical intolerance for the organism and their penetration into the human respiratory system [1].

Many biological, geochemical, and toxicological studies have proved that FSP matter play a vital role for many cardiopulmonary diseases and lung cancer (Valavanidis et. al. 2008). Most studies of monitoring air pollution are done in small scales; they are expensive and time consuming. With the existing instrumentation it is almost impossible to get a spatially comprehensive control over the situation especially in large cities of developing countries with poor environmental laws, and unprecedented vehicular and industrial emissions. It is therefore important to explore new methodologies to improve the spatial characterization of FSP matter [3].

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The application of fast and cost-efficient methods to detect and monitor hazardous suspended dust in fast growing cities of developing countries is applauded. During the past two decades magnetometry was explored as a tool to detect environmental pollution in high-resolution scales with relatively low costs and in less time (Flanders, 1994; Kapicka et al., 2000; Goddu et al., 2004; Jordanova et al., 2008; Meena et al., 2011; Ravi et al., 2017). Magnetic properties are dependent on composition, grain size and source of the material, which enables a differentiation of the magnetic signal caused by natural (lithogenic, pedogenic) and anthropogenic origins (Hanesch et al., 2007; Jordanova et al., 2008; Kapicka et al., 2008). Magnetometry turned out to be especially suitable for detecting heavy metal pollution caused by fly ash; it is based on the fact that during combustion processes both toxic heavy metals and strong magnetic particles (iron oxides or sulphides) are released into the environment (Spiteri et al., 2005; Blaha et al., 2008). Measuring the ferrimagnetic concentration and screening enhanced magnetic signals in polluted soils or sediments, or in road dust, provides a qualitative estimate of the degree of environmental pollution (Mitchell and Maher, 2009; Blaha et al., 2008; Jordanova et al., 2013) [2].

The present study attempts to use magnetometry to detect hazardous levels of particulate matter in Visakhapatnam city (also known as Vizag) and to distinguish between areas affected by traffic and industrial pollution. Previous attempts of studying the degree of environmental pollution using magnetic methods targeted tree leaves and pine needles as natural dust samplers (Gautam et al., 2005; Hoffman et al., 2013). Unavailability of tree leaves of the same species in the study region, and unpredicted rains washing out the dust, limit the possibility for such kind of bio-monitoring. To overcome this limitation Cao et al. (2015) presented an alternative method using simple passive samplers in order to study environmental pollution. In this paper, we suggest another type of simple passive samplers, which are especially suitable for application in city areas (cloth sampling method) [4].

2. STUDY AREA:

The present study is carried out in various industrial and residential zones of Visakhapatnam city. Visakhapatnam is a port city on the southeast coast of India in the state of Andhra Pradesh and often called “The Jewel of the East Coast” and the “City of Destiny”.With a population of 2,091,811 and occupying 681.96 square kilometres (263.31 sq mi), it is the administrative headquarters of Visakhapatnam district, and the second largest city in the state of Andhra Pradesh and the third largest city on the east coast of India. Visakhapatnam is located 625 kilometres (388 mi) east of Hyderabad and 781 kilometres (485 mi) North east of Chennai. It is situated in the middle of Chennai- Kolkata Coromandal Coast. The city is home to several state-owned heavy industries and a steel plant, one of India’s largest seaports and has the country’s oldest shipyard. Visakhapatnam has the only natural harbor on the east coast of India. Major industries, residential areas, heavy traffic zones along with national highways are located in the study area and they mainly deal with production of iron material, smelting, petroleum processing and transport [5]. The map of the study area is shown in the Fig.1 and the elevation map of Visakhapatnam city corresponding to the location of various pollution sources is shown in Fig.2. The elevation map of Visakhapatnam, it is appearing likely as a bowl in shape. The elevation values were mapped with the help portable Global Positioning System (GPS), exactly where latitude and longitude values are taken simultaneously along with leaf samples. The respective longitudes and latitudes are taken along X–axis & Y-axis respectively for 110 measured sites of industrial, residential and heavy traffic zones respectively.

