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RESEARCH ARTICLE

Quantitative assessment of soil metal pollution with principal component analysis, geo accumulation index and enrichment index

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SUMMARY: Total concentration of heavy metals such as Fe, Mn, Zn, Cu, Pb, Cd and Cr in the urban soil of Dindigul town was determined to evaluate the level of contamination. The mean concentration of these metals in the traffic and industrial area were found to be higher compared to residential area. The purpose of this research article was to apply three methods which were enrichment index (EI), geoaccumulation index (I_{geo}) and principal component analysis (PCA) to assess the heavy metals contamination levels in the studied area. Soil pollution assessment showed that the enrichment index for all the eighteen sampling sites were found to be greater than 1 (EI>1) indicating all the three sites were contaminated with heavy metals. The industrial sites showed the enrichment index greater than 2 (EI>2) indicating these sites were seriously affected by the contaminants. The Igeo values revealed that I geo for Cr>= 2 at the industrial sites indicating, these sites were accumulating more of chromium in the soil. I geo for Mn, Zn, Cu and Pb were found in between 0–1 for all the 18 sampling sites indicating these sites were moderately contaminated. Multivariate statistical analysis, principal component analysis and cluster analysis suggest that Mn, Zn, Cu, Cd and Cr were derived from anthropogenic sources, particularly road traffic and leather industrial activities and the extreme proximal parts were heavily contaminated with maximum heavy metals.

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The contamination of the biosphere has been increased as a result of the industrial revolution and urbanization of the landscape. The level of metals in soil may also be elevated by natural sources or by agricultural, industrial, mining and waste disposal practices. Further, soil and sediments are considered as sinks for metals, which are accumulated in high concentrations. The disposal of sewage and industrial sludge is becoming a severe problem in many countries including India. Heavy metal concentrations in past few years have reached to an increasing toxic level due to consequences of anthropogenic activities and urbanization. Now-a-days it is well-known that cities suffer from considerable pollution due to a wide array of substances that contaminate the air, water and soil (Rucandio *et al.*, 2010; Sarala and Prathipa, 2011 a and b). Metal persistence in soil for much longer periods than in other compartments of the biosphere is a matter of serious concern. International agency for research on cancer has classified heavy metals like arsenic, cadmium, chromium, nickel, lead to be carcinogenic to humans and wildlife. Over recent decades, the annual worldwide release of heavy metals reached 22,000t (metric ton) for cadmium, 939,000t for copper, 783,000t for lead and 1, 35,000t for zinc (Singh *et al.*, 2003 and Sarma, 2011).

Mining, industrial processing, pesticide and chemical fertilizer and automobile exhaust are the main sources of heavy metal contamination in the environment (Granero and Domingo, 2002; Lee *et al.*, 2005; Han *et al.*, 2006 and Sarala and Prathipa, 2012 a and b). These metals may accumulate to a toxic concentration level which can lead to

impairment in the quality of human life (Sipter *et al.,* 2008 and Wang *et al.,* 2002). The main threats to human health from heavy metals are associated with exposure to Pb, Cd and Hg. Cd exposure may pose adverse health effects; including kidney damage and possibly also bone effects and fractures (WHO, 1992 and Jarup, 2003). Methyl mercury is highly neutrotoxic and its adverse effects can be expressed in multiple organ systems throughout the life span (WHO, 1990; Bjornberg *et al.,* 2003). deterioration, prolonged reaction times and reduced ability to understand. Children may be affected by behavioural disturbances and learning and concentration difficulties (Jarup, 2003). Cr, Cu and Zn also have non-carcinogenic hazardous effects to human health when exposures exceed the tolerable reference dose (USEPA, 2000).

Modern civilization introduces a wide range of pollutants to the atmosphere through various activities. Most of the heavy metals are essential elements to living organisms but their excess amount is generally harmful to plants and animals. The poison of heavy metals depends a great deal on their chemical form, concentration, residence time (WHO, 1972; Schubrek, 1974; Mielke and Reagan, 1988 and Sarala and Prathipa, 2012 a and b). Traffic emissions on roads are the main cause of heavy metal accumulation on the surrounding environment including vegetation, which might have an ecological effect on them. Elevated levels of heavy metals in urban and industrialized areas atmosphere are reported in many parts of the world (Hampp and Holl, 1974; Ward *et al.,* 1974; Grodzinka, 1977; Karandinos *et al.,* 1985; Momani *et al.,* 2000; Odukoya *et al.,* 2000; Scerbo *et al.,* 2002 and Sarala and Prathipa, 2011 a and b).

