



Assessment of Concentration and Distribution of Contaminants Using Magnetic Susceptibility Measurements

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Article Info	ABSTRACT
<p>Article type: Research Article</p> <p>Article history: Received: 25.05.2022 Revised: 03.07.2022 Accepted: 25.10.2022</p> <p>Keywords: Magnetic Susceptibility heavy metal contamination tropical deciduous forest soil</p>	<p>Magnetic properties are used throughout the world to measure the concentration of (ferri) magnetic minerals in soil, sediment and dust. These minerals in soil come from a variety of sources, including air-borne particulate pollution, parent rock and pedogenesis. Changes in the content of magnetic minerals, as well as their spatial and vertical distribution in soil profiles are caused by human activity. Magnetic minerals are distinguished by their affinity for other elements found in soil, such as heavy metal. As a result, magnetic susceptibility has been widely used as an approximation of heavy metal contamination in soil. The current study was conducted in a tropical deciduous forest in Central Uttar Pradesh, namely the kukrail reserve forest in Lucknow to assess heavy metal contamination levels caused by various anthropogenic activities and to confirm the utility of using MS surveying in these types of studies. The current study was conducted at two sites viz. agricultural area and forest area because these sites are the most contaminated ones. Significant correlation between heavy metal concentration and magnetic susceptibility with $p < 0.005$ is noticed for Co, Cr, Pb, Zn, Cu and Fe of agricultural area. Similarly in forest area significant correlation exists between Cr, Ni, Pb and Zn. The χ_{LF} values show a significant correlation with the concentration of heavy metals except for Cu and Cr in forest area and Pb and Zn in agricultural area. In comparison to the methodologies of chemical analysis, the χ_{LF} measurement techniques provide us with lower cost and less time consuming method for identification of possible soil pollution.</p>

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INTRODUCTION

Soil is considered contaminated when chemical substances are present or other modifications have been made to its local environment. This is frequently resulting from unintentional releases of chemical substances or the fallacious disposal of dangerous waste. Increased inputs of metals and artificial chemical substances in the terrestrial surroundings because of speedy industrialization coupled with inadequate environmental management in the growing country like India, has brought about large scale pollutants to the surroundings. They obviously pose a high threat to the quality of soils, plants, natural waters and human health in the terrestrial environment (Adriano, 2001; Hooda & Naidu, 2004; WHO, 2004). Many countries around the world are faced with the legacy of past industrial activities in the form of contaminated and degraded land. At the very same time new housing and commercial advancements require

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space and are increasingly affecting the green belts of cities and countryside. Contamination of soils with heavy metals has generally taken place in regions of mining, smelting and processing of mineral ores. Sims (1986) mounted that the toxicity and mobility of heavy metals in soil isn't always managed with the aid of using the entire concentration only, however it depends additionally on metal properties (e.g. binding state) and environmental factors (e.g. soil pH, redox condition or organic matter content). Increased emissions from cars, factories and industrial wastewater are the result of rapid urbanization and industrialization has negative effects on the prevailing environment. Heavy metal contamination is taken into consideration as one of these negative outcomes (Kim et al, 2010b). Dust that collects on soil and roadsides in urban areas is an indicator of heavy metal pollution due to atmospheric deposition.

During the last few years, many studies in terms of the content of heavy metals pollution in urban areas, have been reported (Wilcke et al., 1998; Li et al., 2001; Moller et al., 2005; Rimmer et al., 2006; Wong & Selvam, 2006 ; Yongming et al., 2006). In order to evaluate the anthropogenic impact it is important to know the degree of pollution which not only depends on total heavy metal content but also on proportion of their mobile and available forms. The correlation between magnetic susceptibility and heavy metal content has been reported in many recent works (Petrovsky & Ellwood, 1999; Durza, 1999; Petrovsky et al., 2001; Shu et al., 2001). These works describe different relative forms between the analyzed elements, the nature of the analyzed material and the anthropogenic processes concerned in the emissions of ferromagnetic materials. The complexity of these interactions determines how far susceptibility can provide information on heavy metals pollution (Hanesch & Scholger, 2002). In the last years, several proxy method have been used to outline increase level of pollution .One of them is based on measurement of the concentration of (ferri) magnetic mineral of anthropogenic origin .This approach was successfully applied in several European cities and has shown that magnetic parameters (mainly magnetic susceptibility) can be used as a proxy for heavy metal pollution in top soil. Although the technique is well established for studying several urban and water pollution (Dearing et al., 1996), industrial emission and pollution (Petrovsky & Ellwood, 1999), road traffic, fly ash and aerosol (Dekkers & Petersen, 1992; Goddu et al., 2004; Hoffmann et al., 1999 ; Jordanova et al., 2004; Kapicka et al., 1999 ; Muxworthy et al., 2001) by analysing the concentration composition and granulometry of the magnetic material (Evans and Heller, 2003). Heller et al., 1991 and Bityukova et al., 1999 confirmed a strong relationships of magnetic susceptibility to heavy metal pollution in soil by cumulative of chemical and magnetic analyses. Magnetic susceptibility thus provides an indicator of heavy metal contamination of soils. The aim of our study was to trace the distribution and concentration of contaminants (heavy metals) in the soil along the major sires of tropical deciduous forest by using magnetic proxies.