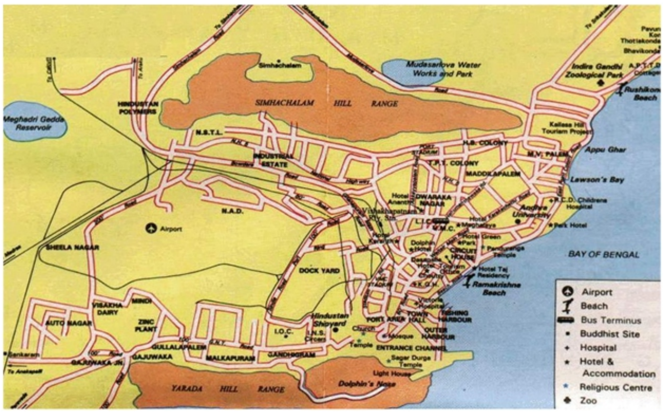

Fig.1 Sketch map of the study area

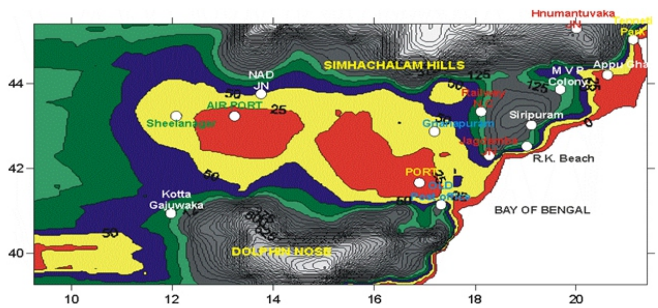

Fig.2 Elevation map of the study area show areas of various expected sources of pollution. It is appearing likely as a bowl in shape.

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3. MATERIALS AND METHODS:

3.1. Sample collection and preparation:

Nap textile medium raised (fuzzy) surface rug cloth was cut into pieces of equal dimension (10x10 cm). The corner of the cloth is pierced with the thread for tying it at the desired height. The cloths were weighed with a digital balance (accuracy 10 mg) in the laboratory and later hanged as dust collectors ca. 2.5 m above the ground level at various locations in the city. The hanged cloth flutters in the wind with both sides exposed and its thickness do not allow itself to fold.

Nap textile medium raised (fuzzy) surface rug cloth (shown in the left side) used for sample collection in the field work and sample preparation in the laboratory as fine magnetic suspended atmospheric dust catcher. The method of collecting textile samplers in the field was shown (on the right side). After recovery, we sealed the cloths in pre-weighted self-locked plastic bags and determined the total weight of the dust trapped by the cloths in the laboratory [6]. The sampling locations to conduct the survey are carefully chosen by using Visakhapatnam city map. The latitude, longitude and elevations are measured with a Global Positioning System (GPS). We choose sampling points avoiding direct exposure to roads, heavy traffic, known contaminated sites, and industries.

To avoid direct influence from rain we placed the cloths in sheltered positions. We left the cloths exposed to air for a period of two months i.e. from end of April to end of June 2012. Sampling points covers almost all major traffic and industrial areas of the Visakhapatnam city with an approximate distance of 500m maintained between them. The numbers of textile samples utilized to monitor air pollution were 200 in number, out of which 118 samples were successfully collected after two months of the initial filed work. Initially, the weights of the empty clothes were measured with a digital electronic balance in the laboratory.

Thereafter, the dust loaded textile samplers from the field were safely collected and preserved in empty covers (whose weights are already known), such that further contamination of the clothes is not possible by any means. Thereafter, the weights of these clothes loaded with magnetic dust from both industrial and heavy road traffic zones are measured [7]. These weights subtracted from the empty cloth weights already determined, gives the amount of dust accumulated from the time of attaching the cloths from the time of their recovery from the field.

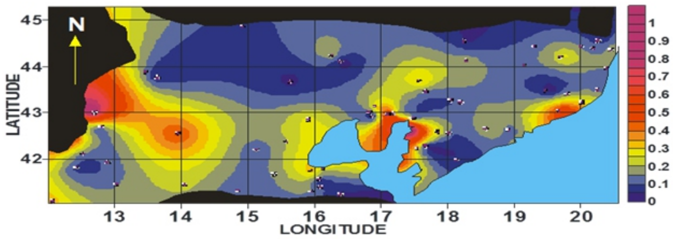

Fig.3 Contour map loaded percentage of accumulated dust on cloth samplers

The spatial distribution of the dust weight provides a first information of the dust load in the study area shown in Fig.3. The above contour map of amount of suspended fine particulate matter that was deposited on the cloth samplers for a period of two months clearly shows and demarcating the zones of dust spots (in miligrams) with relatively high and low magnitudes in the respective industrial and road traffic zones of the Visakhapatnam city. Now, these pre-weighed dust loaded cloth samplers are now prepared into samples in a way suitable for low and high frequency susceptibility measurements using BARTINGTON dual frequency susceptibility meter.

