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RESEARCH ARTICLE

Contamination of road side soil with heavy metals in urban area of Madurai city

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SUMMARY : The purpose of this article is to apply two methods, which are Principal Component Analysis and Geo accumulation Index to assess the heavy metals (Fe, Mn, Zn and Cu) contamination levels in the urban area of Madurai. The concentration of heavy metals were determined at six different sampling sites Site 1 (Kalavasal), Site 2 (Palaganatham), Site 3 (Periyar), Site 4 (Simmakal), Site 5 (Goripalayam) and Site 6 (Mattuthavani) at two different depths, 0-20 cm and 20-40 cm by using Atomic Absorption Spectroscopy (AAS). The mean accumulation level of heavy metal contents were found to be below the critical heavy metal values. The enrichment index was determined for six sampling sites at different depths. The enrichment index for sampling site 2 (Palaganatham) was found to be greater than 2 indicating the soil was enriched with heavy metals. From multivariate statistical technique at depth 0-20 cm two factors were chosen for interpretation accounts for 77 per cent of total variance in the data set and 70 per cent of variance account at depth 20-40 cm. The assessment of geo accumulation index showed that Mn and Cu were highly accumulated at all the sampling sites. Principal component analysis results revealed that sampling site 2 (Palaganatham) and 4 (Simmakal) had high pollution levels of heavy metals. Principal component analysis and geo accumulation index are the important tools to find out heavy metal pollution in soil.

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Soil pollution is one of the main concerns of today's world. The sources of soil pollution in urban areas are different but as non-point source pollution, roads are known as the second largest source of creating pollutions in environment (Fakayode *et al.*, 2003). Emissions from roads and vehicles cause many problems to human health and environment. Roadside soils and dust being contaminated by metals were evaluated by many researchers and they measured vehicular heavy metals in roadside soils with different methods. In many researches, the researchers commonly sampled from roadside soils, dusts or plants and after analyzing samples and comparing to the background levels and standards, they came to result if these observations were anthropogenic or not. Besides that some of them tried to find the relations of concentrations with distance from roads and traffic volumes (Ndiokwere, 1984; Hewitt and Candy, 1990; Garcia and Millan, 1998; Thambavani and Vathana, 2012). In recent year, environmental problems such as air and soil pollution have become increasingly important issue in everyday of life. The widespread contamination with heavy metals in the last decades has raised public and scientific interest due to their dangerous effects on human health (Gilbert, 1984). Heavy metals having great ecological significance are arsenic, zinc, manganese, chromium, lead, cobalt and molybdenum. These elements, unlike most pollutants, are not biodegradable and they undergo ecological cycle (Nurnberg, 1984). Some metals such as iron, zinc, copper, cobalt and manganese are essential to life but can be toxic in high doses. The total trace metal content provides an important information about the pollution level if the background or geochemical composition is known (Salmons and Forstner, 1980). The impact of heavy metals on the environment is a concern to government regulatory agencies and the public (Page and Chang, 1985; Feigin *et al.*, 1991; Tiller, 1992). Soil is very important in ecosystem research as it is the place where many kinds of interactions takes place between minerals, air, water and biota. In the recent past, the soil system, has been subjected to physical stress by input of foreign substances such as heavy metals. This includes the degradation of soil organic matter and lowering of the fertility of the upper soil layer due to erosion. Generally, soil reacts much more slowly to external influences than water and air, as it is able to bind substances into complexes. As a result, the increase in heavy metal concentrations in the soil caused by humans had lead to considerable accumulation in some cases (Al-Muzaini and Jacob, 1996). Plants, which are the basic food of all animals and human life, grow and obtain their nutrition mainly in the top layers of the soil. It is in these top layers, the main rooting zone of the plants, that heavy metals are accumulated and reach high concentrations. Since these heavy metals can become a threat to vegetation and animals, and ultimately affect the quality of human life (Harrison, 1982) through the food chain, it is important continuously to monitor the level of such pollutants in the environment. The purpose of this study was to assess the heavy metal pollution levels of soil in vicinity of traffic area by applying three methods such as Enrichment Index, Principal Component Analysis (PCA) and Geo accumulation Index (I_{geo}). Contents of Fe, Mn, Zn and Cu in soils along traffic area were objectives of the assessment, which were sampled in Kalavasal, Palaganantham, Periyar, Simmakal, Goripalayam and Mattuthavani. Twelve soil samples from each sampling site (depth 0-20 cm and 20-40 cm) were taken for the study.