MATERIALS AND METHODS

Sampling area was carefully selected to cover different land use zones. Sampling stations were divided two zones as agricultural and forest zones. The sampling interval of all the top soil was 0-10 cm. Global Positioning System (GPS) was used to locate all the sampling sites. At each sampling site, a sample was collected using a stainless steel trowel and stored in a plastic bag. In addition samples were dried and stored in bag for use.

To test how far magnetic measurement of soil samples can give information about soil pollution. The soil samples were collected, air-dried, sieved and measured for the bulk magnetic susceptibility at two frequencies (0.47 and 4.47 kHz) using Bartington MS2B susceptibility meter. The sensor operates with an alternating current producing an alternating magnetic field (80 A/m, Bartington Instruments Ltd., 2000). The MS2B dual frequency sensor is used with 10 ml sample containers. The sensor can be operated at two different frequencies, at low frequency 0.47 kHz (LF-Low frequency) and at high frequency 4.47 kHz (HF-High frequency). Samples

were measured at each frequency for studying the frequency dependence of susceptibility. The low frequency is usually selected when single frequency measurements are needed. In this study six measures of MS were taken from each sample and the average was done. The frequency dependence of magnetic susceptibility is expressed as percentage ($\chi_{FD}\%$ -Frequency Dependence):

$$\chi_{FD}\% = [(\chi_{LF} - \chi_{HF}) / \chi_{LF}] \times 100$$

Before taking a reading it is necessary to remove any vegetation to avoid rough surfaces. The depth of response is 0-10 cm at 15 mm and 10% at 60 mm. Five measurements were taken for each sample and the average of these measurements was done.

For chemical analysis the dried sample are disaggregated with mortar and pestle and sieved through a sieve of 2mm. Sample weighing was performed using analytical balance as low as 0.0001g with precision. Samples of 1g of soil were taken in 100ml beaker and digested for 1h on a hot plate with 10ml of aquaregia. The samples are dissolved with 10ml of 2% nitric acid after evaporation to near dryness, filtered and then diluted with double distilled water to 100ml.

Soil Samples are analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES-9000 template, Shimadzu, Japan) for metal ions. In the sample solution the metals are measured by aspirating the sample solution directly into the instruments plasma. Instrument for the individual elements has been standardized. Using generic solution, the calibration curve was obtained for each metal ion. Standard solution of various metals of interest is prepared from 1,000 mg / l stock solution. The minimum metal concentration that the instrument could detect was 10ppb.

Statistical analysis of heavy metal concentration and magnetic measurements were obtained using SPSS software in order to establish the relationship between heavy metal concentration and magnetic measurements in soil samples.

RESULTS AND DISCUSSION

The determination of heavy metals in soils become carried out for the measurement of overall element content and to evaluate the bottom line expertise of soil components with respect to which changes in soil composition are produced via way of means of car pollutants and agricultural inputs in the surrounding fields (Kiikkila, 2003; Oancea et al., 2005; Tahar and Keltoum, 2011).