As a consequence, the adverse effects of poor environmental conditions on human health are most evident in urban environments, particularly in developing countries where urbanization, industrialization and rapid population growth are taking place on an unprecedented scale. Dindigul, one important industrial town in Tamil Nadu has experienced a rapid urbanization and industrialization in the last decades. The rapid growth of industry, population and vehicle exerts a heavy pressure on its urban environment. The main objective of this initial study was to determine the concentration of heavy metals in soil samples collected from Dindigul town and to assess their contaminated level.

EXPERIMENTAL METHODOLOGY

Sampling sites:

The study area is located in the southern part of India, close to Kodaganar river basis, mainly in hard rock terrain. The area is known for its leather industries. It lies between 10°13'44" – 10°26'47" N latitude and 77°55'08" – 78°01'24" E longitude and falls in survey of India Top sheet No. 58 F/15 ; J/3, in the state of Tamil Nadu, India. The selected area is located in the central part of Dindigul town and along Madurai, Batlagundu and Ponmandurai roads. Eighteen sites were selected for the study in Dindigul town.

Sampling procedure:

Sample was collected from Oct., 2011 to Feb., 2012. Five soil samples (the upper 2 cm) were collected from each, at each site, with a stainless steel trowel. The samples were stored in polyethylene bags then treated and analyzed separately.

Sample preparation and analysis:

500g of each air dried composite sample was ground separately to pass through a 2 mm sieve. About 5 g of the homogenized sample from each group was ground into fine powder using agate mortar and pestle and further dried in hot air oven at 70°C for 72 hrs to constant weights (ISO, 1995). Exactly 1g from each of these finely ground soil samples were weighed out using an electronic balance into property cleaned 250 ml glass beakers.

Digestion was performed by adding 12ml of aqua regia (3:1,v/v, concentrated HCl to concentration HNO_3) into the beaker covered with watch glasses on a hot plate for 3 hrs at 110°C. After evaporation to near dryness carefully, the sample was diluted with 20 ml of 2 per cent (v/v with water) nitric acid and transferred into a 100 ml volumetric flask after filtering through Whatman no:42 filter paper and diluted to 100 ml with double distilled water (Chen and Ma, 2001and Hseu *et al.,* 2002) and used for chemical analyses. Heavy metal analysis was carried out with the flame atomic absorption spectrophotometer. Quantitation of Fe, Mn, Zn, Cu, Pb, Cr and Cd was carried out using standard solutions in the same acid matrix. Reagents blanks for soil was also prepared by carrying out the whole extraction procedure, but without samples.

Descriptive analysis:

Geo accumulation index:

Index of geo accumulation (Igeo), which was proposed to assess the pollution levels of bottom sediments by Muller (1969), was applied to assess the contamination levels of heavy metals in stream sediments by previous researchers (Howari *et al.,* 2001 and Ghrefat and Yusuf, 2006). This technique can also be used to the assessment of soil pollution (Teng *et al.,* 2002 and Loska *et al.,* 2003). Igeo is computed by the equation (1):

$$\text{Igeo} = \log_2 (C_n / 1.5\ B_n) \text{ ———— eqn} \quad (1)$$

where

C_n is content of trace element in soil, Bn is the geo chemical back ground content in soil, the 1.5 is the factor compensating the back ground content due to lithogenic

effects .The Igeo is classified into seven grades (Forstner *et al.*, 1990) or five grades (Martin, 2000) as shown in Table A. It can be indicated by the procedure of determine the value of Igeo that the contents of elements in soil of highest class more than 150 folds of back ground contents. In order to avoid that the assessed results with lower differentiation, the classified methods of seven grades was selected for assessing the contamination levels of heavy metals in soils.

The key part of this technique is the selection of back ground contents of heavy metals in sample soils. Although the equation, which determines the value of Igeo, includes the factor which compensates the back ground content of lithogenic effects, incorrect back ground contents of heavy metals will lead to the mistaken results. Previous research results have indicated that there are linear differences among the assessed results of different back grounds (Teng *et al.*, 2002). The back ground concentrations of heavy metals in soil of Dindigul town (Lakshmanapuram) are selected for the analysis of Igeo in this study.

Enrichment index for top soil:

Generally, the extent of anthropogenic contamination can be expressed using the enrichment index (Kribek and Nyambe, 2002). The EI is based on the average ratio of the actual and median concentrations of the given contaminants.

$$EI = \frac{\left(\frac{Fe}{M_{Fe}} + \frac{Mn}{M_{Mn}} + \frac{Zn}{M_{Zn}} + \frac{Pb}{M_{Pb}} + \frac{Cu}{M_{Cu}} + \frac{Cd}{M_{Cd}} + \frac{Cr}{M_{Cr}}\right)}{7}$$

where,

M_{me} is the median value of concentration for a given metal in top soil. The enrichment index actually reflects a higher than median or lower than median average content for the six elements. Nevertheless, the EI values correlate well with the ratio of top soil to subsurface with soil metal contents. This indicates that the EI values to a large degree reflect the enrichment from anthropogenic sources. Boundaries between individual intervals of EI values were established based on the statistical distribution of data and are expressed are percentile.