EXPERIMENTAL METHODOLOGY

Sampling sites :

Madurai is the administrative headquarters of Madurai district in the South Indian state of Tamil Nadu. It is the third largest city and the second largest municipal corporation in Tamil Nadu. Located on the banks of river vaigai. Madurai has been a major settlement for two millennia and is one of the oldest continuously inhabited cities in the world. For the study six areas are selected namely Kalavasal (Site 1), Palaganatham (Site 2), Periyar (Site 3), Simmakal (Site 4), Goripalayam (Site 5) and Mattuthavani (Site 6). Roadways were selected on the basis of traffic load, population, density and anthropogenic activities. A detailed description of the selected sites is given in Table A.

Table A: Description of sampling sites

Site No.	Name of the site	No. of vehicle/hr	Site description
S_1	Kalavasal	3475	Medium traffic area
S_2	Palganatham	3976	High traffic area
S_3	Periyar	3754	High traffic area, commercial area
S_4	Simmakal	4672	High traffic area
S_5	Goripalayam	4533	High traffic area
S_6	Mattuthavani	3419	Medium traffic, industrial area

Sampling procedure :

Sample was collected from June 2011-May 2012. Twelve soil samples (depth 0-20 cm and 20-40 cm) were collected from each site with a stainless steel trowel. The samples were stored in polyethylene bags then treated and analyzed separately.

Sample preparation and analysis :

500 g 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 70^0C for 72 hrs for a constant weights (ISO, 1995). Exactly 1g from each of these finely ground soil samples were weighted out using an electronic balance into properly 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 plated for 3 hr at 11^0C. 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 100ml volumetric flask after filtering through Whatman no:42 filter paper and diluted to 100 ml with double distilled water (Chen and Ma, 2001 and 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 and Cu was carried out using standard solutions in the same acid matrix. Reagent 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 (I_{geo}), which was proposed to assess the pollution levels of bottom sediments by Muller in 1969 , was applied to assess the contamination levels of heavy metals in stream sediments by previous researchers (Howari *et al.*, 2001). This technique can also be used to the assessment of soil pollution (Teng *et al.*, 2002 and Loska *et al.*, 2003). I_{geo} is computed by the equation (1):

$$I_{geo} = \log_2 \frac{Cn}{1.5\, B_n} \qquad (1)$$

where, C_n is content of trace element in soil, Bn is the geochemical background content in scale, the 1.5 is the factor compensating background content due to lithogenic effects. The I_{geo} is classified into seven grades (Forstner *et al.*, 1990) or five grades (Martin, 2000), as shown in Table 1. It can be indicated by the procedure to determine the value of I_{geo} that the contents of elements in soil of highest class more than 150 folds of background 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 selection of background contents of heavy metals in sample soils. Although the equation, which determines the value of I_{geo}, includes the factor which compensates the background content of lithogenic effects, incorrect background 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 background (Teng *et al.*, 2002). The background concentrations of heavy metals in soil of Madurai traffic area was selected for the analysis of I_{geo} in this study.

Enrichment index:

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

$$EI = \frac{Fe/M_{Fe} + Mn/M_{Mn} + Zn/M_{Zn} + Pb/M_{Pb} + Cu/M_{Cu} + Cd/M_{Cd} + Cr/M_{Cr}}{7}$$

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 four elements. Neverthless, 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 as 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 origin of trace elements and air pollutants (Manno *et al.*, 2006; Shah and Shaheen; 2007 and Ragosta *et al.*, 2008).

Principal component analysis (PCA) :

Principal component analysis (PCA), a multivariate statistical method. It is generally employed to reduce the dimensionality of a data set while, attempting to preserve the relationships present in the original data (Loska *et al.*, 2003). In order to assess the soil heavy metal pollution levels by PCA, the principal components of data set should be first identified. The principal components, which contain most part of information of assessed indexes, can present the contamination levels of heavy metals in soil correctly. During the processes of PCA, we seek to maximize the variance of a linear combination of the variables data set. The values of principal components can be calculated by the contents of heavy metals in soils and the contamination levels of heavy metals in soil can be assessed by weight sum of different principal component values.