Table 1 shows the concentration of different heavy metals for soil samples. We examined only seven heavy metals to show pollution changes. The soil of agricultural area contain high concentration of heavy metals Co (9.84 $\mu\text{g/g}$), Cr (73.69 $\mu\text{g/g}$), Ni (55.85 $\mu\text{g/g}$), Pb (23.88 $\mu\text{g/g}$), Zn (56.4 $\mu\text{g/g}$), Cu (23.48 $\mu\text{g/g}$) and Fe (944.13 $\mu\text{g/g}$). Similarly the concentration of heavy metals in forest soil is Co (33.09 $\mu\text{g/g}$), Cr (95.22 $\mu\text{g/g}$), Ni (65.21 $\mu\text{g/g}$), Pb (26.03 $\mu\text{g/g}$), Zn (94.35

Table 1. Heavy metal concentration

S. No	Heavy metals	Forest Area ($\mu\text{g/g}$)	Agricultural Area ($\mu\text{g/g}$)
1	Cobalt (Co)	33.09	9.84
2	Chromium (Cr)	95.22	73.69
3	Nickel (Ni)	65.21	55.85
4	Lead (Pb)	26.03	23.88
5	Zinc (Zn)	94.35	56.4
6	Iron (Fe)	1010.48	944.13
7	Copper (Cu)	42.96	23.48

$\mu\text{g/g}$), Cu (42.96 $\mu\text{g/g}$) and Fe (1010.48 $\mu\text{g/g}$). Thus the high concentration of heavy metals in forest area indicates the presence of magnetic particles along with heavy metals.

Tables 2 and 3 gives the values of magnetic susceptibility at low and high frequency (χ_{lf} , χ_{hf}), the derived value χ_{fd} % of sample collected in the study area. In the forest area, the values of magnetic susceptibility at low frequency varied from 9.64 to $17.47 \times 10^{-8} \text{ m}^3/\text{kg}$ with the mean value of $13.205 \times 10^{-8} \text{ m}^3/\text{kg}$ (Table 2). In the agricultural land χ_{lf} susceptibilities varying from 19.04 to $28.50 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$ with a mean value of $24.04 \times 10^{-8} \text{ m}^3/\text{kg}$ (Table 3).

Similarly susceptibility at higher frequency varied from 9.01 to $16.54 \times 10^{-8} \text{ m}^3/\text{kg}$ with a mean value of $12.496 \times 10^{-8} \text{ m}^3/\text{kg}$. In the agricultural land χ_{hf} susceptibilities varying from 18.04 to $27.45 \times 10^{-8} \text{ m}^3/\text{kg}$ with a mean value of $23.16 \times 10^{-8} \text{ m}^3/\text{kg}$.

The Kukrail Reserve Forest soils from forest land can be considered to be highly magnetic while those from agricultural land would be moderately magnetic. In general, there are many factors that cause magnetic susceptibility variations (MS), such as the differences in lithology (lithogenic/geogenic), soil forming processes (pedogenesis), and anthropogenic contribution of magnetic material (Dearing et al., 1996; Hanesch and Scholger, 2005). Sadiki et al., 2009 confirmed that the lithology is the main factor contributing to the magnetic susceptibility variation.

Large MS value suggest a high concentration of ferromagnetic minerals which could be either neoformed (Paedogenic origin), acquired from the substructure or allochthonous. The latter are often the consequences of atmospheric pollution (e.g. loess or polluted dust). Paedogenic ferromagnetic minerals have been reported to be created by oxidation of Fe^{+2} in iron bearing minerals in soils subject to moist drying cycles, which have been the features of climatic conditions (Hanesch and Scholger, 2005). Thus, the MS in the upper soil would represent the type of soil as well as the parent mineral components.

The mean magnetic susceptibility (MS) in the forest cover is high in comparison to the

Table 2. Magnetic parameters measured on the different samples of Kukrail Reserve Forest land.

S.No	SAMPLE ID	χ_{LF}	χ_{HF}	χ_{FD} %
1	KRFF1	14.38	13.21	2.82
2	KRFF2	14.69	14.01	2.95
3	KRFF3	16.78	15.43	3.12
4	KRFF4	13.24	12.98	2.04
5	KRFF5	9.64	9.32	1.84
6	KRFF6	11.24	10.51	2.41
7	KRFF7	13.74	12.84	2.18
8	KRFF8	15.56	14.31	3.04
9	KRFF9	17.47	16.54	3.24
10	KRFF10	10.41	9.21	1.98
11	KRFF11	10.24	9.01	1.76
12	KRFF12	11.38	10.62	2.51
13	KRFF13	14.54	13.98	2.87
14	KRFF14	13.44	12.98	2.31
15	KRFF15	13.01	12.45	1.97
16	KRFF16	12.64	11.95	2.41
17	KRFF17	10.48	10.12	1.84
18	KRFF18	13.18	13.01	1.86
19	KRFF19	14.56	14.23	2.88
20	KRFF20	13.48	13.21	2.24

Table 3. Magnetic parameters measured on the different samples of Kukrail Reserve Agricultural land.