Multivariate analysis:

Principal component analysis (PCA) and cluster analysis (CA) are the most common multivariate statistical methods used in atmospheric deposition studies to explore associations and origins of trace elements and air pollutants (Wong *et al.*, 2003; Manno *et al.*, 2006 and Shan and Shaheen, 2007).

Principal component analysis (PCA):

Principal component analysis (PCA) is generally employed to reduce the dimensionality of a dataset while, attempting to preserve the relationships present in the original data (Loska and Wiechula, 2003). Many researchers (Daniela *et al.*, 2002; Wong *et al.*, 2002; Manno *et al.*, 2006; Shan and Shaheen, 2007) have used PCA in the evaluation of environmental data obtaining interesting conclusions that are not immediately obvious. The concentrations of the trace elements evaluated in this study vary by different order of magnitude. Thus, each variable was normalized to unit variance. After checking the suitability of the data set for factor analysis, PCA with varimax rotation was run only components with eigen values greater than unit after rotation were retained.

Cluster analysis (CA):

Cluster analysis (CA) was performed to further classify the elements into groups representing different sources on the basis of similarities in their chemical properties. The hierarchical CA was conducted to identify relatively homogenous groups of variables, using an algorithm that starts with each variable in a separate cluster and combines cluster until only one is left. Before cluster analysis, the variables were standardized by means of Z-scores; then Euclidean distances for similarities in the variables were calculated. A dendrogram was constructed to assess the cohesiveness of the clusters formed, in which correlations among elements

Table A: The classes of the value of geo accumulation index (I_{geo})

Seven grades			Five grades		
Igeo	Class	Soil quality	Igeo	Class	Soil quality
Igeo ≤ 0	1	Practically unpolluted	Igeo ≤ 0	1	Uncontaminated/Slightly
0<Igeo ≤ 1	2	Unpolluted to moderately polluted	0<Igeo ≤ 1	2	Moderately contaminated
1<Igeo ≤ 2	3	Moderately polluted	1<Igeo ≤ 3	3	Moderately/Strongly contaminated
2<Igeo ≤ 3	4	Moderately strongly	3<Igeo ≤ 5	4	Strongly contaminated
3<Igeo ≤ 4	5	Strongly polluted	5<Igeo	5*	Extremely contaminated
4<Igeo ≤ 5	6	Strongly to very strong			
5<Igeo	7*	Very strong pollution			

* This class is an open class and indicates all values of Igeo higher than 5

can readily be seen.

Descriptive analysis and correlation analysis:

Descriptive data analysis, including mean, standard deviation, minimum and maximum concentration was performed on the concentration of heavy metals present in the soil. Correlation coefficients were also calculated to analyze the relationships among different elements in order to identify similar sources of elements.

EXPERIMENTAL FINDINGS AND DISCUSSION

The experimental findings of the present study have been presented in the following sub heads:

Trace element concentration:

Table 1 and 2 shows the statistical summary for the concentration of heavy metals in soil samples analysed in the study area. The mean concentration of heavy metals were in the order Mn (13.85) > Fe (9.13) > Cu (6.73) > Zn (2.21)> Cr (1.92) >Pb (0.81)> Cd (0.080). Sampling station (S_{15}) has the highest mean concentration (11.54) and the least concentration (6.74) at the sampling station. Sampling sites from S_7 to S_{18} have the higher concentration than mean concentration of Fe (9.14). Manganese had the range between 9.58 (S_{12}) to 19.26 (S_2). Sampling sites S_1 to S_6 and S_{13} to S_{15} have manganese concentration higher than mean concentration (13.16). Sampling site (14) has the maximum concentration of Zn (3.02) and the minimum concentration of Zn (1.21) at the sampling site (S_1). It was inferred that from sampling site S_7 to S_{18} have higher zinc concentration than the mean concentration of Zn (2.13) .The sampling sites exposed to industrial activity and traffic loaded area (S_7 to S_{18}) have the higher concentration of zinc compared to S_1 to S_6 which are said to control area. The concentration of copper ranged from 2.72 (S_4) to 9.21 (S_{15}). The higher concentration of Cu was found out in the sampling site S_7 to S_{18} which are more urbanized site with more of human activity. These sites have more concentration of Cu than the mean value of Cu (6.73).