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:

Heavy metal concentration :

Table 1 shows the concentration of heavy metals in soil samples analyzed in the study area. At Kalavasal sampling site the concentration of Fe (14.71 $\mu g/m^3$) > Mn (10.08 $\mu g/m^3$)

Table 1: 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 contaminated
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 to 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			

> Zn (4.38 µg/m^3) > Cu (1.88 µg/m^3) at the depth 0-20 cm. The concentration of all the heavy metals showed less concentration at the depth (20-40 cm) compared to 0-20 cm depth at the same sampling site {Zn(2.05 µg/m^3) > Mn (1.71 µg/m^3) > Fe (1.55 µg/m^3) > Cu (0.86 µg/m^3)}. At the sampling site Palaganatham, the concentration of heavy metals was in the order of Fe (14.41 µg/m^3) > Zn (7.22 µg/m^3) > Mn (5.36 µg/m^3) > Cu (5.03 µg/m^3). On comparing with that of depth 20-40 cm, the concentration of all the heavy metals was in the decreasing order {Fe (7.21 µg/m^3) > Zn (4.22 µg/m^3) > Cu (2.26 µg/m^3) > Mn (1.22 µg/m^3)}. The result revealed that the concentration of heavy metals at Periyar sampling site was found to be Fe (18.09 µg/m^3) > Mn (8.95 µg/m^3) > Zn (7.14 µg/m^3) > Cu (2.15 µg/m^3). The concentration of all the heavy metals showed decreasing concentration at the depth 20 – 40 cm, compared to 0 – 20 cm depth at the sampling site { Fe (8.11 µg/m^3) > Mn (2.45 µg/m^3) > Zn (2.0 µg/m^3) > Cu (0.9 µg/m^3)}. It has been found that the concentration of heavy metals at Simmakal sampling site at the depth 0 – 20 cm was in the order of Fe (21.6 µg/m^3) > Mn (6.69 µg/m^3) > Zn (6.14 µg/m^3) > Cu (2.44 µg/m^3). On comparing the concentration of all the heavy metals at the depth 20 – 40 cm was found to be lower than that of at the depth 0 – 20 cm{ Zn (12.25 µg/m^3) > Fe (11.63 µg/m^3) Cu (6.21 µg/m^3) > Mn (1.09 µg/m^3)}. At Goripalayam sampling site, the concentration of Mn (16.25 µg/m^3) > Fe (11.96 µg/m^3) > Zn (5.88 µg/m^3) > Cu (2.27 µg/m^3) at the depth 0 – 20 cm. The concentration of all the heavy metals showed decrease in concentration at the depth 20 – 40 cm compared to 0 – 20 cm depth at the same sampling site {Zn (8.36 µg/m^3) > Fe (6.63 µg/m^3) > Cu (3.31 µg/m^3) > Mn (1.27 µg/m^3)}. The results implies that the heavy metal concentration at sampling site Mattuthavani at the depth 0 – 20 cm was found to be in the following order Fe (15.71 µg/m^3) > Mn (9.14 µg/m^3) > Zn (4.95 µg/m^3) > Cu (1.58 µg/m^3). But the concentration of all the heavy metals showed less concentration at the depth 20 – 40 cm compared to 0 – 20 cm at the same sampling site { Fe (3.02 µg/m^3) > Zn (2.46 µg/m^3) > Mn (1.35 µg/m^3) > Cu (0.96 µg/m^3)}. The concentration of Fe analyzed at the six sampling sites and at the depth 0 – 20 cm showed the following results.