S.No	SAMPLE ID	χ_{LF}	χ_{HF}	χ_{FD} %
1	KRFA1	27.03	26.91	1.47
2	KRFA2	28.50	27.45	1.42
3	KRFA3	19.45	18.32	2.36
4	KRFA4	19.04	18.04	2.41
5	KRFA5	26.14	25.32	1.01
6	KRFA6	22.45	21.62	2.28
7	KRFA7	24.12	23.47	2.31
8	KRFA8	25.44	24.13	2.34
9	KRFA9	27.98	26.54	1.43
10	KRFA10	20.31	19.84	2.15

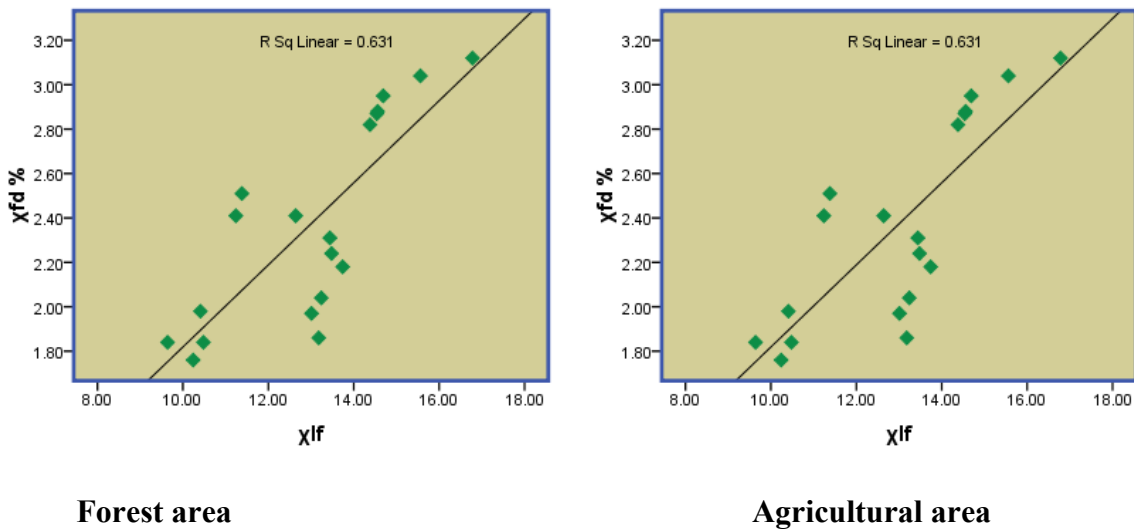


Fig. 1. Interdependence between χ_{fd} and χ_{lf}

agricultural land. This difference plays an essential role, as it suggest that the protected natural soils are much more stable than the agricultural land and be regarded as undisturbed areas due to the density of vegetal cover that serves to protect the soil from erosion.

Smaller values in agricultural area are likely due to the combined effects of magnetic signal dilution due to the weakly limestone soil element and the erosion of surface soil.

In all the soil profile χ_{lf} has higher value than χ_{hf} . This difference is due to the addition of fine-grained supermagnetic grains which at high frequency have relaxation time shorter than the measurement time, are magnetically blocked and therefore do not contribute to the measured signal. The difference thus indicates the presence of ultrafine ferri magnetic minerals (Sangode et al., 2010 ;Dearing et al., 1996).

The differentiation between χ_{lf} and χ_{hf} can be expressed as a relatively loss of susceptibility (χ_{fd}), this difference is significant as shown in Table 2 and 3. In the forest soil χ_{fd} ranges from 1.76 and 2.95 % with a mean of 2.413 %. In the agricultural soil χ_{fd} varied between 1.01 to 2.36% with a mean of 1.89 %. Low χ_{fd} % values are likely to indicate the beginning of pedogenic formation of magnetic particles in soil.