3.2 Magnetic susceptibility (MS):

Magnetic susceptibility is a dimensionless proportionality constant that indicates the degree of magnetization of a material in response to an applied magnetic field.

$$\kappa = M / H$$

where, κ = Magnetic Susceptibility

M=Magnetisation

H=Applied Field

There are two types of susceptibility measurements:

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» Mass specific measurements:

The sensor is calibrated for a sample mass of 10g. Mass specific measurements are the preferred method of expressing measurements using this sensor. For dry materials and for materials of known density this provides the most useful measurement because simple weighing of the material is all that is required. Where sample mass departs from calibration mass the corrected value will be:

χ = Measured value of susceptibility / Sample density

» Volume specific measurements:

Where comparison only between identically prepared samples is required or where it is not desired to dry out wet samples then "volume" susceptibility can be recorded directly. Where sample volume departs from calibration volume the corrected value will be:

k = Measured value of susceptibility / Sample volume

3.3 Magnetic measurements in the laboratory:

The magnetic susceptibility system comprises a meter with a range of sensors for measuring the magnetic susceptibilities of many types of materials. The MS2 device measures the magnetic susceptibility. It operates by generating a low frequency, low intensity AC magnetic field around the sensor. The meter displays the value of magnetic susceptibility, when the materials are brought within the influence of the sensor by resulting change in the AC magnetic field. The resolution of the system is 2×10^{-6} SI units. The range of sensors allow measurements of individual soil or rock samples, sediment cores, soil surfaces, rock outcrops etc., in the laboratory as well as in the field. The measurements on the samples are non-destructive in the sense that, they retain the original sample magnetic characteristics [8].

The dust loaded leaf samples are now used for low frequency and high frequency susceptibility measurements using BARTINGTON MS 2B Dual Frequency Sensor. This laboratory sensor is specifically calibrated for use with a 10cc sample container with internal dimensions 24 mm diameter × 23 mm height and a base external diameter of 26 mm maximum. Sample insertion and removal is facilitated by a hand operated moving platen with a 27.5 mm stem.. This is a single sample dual frequency sensor accepts 10 cubic cm samples in plastic pots supplied by Bartington instruments. Suitable polystyrene sample containers produced from virgin plastic and sealed with a polyethylene lid are available from Bartington instruments. This is a portable laboratory sensor which has the facility of making measurements at two different (low and high) frequencies. The Bartington Instruments MS 2B Dual Frequency Sensor measures mass dependent susceptibility (χ) in [m^3 kg^{-1}], within an AC magnetic field amplitude of 80 Am^{-1} at low frequency (0.465 kHz or 465 Hz) and high frequency (4.65 kHz or 4650 Hz) ± 1%. Measurements made at these two frequencies are corrected for mass to account for any bulk density differences between the samples. Samples were measured at each of the above two frequencies, i.e., low-frequency mass-dependent susceptibility (χ_{lf}) and high-frequency mass-dependent susceptibility (χ_{hf}), both are measured in [m^3 kg^{-1}]. When dual frequency measurements are not required, the results with best precision are obtained by LF (low frequency) measurements. This is shown in Fig.4.

Fig .4: Magnetic Susceptibility System - BARTINGTON MS 2B dual frequency sensor.

The coefficient of frequency dependency (χ_{fd}) can be expressed as the change in susceptibility per decade frequency divided by the low-frequency susceptibility (χ_{lf}) where the low frequency susceptibility will always have the higher value. Materials containing fine grained magnetic particles exhibit frequency dependent susceptibility and this is particularly significant if there are single domain grains with their diameter is of the order of 0.03µm. If there are relatively small changes in diameter, then there occurs very rapid change in frequency dependency. These single domain grains are widely distributed in naturally occurring materials (like road dusts, suspended dusts on leaves of plants etc.,) in varying sizes which give rise to a fairly uniform frequency dependency of susceptibility in the low kHz range in which MS2 meter operates.
Frequency-dependent magnetic susceptibility (χ_{fd}) can be expressed as a percentage loss of susceptibility,