The mean concentration of Pb was 0.826. The sampling site (S_6) has minimum concentration (0.42) but sampling site (S_9) had maximum concentration (0.98). Sampling site from S_7 to S_{18} (traffic and industrial area) had higher concentration of lead than the mean concentration and also the residential area (S_1 to S_6). The range of cadmium in the sampling site showed that sampling site (S_6) had minimum concentration (0.013) and maximum concentration (0.154) at S_{16}. The sampling site from S_7 to S_{18} had the higher concentration of cadmium than the sampling site S_1 to S_6 and also the mean concentration (0.079). The concentration of chromium was found to be in the elevating level from S_{13} to S_{18}. These six sampling sites (S_{13} to S_{18}) have the two times of Cr concentration than the mean Cr concentration (1.98). Sampling site S_6 was found to have minimum concentration (0.88) and S_{14} had maximum concentration (4.74).

From the analysis of heavy metals, it was inferred that sampling sites S_1 to S_6 had minimum concentration Fe (S_4), Mn (S_2), Zn (S_5), Cu (S_4), Pb (S_6), Cd (S_6) and Cr (S_6). The maximum concentration of heavy metals was Fe (S_{15}), Mn (S_{12}), Zn (S_{14}), Cu (S_{15}), Pb (S_9), Cd (S_{15}) and Cr (S_{14}). The concentration of

Table 1: Heavy metal concentration (mg/kg) in urban soil collected from Dindigul town

Metals	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}	S_{16}	S_{17}	S_{18}
Fe	8.49	8.62	8.60	6.74	6.90	6.88	10.29	10.22	10.32	8.83	8.91	8.81	10.82	11.09	11.54	9.13	9.14	9.04
Mn	19.21	19.26	19.16	17.51	17.48	17.58	11.55	11.56	11.46	9.65	9.68	9.58	14.72	14.71	14.52	10.58	10.6	10.5
Zn	1.96	2.03	1.93	1.24	1.21	1.31	2.5	2.46	2.56	2.05	2.12	2.02	2.95	3.02	2.92	2.48	2.46	2.56
Cu	3.28	3.25	3.35	2.72	2.79	2.69	8.4	8.42	8.32	8.16	8.19	8.09	9.12	9.11	9.21	8.73	8.74	8.64
Pb	0.75	0.7	0.8	0.49	0.52	0.42	0.95	0.88	0.98	0.907	0.925	0.825	0.973	0.892	0.992	0.85	0.92	0.82
Cd	0.016	0.030	0.038	0.017	0.018	0.013	0.15	0.12	0.22	0.055	0.133	0.033	0.135	0.054	0.154	0.105	0.124	0.024
Cr	1.085	1.12	1.02	0.90	0.98	0.88	1.35	1.36	1.26	0.92	0.99	0.89	4.68	4.74	4.64	2.53	2.52	2.62

Table 2: Heavy metal concentration (mg/kg) in urban soil collected from Dindigul town

Metals	Minimum	Maximum	Mean	Std. deviation	Median
Fe	6.74	11.54	9.132	1.402	8.975
Mn	9.58	19.26	13.850	3.683	13.04
Zn	1.21	3.02	2.21	0.554	2.29
Cu	2.69	9.21	6.73	2.731	8.255
Pb	0.42	0.992	0.810	0.173	0.865
Cd	0.013	0.22	0.080	0.063	0.055
Cr	0.88	4.74	1.916	1.400	1.19

heavy metals in the soil samples at different site in the study area exhibited great variability and are affected by anthropogenic sources.

Evaluation of the enrichment index:

The enrichment index (EI) is used by numerous authors in order to establish the degree of contamination of heavy metals (Nishida *et al.,* 1982; Chon *et al.,* 1995; Kim *et al.,* 1998; Lee *et al.,* 1998; 2001 and Dasilva *et al.,* 2005). The enrichment index in this study was modified so that it is expressed as a ratio of the concentration of the measured element to the hazard criteria but as a shared average of actual and median concentration of potential contaminants Fe, Mn, Zn, Cu, Cd, Pb and Cr. Areas with EI >1 are suspected to be affected by industrial activity. However, it should be pointed out that in cases where the EI value falls in the range of 1 – 2, it must be significantly influenced by various in the geochemical character of the soil. For this reason, only areas with EI > 2 are considered to have been seriously affected by contamination.

The results of Table 3 showed that enrichment index ranged between 0.601to 2.02. The minimum enrichment index was assessed for the sampling site S_1 to S_6. Since the EI value for these sampling site (S_1 to S_6) lie below one indicated that these sampling site are not affected by industrial activity. But the sampling site S_7 to S_{18} had the enrichment index greater than 1 indicating these sites are contaminated and affected by industrial activity. It was very obvious from Table 3 that sampling site S_9, S_{13}, S_{14} and S_{15} had enrichment index (EI >=2) greater than or equal to two indicating that these sampling soils were seriously affected by contamination. The order of enrichment index in the various sampling sites was:

S_9(2.02) >S_{15}(1.81) >S_{13}(1.75) >S_{14}(1.54) >S_{16}(1.44) >S_{17} (1.35) >S_7(1.30) >S_8(1.22) >S_{11}(1.11) >S_{18}(1.00) >S_{10}(0.911) >S_2(0.85) >S_{12}(0.84) >S_1(0.82) >S_3(0.788) >S_5(0.676) >S_6(0.631) >S_4(0.609).