The concentration of Fe was greater at Simmakal (21.6 µg/m^3) followed by Periyar (18.09 µg/m^3), Mattuthavani (15.71 µg/m^3), Kalavasal (14.71 µg/m^3), Palaganatham (14.41 µg/m^3) and goripalayam (11.96 µg/m^3). The concentration of Mn showed trend like Goripalayam (16.25 µg/m^3) > Kalavasal (10.08 µg/m^3) > Matuthavani (9.14 µg/m^3) > Periyar (8.95 µg/m^3) > Simmakal (6.69 µg/m^3) > Palaganatham (5.36 µg/m^3). The analyzed results of Zn contamination in the road soil revealed that Palaganatham (7.22 µg/m^3) soil had more concentration followed by Periyar (7.14 µg/m^3), Simmakal (6.14 µg/m^3), Goripalayam (5.88 µg/m^3), Mattuthavani (4.95 µg/m^3) and Kalavasal (4.38 µg/m^3). The concentration on Cu in the different sampling sites revealed the trend Palaganatham (5.03 µg/m^3) > Simmakal (2.44 µg/m^3) > Goripalayam (2.27 µg/m^3) > Periyar (2.15 µg/m^3) > Kalavasal (1.88 µg/m^3) > Mattuthavani (1.58 µg/m^3). The concentration of Fe analyzed at the six sampling sites and at the depth 20 – 40 cm showed the following results. The concentration of Fe was greater at Simmakal (11.63 µg/m^3) followed by Periyar (8.11 µg/m^3), Palaganatham (7.21 µg/m^3), Goripalayam (6.63 µg/m^3), Mattuthavani (3.02 µg/m^3) and Kalavasal (1.55 µg/m^3). The concentration of Mn showed the trend Periyar (2.45 µg/m^3) > Kalavasal (1.71 µg/m^3) > Mattuthavani (1.35 µg/m^3) > Goripalayam (1.27 µg/m^3) > Palaganatham (1.22 µg/m^3) > Simmakal (1.09 µg/m^3). The analyzed result of Zn contamination in traffic implies that Simmakal (12.25 µg/m^3) has more concentration followed by Goripalayam (8.36 µg/m^3), Palaganatham (4.22 µg/m^3), Mattuthavani (2.46 µg/m^3), Kalavasal (2.05 µg/m^3) and Periyar (2.0 µg/m^3). Similarly the concentration of Cu in the different sampling site revealed the following order Simmakal (6.21 µg/m^3) > Goripalayam (3.31 µg/m^3) > Palaganatham (2.26) > Mattuthavani (0.96) > Periyar (0.9) > Kalavasal (0.86 µg/m^3).

The concentration Fe was greater in the Simmakal sampling site at both sampling depth (0 – 20 cm and 20 – 40 cm). The concentration of Mn was more at Goripalayam soil sample (16.25µg/m^3) at a depth 0 – 20 cm and Periyar soil sample (2.45µg/m^3) at depth 20 – 40 cm. The concentration of Zn and Cu was maximum at Palaganatham soil sample 7.22µg/m^3 and 5.03 µg/m^3, respectively at depth 0 – 20 cm. The concentration of Zn and Cu was maximum at Goripalayam soil samples at depth 20–40 cm (8.36 µg/m^3 and 3.31µg/m^3), respectively (Table 2).

Evaluation of the enrichment index :

The Enrichment Index (EI) has been 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 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 and Cu. 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 geochemical character of the soil. For this reason only, areas with EI > 2 considered to be seriously affected by contamination.

The results of the Table 3 showed EI ranged from 0.983 to 4.39 for the six sampling sites. Since the EI for all the sampling sites and at two different depths were found to be below 1. It indicated that these sampling sites were not much affected by industrial and traffic activity. But the sampling site, Palaganatham (0 -20 cm) showed the enrichment index greater

Table 2: Contents of heavy metal concentration (μg/m³) in study area

Sampling site	Depth (cm)	Fe	Mn	Zn	Cu
Kalavasal	0-20 cm	14.71	10 .08	4.38	1.88
	20-40 cm	1.55	1.71	2.05	0.86
Palaganantham	0-20 cm	14.41	5.36	7.22	5.03
	20-40 cm	7.21	1.22	4.22	2.26
Periyar	0-20 cm	18.09	8.95	7.14	2.15
	20-40 cm	8.11	2.45	2.00	0.90
Simmakal	0-20 cm	21.6	6.69	6.14	2.44
	20-40 cm	11.63	1.09	12.25	6.21
Goripalayam	0-20 cm	11.96	16.25	5.88	2.27
	20-40 cm	6.63	1.27	8.36	3.31
Mattuthavani	0-20 cm	15.71	9.14	4.95	1.58
	20-40 cm	3.02	1.35	2.46	0.96