Figures1 is the graphs of χ_{fd} versus χ_{lf} in the topsoil of Kukrail Reserve Forest. The low filed magnetic susceptibility is strongly correlated with the specific mass frequency dependent

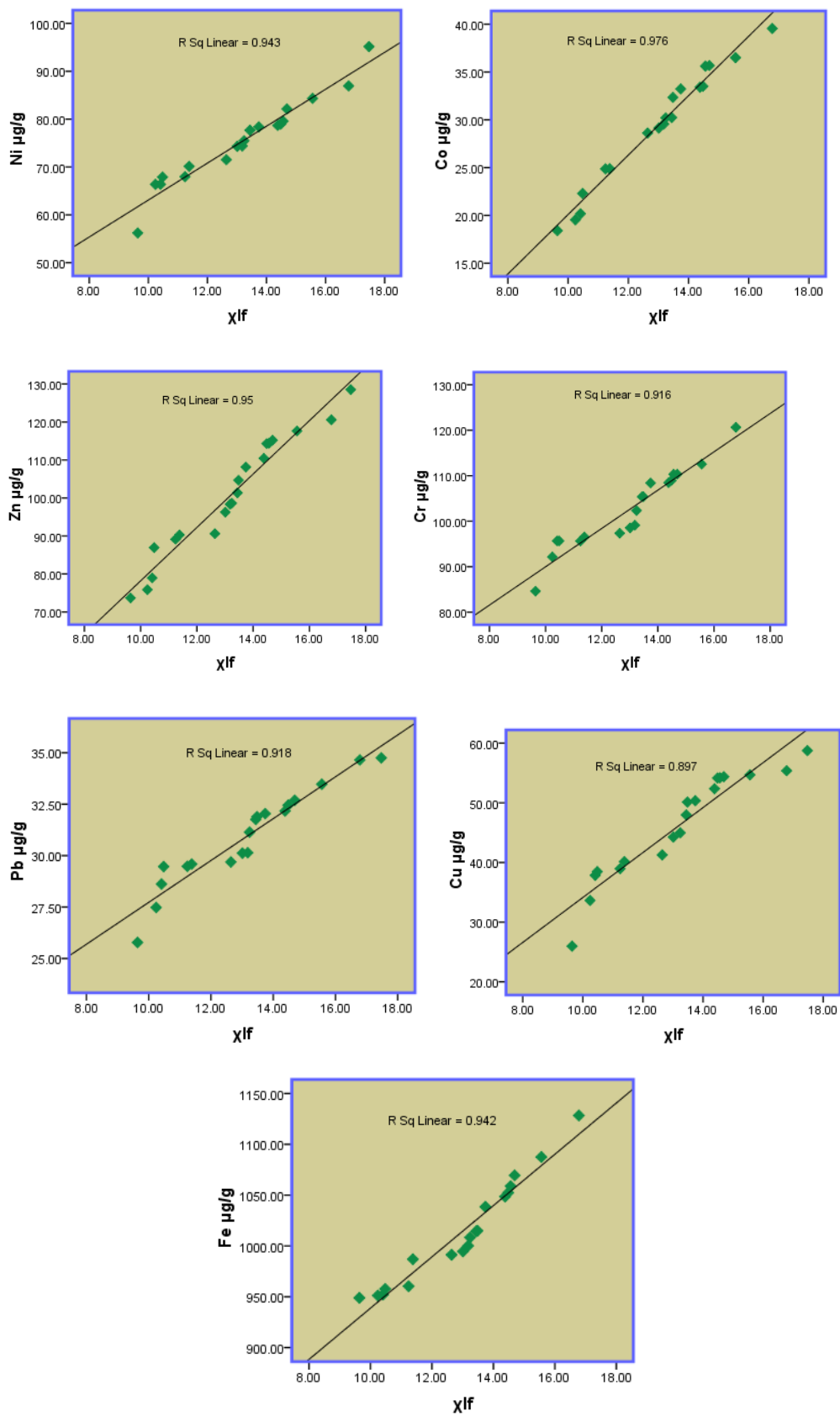


Fig. 2. Correlation coefficients (R^2) between the χ_{lf} and heavy-metal contents (Forest area)