Analysis and comparison of geo-accumulation index results:

The geo accumulation index is shown in Table 3 and 3a. According to the assessment result of Igeo, geo accumulation index for Fe lied between 0 to 1 indicating that all the eighteen sampling sites were moderately contaminated by Fe and lied under the class 1. But the sampling sites S_{13}, S_{14}, S_{15}, S_1, S_2 and S_3 had higher Fe geo accumulation index than any other site. Geo accumulation index for Mn, Zn, Cu and Pb, were found to be in between 0 to 1 for all the eighteen sampling sites indicating that these sampled soils were moderately contaminated by manganese, zinc, copper and lead. Geo accumulation index for cadmium was found to be greater than 1 for the sampling site S_2, S_3 and S_9. But the remaining sites had less than one geo accumulation index for cadmium. Sampling sites S_2, S_3 and S_9 were said to be strongly contaminated by cadmium. Sampling from S_1 to S_{12} had less than one geo accumulation index for chromium, but the sites such as S_{13}, S_{14} and S_{15} had greater than two Igeo (Cr) > 2 and sites such as S_{16}, S_{17} and S_{18} had

Table 3: Assessed results of PCA, enrichment index and geo accumulation index technique

Site	PCA	EI	Fe	Mn	Zn	Cu	Pb	Cd	Cr
S_1	155.95	0.823	0.333	0.243	0.742	0.303	0.075	0.803	0.286
S_2	156.93	0.851	0.339	0.244	0.769	0.301	0.070	1.51	0.296
S_3	154.79	0.788	0.338	0.243	0.731	0.301	0.080	1.906	0.261
S_4	139.05	0.609	0.265	0.222	0.469	0.252	0.049	0.853	0.238
S_5	128.92	0.676	0.271	0.221	0.458	0.258	0.052	0.903	0.259
S_6	140.09	0.631	0.270	0.223	0.496	0.249	0.042	0.652	0.232
S_7	115.89	1.304	0.278	0.297	0.301	0.213	0.221	0.886	0.502
S_8	120.92	1.223	0.276	0.299	0.305	0.213	0.213	0.708	0.505
S_9	114.95	2.015	0.279	0.296	0.317	0.211	0.237	1.298	0.468
S_{10}	100.2	0.911	0.239	0.241	0.254	0.207	0.219	0.325	0.342
S_{11}	100.04	1.114	0.241	0.25	0.263	0.208	0.224	0.785	0.368
S_{12}	100.06	0.841	0.238	0.245	0.250	0.205	0.191	0.195	0.331
S_{13}	131.05	1.752	0.308	0.457	0.290	0.222	0.3251	0.502	2.683
S_{14}	131.75	1.542	0.316	0.456	0.297	0.222	0.233	0.201	2.718
S_{15}	133.56	1.809	0.328	0.450	0.287	0.224	0.259	0.572	2.660
S_{16}	100.34	1.443	0.251	0.328	0.244	0.223	0.222	0.390	1.451
S_{17}	104.31	1.346	0.260	0.329	0.242	0.213	0.240	0.461	1.45
S_{18}	103.33	1.004	0.259	0.326	0.252	0.210	0.214	0.0891	1.50

EI-Enrichment factor
PCA-Principal component analysis

Table 3a: Results of geo accumulation index

Geo-accumulation index	Sampling site	Class	Soil quality
I geo Fe [0-1]	$S_1 - S_{18}$	1	Slightly contaminated
I geo Mn[0-1]	$S_1 - S_{18}$	1	Slightly contaminated
I geo Zn[0-1]	$S_1 - S_{18}$	1	Slightly contaminated
I geo Pb[0-1]	S_1-S_{18}	1	Slightly contaminated
I geo Cd [0-1]	S_1, $S_4 - S_8$, $S_{10} - S_{18}$	1	Slightly contaminated
I geo Cd [1-2]	S_2,S_3,S_9	2	Moderately contaminated
I geo Cr [0-1]	$S_1 - S_{12}$	1	Slightly contaminated
I geo Cr [1-2]	$S_{16} - S_{18}$	2	Moderately contaminated
I geo Cr [2-3]	$S_s - S_{15}$	3	Strongly contaminated

greater than one I geo (Cr) >1 indicating, these sites were strongly affected by chromium.