$$\chi_{fd\%} = \frac{[(\chi_{lf} - \chi_{hf})]}{\chi_{lf}} \times 100$$

Magnetic susceptibility is a measure of the degree to which a substance affects a known magnetic field and is a function of the concentration, grain-size, and type of magnetic minerals present in a sample (Begét et al., 1990). The above two types of magnetic susceptibility measurements are commonly used to infer specific magnetic grain-sizes and concentrations. Measurements made at the two frequencies mentioned above are generally used to detect the presence of ultrafine (< 0.03 µm) superparamagnetic (SP) minerals occurring as crystals produced by bacteria or by mineral authigenic chemical processes occurring in soils.

Samples where SP minerals are present will show slightly lower values when measured at high frequency; samples without the superparamagnetic minerals will show identical κ values at both frequencies (Dearing, 1999). Table 1 outlines the suggested $\chi f_{d\%}$ values for the occurrence SP grains in a environmental samples.

Table 1 Interpretation of $\chi_{fd\%}$ values. When $\chi_{fd\%}$ > 10% use $\chi_{fd\%}$ as an estimate of SP concentration. (From Dearing, 1999).

Low $\chi_{fd\%}$	< 2.0	Virtually no SP grains
Medium $\chi_{fd\%}$	2.0 – 10.0	Mixture of SP and coarser grains, or SP grains < 0.05µm
High $\chi_{fd\%}$	10.0 – 14.0	Virtually all SP grains
Very High $\chi_{fd\%}$	> 14.0	Erroneous measurement, anisotropy, weak sample or contamination

Environmental pollutants caused by anthropogenic sources are strongly magnetic in many cases, e.g., effluents of power plants, combustion of fossil fuel, metallurgical industries, smelters and road traffic are accompanied by significant emissions of strongly magnetic fine particles.

They main magnetic phases observed are magnetite, maghemite and iron which causes the increase in the magnetic susceptibility and thereby enhancing the magnetic properties of the suspended atmospheric dust. Another source of pollution is the vehicular transport due to abrasion and exhaust emissions which are mainly accumulated at the edges of the roads.

Fig.5 shows the major sources of air pollution from anthropogenic origin containing fine grained magnetic paricles:

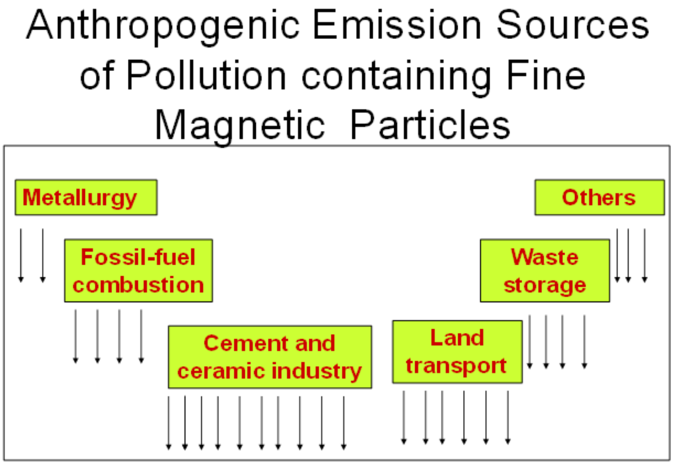
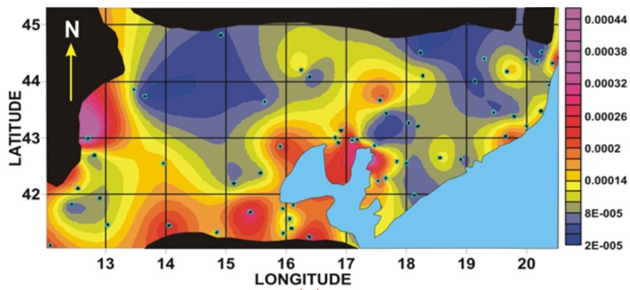
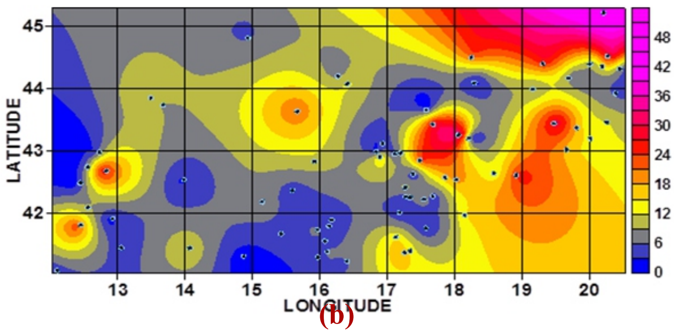