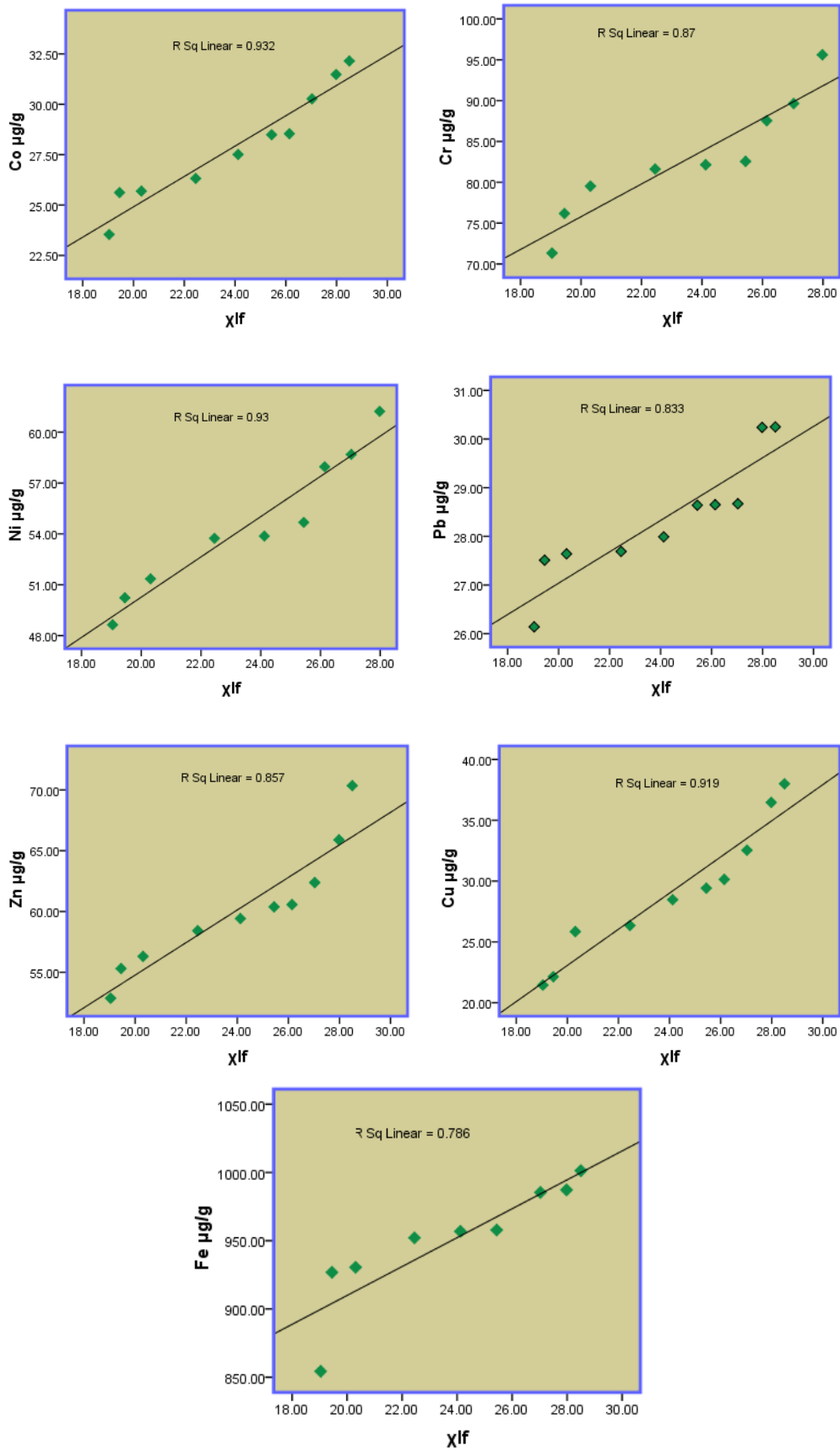


Fig. 3. Correlation coefficients (R^2) between the χ_{lf} and heavy-metal contents (Agricultural area)

Table 4. Pearson's Correlation coefficients between heavy metal concentrations and Magnetic Susceptibility

Agricultural Area							
	Co	Cr	Ni	Pb	Zn	Cu	Fe
χ_{lf}	0.405	0.263	-0.333	0.330	0.198	0.206	0.472
Forest Area							
	-0.302	0.175	0.003	0.259	0.011	-0.106	-0.150

susceptibility. This linear correlation has been confirmed by Forster et al., 1994 for paleosols on loess substrate in which the rising susceptibility is regulated by the pedogenic (fine grain size) magnetic fraction contribution. A significant negative correlation between χ_{fd} and χ_{lf} also exhibit great homogeneity in soil and particle size magnetic mineralogy despite a change in land use. χ_{lf} value is very low as compared to the mean of χ_{fd} values obtained for each land use and is related with the susceptibility of unaltered parent material of the soil. Thus, the MS Enhancement is attributed to pedogenesis, being consistent with Dearing et al., 1999 analysis and Gautam's soil classification.