Determination of contamination levels of soil by principal component analysis (PCA):

Set the matrix x present the data set of contents of heavy metals in soil samples. $X = (C_{ij})$ where C is the concentration of heavy metals in soils and i is the different heavy metals, (i = Fe, Mn, Zn, Cu, Cd, Pb and Cr), j is the sampling sites (*i.e.*) j= (1-18). The result of principal component analysis was shown in Table 4. Due to the first two principal components account for 99.25 per cent of the total variance, they can represent the soil heavy metal contamination levels in study area.The values of these two principal components can be presented by the contents of heavy metals in soil and the eigen vectors of principal components (eqn 1 and 2)

$$\mathbf{Z_1 = 3.75C_{Fe}+7.380C_{Mn}+2.378C_{Zn}+1.892C_{Cu}+3.628C_{Pb}+2.661C_{Cr}} \quad \mathbf{(1)}$$

$$\mathbf{Z_2 = +0.366\ C_{Fe}+(-0.556\ C_{Mn}) + (-0.187C_{Zn}) + 0.930\ C_{Cu}+ (-0.507C_{Pb})) + (-0.583C_{Cd}) + 0.537\ C_{Cr}} \quad \mathbf{(2)}$$

where,

Z_1 and Z_2 are the values of first two principal components respectively, C is the concentration of heavy metals in the study soil. In order to get the comprehensive contamination levels of heavy metals of different samples, the values of Z_1 and Z_2 should be weight sum by each eigen value of their. The following will take sample 1(S_1) as an example to explain the computational process of comprehensive contamination levels by PCA (Fig. 1).

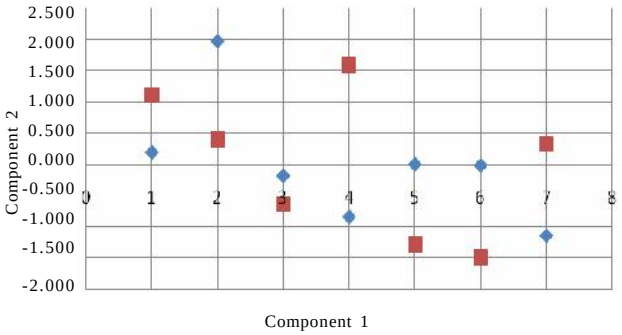

Fig. 1: Loading plots of PCA analysis of heavy metals

The values of Z_1 and Z_2 of sampling site (S_1) (Z_1S_1 and Z_2S_1) can be calculated by equation (1) and (2) and the contents of heavy metals in soil, which is Z_1S_1=169.48 and Z_2S_1=-4.313, respectively. And then, the comprehensive contamination levels of heavy metals in S_1 can be obtained, which is,

$$\mathbf{PCAS_1 = Z_1S_1\ x\ (16.476/16.476+1.389) = Z_2S_1\ x\ (1.389/16.476+1.389)}$$
$$\mathbf{PCAS_1 = 155.95}$$

Table 4: The results of principal component analysis

	Eigen values			Eigen vectors		
Sr. No.	Eigen value	Proportion	Cumulative	Elements	PCA1	PCA2
1.	16.476	91.53	91.533	Fe	3.750	0.366
2.	1.389	7.719	99.25	Mn	7.380	-0.556
3.	0.094	0.521	99.77	Zn	2.378	-0.187
4.	0.006	0.032	99.80	Cu	1.892	0.930
				Pb	3.628	-0.507
				Cd	4.282	-0.583
				Cr	2.661	0.537

Similarly, the comprehensive examination levels of heavy metals in other samples can be calculated by this procedure, and the results were shown in Table 3.

According to the result of principal component analysis (PCA) (Table 3), the comprehensive pollution levels of heavy metals in soil were determined by the concentration distribution of all elements. The comprehensive pollution levels of heavy metal in sampling site S_1 to S_6 ranged between 128.92 to 156.93. The higher pollution level was found due to the contamination of zinc and cadmium in these sampling sites. The comprehensive pollution levels of heavy metal in sampling site S_7 (115.89), S_8 (120.92) and S_9 (114.95) were observed due to the higher level of geo accumulation index of cadmium and chromium in these sampling sites. The comprehensive pollution levels of heavy metals in sampling site S_{10} (100.2), S_{11} (100.04) and S_{12} (100.06) were less because the geo accumulation index of all the metals (Fe, Mn, Zn, Cu, Cd, Pb and Cr) were below 0.5 (Igeo<0.5). Sampling sites such S_{13}, S_{14} and S_{15} had higher pollution level of heavy metals (131.05, 131.75, and 133.56) because of high geo accumulation index of Cd, Mn and Cr. The comprehensive pollution levels of heavy metals in sampling site S_{16} to S_{18} ranged between 100.34 to 104.31. These sampling sites had higher geo accumulation index for chromium only.