Table 3 : Enrichment index of study area

Sr. No.	Depth	Sampling site					
		S_1	S_2	S_3	S_4	S_5	S_6
1.	0 – 20 cm	1.00	4.39	0.998	0.995	1.00	0.986
2.	20 – 40 cm	0.983	1.01	0.980	1.00	0.980	1.00

than 2. It is inferred that Palaganatham sampling soil was seriously affected by heavy metal contamination (Table 3).

Analysis of geo accumulation index :

The geo accumulation index has been shown in Table 4 and Table 4a.

According to the assessment results of geo accumulation index in the sampling site 1 (Kalavasal 0-20 cm), it was found to be I_{geo} = 0, which is coming under class I. The five grade classification indicated the soil quality came under class I which means it was contaminated by the heavy metals Fe, Mn, Zn and Cu. But in the same site at depth 20-40 cm, the geo accumulation index for Mn and Cu was found to be $0 < I_{geo} < 1$ which came under class II. Class II indicated that the soil of Kalvasal at depth 20-40 cm was moderately contaminated by Mn and Cu but uncontaminated by Fe and Zn (I_{geo} =0). The geo accumulation index for the sampling site 2 (Palaganatham 0-20 cm) indicated that I_{geo} for all the heavy metals were found under class I which means the soil quality were uncontaminated (or) slightly contaminated (I_{geo} for Fe, Mn, Zn and Cu = 0). In the same sampling site at depth 20-40 cm I_{geo} for Mn was found to be $0 < I_{geo} < 1$ which indicated that the soil was contaminated with Mn heavy metal. But at depth 20-40 cm, the soil was not contaminated with Fe, Zn and Cu since I_{geo} for Fe, Zn and Cu = 0). The soil quality analysis at sampling site 3(Periyar) gave the following results with the geo accumulation index. I_{geo} for Fe, Zn, Mn and Cu was = 0 at depth 0-20 cm which came under Class I and which denoted that the soil was uncontaminated (or) slightly contaminated with the heavy metals. But at depth 20-40 cm, I_{geo} for Cu was $0 < I_{geo} < 1$ which came under Class II and which indicated that the soil was moderately contaminated with Cu but it was uncontaminated by Fe, Zn and Mn because I_{geo} for Fe, Mn and Zn = 0. The geo accumulation index for the sampling site 4 (Simmakal 0-20 cm) indicated that the soil was uncontaminated with Fe, Mn, Zn and Cu. The geo accumulation index for Mn at depth 20-40 cm was found to be $0 < I_{geo} < 1$. It came under Class II which represented that the soil depth was moderately contaminated by Mn but uncontaminated by Fe, Zn and Cu. The assessment result of geo accumulation index for sampling site 5 (Goripalayam 0-20 cm) indicated that geo accumulation index of Fe, Mn, Zn and Cu at depth 0-20 cm came under Class I indicating the soil was uncontaminated by Fe, Mn, Zn and Cu. But at depth 20-40 cm the soil was moderately contaminated by Mn but uncontaminated by Fe, Zn and Cu (I_{geo} for Mn $0 < I_{geo} < 1$ and Igeo for Fe, Zn and Cu I_{geo} = 0). The geo accumulation index for sampling site 6 (Mattuthavani) at depth 0-20 cm and 20-40 cm was found to I_{geo} = 0 which came under Class I indicating uncontaminated by heavy metals. Surprisingly the depth soil 0-20 cm and 20-40 cm were contaminated with Cu since I_{geo} for Cu $0 < I_{geo} < 1$ (Table 4 and 4a).