Fig.5 Major sources of air pollution – Sources of particulate matter

Magnetic susceptibility measurements were done in the laboratory, for all the 118 dust loaded cloth samplers collected at the sampling sites at their respective latitudes and longitudes. Using BARTOSOFT software, the mass specific and frequency dependence of the susceptibility on the collected textile dust loaded samples were studied and their corresponding contour maps were prepared. The low frequency (LF) and high frequency (HF) measurements give an idea of fine magnetic matter content and its behavior. The susceptibility contours were shown in Fig.6. Susceptibility data collected from various sites of Visakhapatnam city which clearly demarcate the zones of low, intermediate and high pollution levels (shown by scale on the right) in the figures 6 (a) & 6(b).



(a)



(b)

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Fig.6 Magnetic susceptibility measurements on the dust loaded cloth samplers
(a) Mass specific susceptibility contours
(b) Frequency dependent susceptibility contours

4.RESULTS AND DISCUSSION:

The major inputs for anthropogenic sources of air pollution containing fine grained magnetic particles deposited as suspended particulate matter on the textile samplers came from different sources (Fig.5). But, at the sampling locations the effect of local pollution sources was believed to be more predominant. The percent dust loaded contour map clearly reveals the spatial distribution of suspended dust obtained at different areas which may indicate the tentative hotspots of pollution in the study area. In general, suspended particles that evolved from natural processes such as wind erosion are coarser then those that originated from combustion processes like vehicular and industrial emissions (Mbengue et al., 2014, Kozlowska et. al. 2015) [9].

The highest amounts of collected dust mass were found at the port, in the industrial area and in heavy traffic zones as expected. The frequency dependent susceptibility measurements clearly point the presence of the deposition of fine grained particulate matter. The spatial distribution of accumulated dust weight along with the variations of mass specific and frequency dependent susceptibilities among various zones in the contour patterns indicates that, the magnetic concentration signal is dominated by the ferrimagnetic fraction [10]. The range of magnitudes of susceptibility values in our study area are higher closer to the industrial and port zones, whereas medium to low values occur at traffic zones and residential areas as depicted by the contour patterns.

This could indicate that the susceptibility values are controlled by different local sources of pollution or that there is a distance effect to larger sources. Thus, the above studies more or less reveal the fact that the magnetic signal is influenced by the different sources of pollution with a distance effect in the study area. Traffic related dust seems to contain a larger fraction of fine suspended particulate matter (FSP) than in industrial areas, while the dust in the residential areas is containing relatively more magnetite. The latter seems to be related the influence of the industrial emissions that influence the atmospheric FSP over longer distances than traffic emissions which mostly contain ultrafine super paramagnetic particles. In high traffic zones, both contributions are important.

These studies shows that, it is possible to distinguish the contribution of various zones (industrial, road traffic and residential) of the city, in producing distinct magnetic signatures based on the mass and frequency dependence magnetic susceptibility patterns and air pollution hot spots from the estimated dust load [9] [10]. These observations show that the applied simple sampling technique is reliable. Besides providing the opportunity for a time-saving and spatially high-resolution monitoring, the cloth samplers have also the advantage of collecting only finer particles because coarser ones will easily drop down due the gravity effect.

5. CONCLUSIONS:

Cloth samplers method was proved to be a simple, cost-effective and fast tool to detect atmospheric pollution sources and to monitor suspended particulate matter. The measurements of susceptibility and weight of the suspended dust load using textile method indicate that the susceptibility can be used as a proxy for monitoring the spatial distribution of pollution levels in the city. Also it is evident that, the magnetic concentration signal of the suspended dust is largely controlled by the pollutants from local source than from the far distance. Thus, the results enable us to know the extent of pollution zones. Moreover, the frequency dependent susceptibility measurements clearly indicate that, fine suspended particulate matter (FSP) released from vehicular traffic was more hazardous to human health.

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