Table 4a: PCA range and geo-accumulation index

Sampling sites	PCA range	Geo accumulation index
$S_1 – S_6$	128.92 – 156.93	I geo Zn and I geo Cd > 0.5
$S_7 – S_9$	114.95 – 120.92	I geo Cd and I geo Cr > 0.5
$S_{10} – S_{12}$	100.04 – 100.2	I geo for Fe, Mn, Zn, Cu, Cd, Pb, Cr > 0.5
$S_{13} – S_{15}$	131.05 – 133.56	I geo Zn I geo Cd and I geo Cd > 0.5
$S_{16} – S_{18}$	100.34 – 104.31	I geo Cr > 1.0

The results of PCA can give the comprehensive information of heavy metals contamination in soil. The combination of results of PCA and I geo can identify the comprehensive and single pollution levels of different metals in soils, which is very important for defining the extent of heavy metal pollution in soil.

Pollution source identification:

Factor analysis was applied to assist in the identification of the sources of the heavy metals. The results of factor analysis are shown in Table 4. According to the Kaiser criterion, the first two components with eigen values larger than 1.0 have dominant influences. The two principal components contributed 99.25 per cent of the total variance in the samples. The initial eigen value of the first factor was the largest 16.476, accounting for 91.53 per cent of the total variance, which suggests the existence of one dominant emission source or a group of emission sources of some elements. By VARIMOX rotation, the final values of eigen vectors are obtained, which are considered as for prints of emission sources (Dordevic and Tainsho, 2005). The two principal component analyses are shown in Fig. 2.

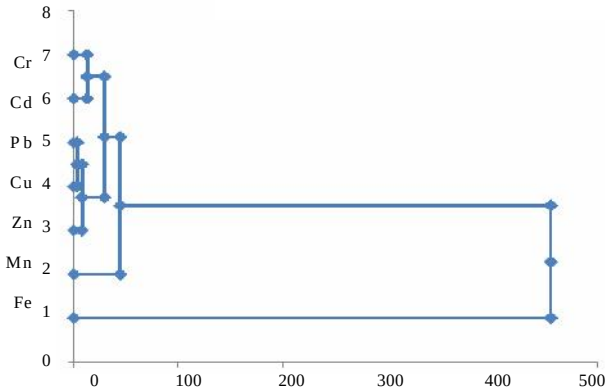

Fig. 2: Two principal component analysis

The first factor is mainly characterized (Mn=1.985), (Cu = -0.842) and (Cr = - 1.145). The association between these elements showed the existence of a common emission source of these elements. This result confirms the strong positive relationship among them except manganese. The factor must be associated with anthropogenic sources represented by traffic since all of these elements were reported to be contributed by road traffic emission. Road traffic emission contains not only vehicles exhaust but also tire end brake wear and resuspended dust. Brake dust has been recognized as an important carrier of copper in the composition of aerosol (Adachi *et al.*, 2004). Copper is generally used in breakes to control heat transport (De – Miquel *et al.*, 1997). Cu, Zn, and Cd in atmospheric deposition were considered to be emitted from road traffic (Berm *et al.*, 2003 and Stern beck *et al.*, 2002). Factor 1 also represents the high score of chromium, which indicate the urban soil of Dindigul which is leather industrialized town, contaminated with the same.

The factor F_2 is characterized by (Cu =1.589), (Fe = 1.107), (Pb= -1.282), (Cd=-1.492) and (Zn = -0.639). The association between these element can be seen in the loading plot (Fig. 2). Copper has relatively high loading in F_2 (Cu= +1.589). The high loading for these five elements also confirm their strong positive relationship. The result suggests that the concentration of these metals originate from the influence of road traffic. This result also suggests that, other elements with high loading in F_1 might be also contributed by resuspension of local soil particles provoked by vehicle activities.

Table 5: Correlation matrix (Pearson n)

Variables	Fe	Mn	Zn	Cu	Pb	Cd	Cr
Fe	1	-0.384	0.957	0.803	0.883	0.705	0.435
Mn		1	-0.449	-0.833	-0.615	-0.509	0.044
Zn			1	0.851	0.879	0.637	0.327
Cu				1	0.861	0.676	0.232
Pb					1	0.750	0.265
Cd						1	0.296
Cr							1

Cluster analysis:

Cluster analysis was performed on the basis of information assessed from principal component analysis, hierarchical cluster analysis (Gotelli and Ellison, 2004). Three main clusters can be distinguished in the dendrogram obtained from the cluster analysis performed on the analyzed parameters with ward's method and the squared Euclidean distance as a similarity measures. The distance cluster represents the degree of association between elements. The lower the value on the distance cluster, the more significant is the association. Pb, Cu, and Zn form a cluster (1) which suggests that the association between these elements is very significant and their sources are similar cluster 1 include Pb, Cu and Zn which were identified as contaminants derived from anthropogenic sources. These findings confirm the results of correlation matrix. Cluster 2 contains Cr and Cd which form a distinct cluster 2 contains Cr and Cd which form a distinct cluster at longer distance, showing that they are from similar sources that is due to industrial activity and vehicular output. Cluster 2 contains Cr and Cd which is mostly controlled by anthropogenic sources. Cluster 3 contains Fe and Mn which are attributed of a main origin from road traffic emission. It has revealed that the elevated concentration of the metals could be related to land based point source discharge related to rapid urbanization.

Correlation matrix:

Interelement relationships in soil matrix provide information on heavy metal sources and pathways in the geo environment (Dragovic *et al.*, 2008). In general, correlation between metals was useful to confirm the new association between metals. According to the values of pearson correlation co-efficient Table 5, a significant positive correlation (P<0.01) existed between Fe vs Zn (r=+0.957, P<0.01), Cu (r=-0.803, p<0.01), Pb (r =+0.883), p<0.01), Cd (r =+0.705, P<0.01), weak correlation with Cr (r =+0.435, r<0.01) and negative correlation with Mn (r =-0.384, P<0.01). Manganese showed negative and significant correlation with Zn (r=-0.449, P<0.01), Cu (r=-0.8333, p<0.01), Pb(r=-0.615, p<0.01), Cd (r =-0.509, p<0.01) but insignificant positive correlation with Cr (r=+0.044, r<0.01). Zinc showed positive and significant correlation with Cu (r=0.851, p<0.01), Pb (r=+0.879, P=0.01), Cd (r=+0.637, p=0.01) and weak correlation with Cr (r=+0.327, p<0.01). The significant and positive correlation existed between Cu and Pb (r=+0.861, p<0.01) and Cd (r=0.676, p<0.01) and insignificant correlation with Cr (r=+0.232, P<0.001). Pb showed positive and significant correlation with Cd (r =+0.750, p<0.01) and insignificant correlation existed between Pb and Cr (r=+0.265, p<0.01) and Cd and Cr (r=+0.296, p<0.01). The strong correlations among elements indicate their common origin. The significant positive correlation among Fe, Zn, Cd, Pb and Cu indicate their similar sources that are anthropogenic sources.

Conclusion:

Different useful tools, methods and indices have been employed for evaluation of soil pollution in the urban area. Analysis of soil samples from 18 sampling site in the traffic and industrialized area showed variation of heavy metals Fe, Mn, Zn, Cu, Pb, Cd and Cr. The maximum concentration of Fe, Mn, Zn, Cu, Pb, Cd and Cr was identified from the soils sampled from industrial and traffic area that is sampling sites S_7 to S_{18} . The evaluation of enrichment index of the metals Fe, Mn, Zn,Cu, Pb,Cd,and Cr showed that they sampling S_7 to S_{18} had higher enrichment index (*i.e.*) EI>=2 which is indicating that these sampling sites are seriously contaminated by heavy metals. Analysis of geo accumulation index result indicated that sampling sites 13 to 18 were contaminated by chromium because in these sites Igeo for chromium was greater than 2. Sampling site S_2, S_3 and S_9 were also contaminated cadmium since Igeo for Cr was more than 1. This study also suggests that the metal contamination can not be simply evaluated by examining metal concentrations alone. A complementary approach that integrates enrichment factor and geo accumulation index should be considered in order to provide a more accurate appraisal of the fate and transport of metals from anthropogenic sources and the resultant environmental impact of these materials on soil.

Multivariate analysis (PCA, CA) and correlation matrix used in this study provided important tools for better understanding of the source identification and dynamics of pollutants. The PCA applied on the investigated heavy metals identified two components. Among them PC1 was loaded Mn, Cu and Cr. Mn, Cu and Cr were related to the anthropogenic sources. PC2 was loaded with Fe, Zn, Cu, Pb and Cd which

were related to the anthropogenic sources. A significant positive correlation was observed among Fe, Zn, Cu, Pb and Cd. Negative correlation was observed with manganese and insignificant positive correlation was observed with chromium. It is very obvious from the results that Fe, Zn, Cu, Pb and Cd were anthropogenic sources mainly from road traffic emission. The positive correlation of Cr indicates that it is from industrial activity that is from leather industry. A significant positive correlation among these elements indicates that these metals have similar geo chemical behaviour. The method of principal component analysis relates to the concentration distribution of all elements in soils. Combination of principal component analysis and geo accumulation index can determine both the comprehensive and single factor pollution levels of different elements in soils, thus being of particular important to soil contamination assessment.

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