According to Chan et al., 1997 certain heavy metals Pb, Zn and Cu are preferably absorbed to the outer surface of fly ash and industrial emission aerosols which often contain significant amount of Fe oxides. As a result a strong and positive correlation between heavy metals and χ_{lf} is expected. It is therefore, observed that the coefficient of correlation between χ_{lf} measurements and the heavy metal concentrations could be used as a pollutant indicator.

The scatter plot of MS versus Co, Cr, Ni, Pb, Zn, Cu and Fe were given in Fig2 and 3 where the correlation coefficient and the regression equation is also given. In forest area all the heavy metals except Cu and Cr show good association with χ_{lf} . The highest correlation coefficient between MS and heavy metal Co ($r^2= 0.976$), whereas correlation between MS and other heavy metal concentration is as follows: Cr ($r^2= 0.916$), Ni ($r^2= 0.943$), Pb ($r^2= 0.918$), Zn ($r^2= 0.95$), Cu ($r^2= 0.897$) and Fe ($r^2= 0.942$).

Similarly in agricultural area all the heavy metals (Co, Cr, Ni, Zn, Cu) show good association with χ_{lf} while Pb and Zn have a moderate coefficient with magnetic susceptibility. The highest correlation coefficient between MS and heavy metal Co ($r^2= 0.932$), whereas correlation between MS and other heavy metal concentration is as follows: Cr ($r^2= 0.87$), Ni ($r^2= 0.93$), Pb ($r^2= 0.833$), Zn ($r^2= 0.857$), Cu ($r^2= 0.919$) and Fe ($r^2= 0.786$). Lu et al. (2007) reported that Pb, Zn, Cd, Cu exhibit high correlation between heavy metal. According to Lu et al. (2007) the correlation between MS and heavy metal content tell us about the relation between iron oxide and heavy metals in the soil.

Pearson's Correlation coefficient between heavy metal concentrations and magnetic susceptibility are listed in Table 4. Significant correlation between heavy metal concentration and magnetic susceptibility with $p<0.005$ is noticed for Co, Cr, Pb, Zn, Cu and Fe of agricultural area. Similarly in forest area significant correlation exists between Cr, Ni, Pb and Zn.

CONCLUSIONS

Presently, there seems to be an increasing interest among researchers in field tool for determining contamination of soil in urban areas, where high spatial variations in the concentration of heavy metals necessitate an analysis of high number of samples to highlight technogenic anomalies. Magnetic susceptibility assessment is one of such methods. It is concerned with the study of contamination of soil by magnetite and heavy metals. The use of magnetic susceptibility (MS) survey has an initial step in the surveying of heavy metal pollution has demonstrated its usefulness by providing a fast, non destructive and affordable

tool. The present study was carried out in tropical deciduous forest of Central Uttar Pradesh i.e. Kukrail Reserve Forest, Lucknow to evaluate the contamination levels with heavy metals due to various anthropogenic activities and to confirm the usefulness of using MS surveying in this kind of studies. The magnetic susceptibility (MS) survey together with laboratory soil analysis was undertaken in the study area. Two sites were expected to carry out the present study as these sites are mostly affected by contamination. The χ_{LF} values show a significant correlation with the concentration of heavy metals except for Cu and Cr in forest area and Pb and Zn in agricultural area. It's been showed that there is a correlation between magnetic susceptibility and total soil heavy metal content. In comparison to the methodologies of chemical analysis, the χ_{LF} measurement techniques provide us with lower cost and less time consuming method for identification of possible soil pollution. In addition, we have shown that the χ_{LF} measurement techniques can be used as a measurement tool for the degree of accumulation of heavy metal, revealing the distribution of polluted parts in areas. The following conclusions are drawn;

- Assessed values of χ_{LF} with higher heavy metal content of soil samples consistently proven to be a good indicator of anthropogenic contribution in soil.

- χ_{LF} measurements could yield useful information on the degree of pollution. This study shows that χ_{LF} shows strong correlations with heavy metals such as Pb, Zn, Co and Ni; and weak correlations with Cu and Cr.

- χ_{LF} measurements show that the main magnetic components in urban soil samples are multidomain grains of ferromagnetic minerals, which are introduced by various anthropogenic activities and deposition of atmospheric particulates.

It is highly recommended carrying out a remediation action in study area and surroundings using suitable techniques in order to remove the contamination effects and to safe the human health and environment.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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