Table 4: Analysis of geo accumaulation index

Heavy metals	Depth	Sampling site					
		Kalavasal	Palaganantham	Periyar	Simmakal	Goripalayam	Mattuthavani
Fe	0-20 cm	-0.54	-0.54	-0.53	-0.57	-0.54	-0.56
	20-40 cm	+0.05	-0.43	-0.49	-0.48	-0.46	-0.31
Mn	0-20 cm	-0.59	-0.39	-0.51	-0.40	-0.51	-0.47
	20-40 cm	_0.19	+0.19	-0.29	+0.28	+0.28	0
Zn	0-20 cm	-0.45	-0.39	-0.40	-0.38	-0.45	-0.27
	20-40 cm	-0.13	-0.36	-0.36	-0.53	-0.47	-0.29
Cu	0-20 cm	-0.16	-0.39	-0.17	-0.22	-0.17	+0.14
	20-40 cm	+0.52	-0.09	+0.25	-0.43	-0.29	+0.10

Table 4 a: Analysis of geo-accumulation index

Geoaccumulation index	Depth	Sampling site					
		S_1	S_2	S_3	S_4	S_5	S_6
I_{geo}	0 – 20 cm	I_{geo} Fe<0	I_{geo} Fe<0	I_{geo} Fe<0	I_{geo} Fe<0	I_{geo} Fe<0	I_{geo} Fe<0
		I_{geo} Mn<0	I_{geo} Mn<0	I_{geo} Mn<0	I_{geo} Mn<0	I_{geo} Mn<0	I_{geo} Mn<0
		I_{geo} Zn<0	I_{geo} Zn<0	I_{geo} Zn<0	I_{geo} Zn<0	I_{geo} Zn<0	I_{geo} Zn<0
		I_{geo} Cu<0	I_{geo} Cu<0	I_{geo} Cu<0	I_{geo} Cu<0	I_{geo} Cu<0	I_{geo} Cu>0
	20-40 cm	I_{geo} Fe<0	I_{geo} Fe<0	I_{geo} Fe<0	I_{geo} Fe<0	I_{geo} Fe<0	I_{geo} Fe<0
		I_{geo} Mn>0	I_{geo} Mn>0	I_{geo} Mn<0	I_{geo} Mn>0	I_{geo} Mn>0	I_{geo} Mn<0
		I_{geo} Zn<0	I_{geo} Zn<0	I_{geo} Zn<0	I_{geo} Zn<0	I_{geo} Zn<0	I_{geo} Zn<0
		I_{geo} Cu>0	I_{geo} Cu<0	I_{geo} Cu>0	I_{geo} Cu<0	I_{geo} Cu<0	I_{geo} Cu>0

Determination of contamination levels of soil by principal component analysis :

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 soil, I is the different heavy metals, i= Fe, Mn, Zn and Cu, j is the sample number, j = (1,2,…….12). The results of Principal Component Analysis has been shown in Table 5. Due to the first two principal component account for nearly % of the total variance, they can present the soil heavy metal contamination levels in study area. While computing Principal Component Analysis, we have retained components with eigen values = 1.0 and accounting the more than 60 per cent of variance. The components with eigen value < 1.0 explain less variance and hence discarded (Johnston, 1978; Kim and Mueller, 1994). 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 (equation 1 and 2):

$$Z_1 = (0.378 \times C_{Fe})+(-0.533 \times C_{Mn})+(0.462 \times C_{Zn}+(-0.600 \times C_{Cu}) \quad (1)$$

$$Z_2 = (-0.781 \times C_{Fe})+(0.223 \times C_{Mn})+(0.174 \times C_{Zn})+(0.556 \times C_{Cu}) \quad (2)$$

where, Z_1 and Z_2 are the values of first two principal components respectively, Cij = (Fe, Mn, Zn and Cu) is the contents of heavy metals in 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 values of their. The following will take sample (1) Kalavasal sampling site (S_1) at depth 0-20 cm as an example to explain the computational process of comprehensive contamination levels by principal component analysis.

The values of Z_1 and Z_2 of site 1 (S_1) (Z_1S_1 and Z_2S_1) can be calculated using the equation 1 and 2, the contents of heavy metals in soil, which is Z_1S_1 = 3.33 and Z_1S_2 = -7.41. And then, the comprehensive contamination levels of heavy metals

Table 5: The results of principal component analysis

Eigen values				Eigen vectors			
Sr. No.	Eigen values	Proportion	Cumulaive	Element	Prin 1	Prin 2	Prin 3
1.	1.838	45.950	45.950	Fe	0.378	-0.781	0.259
2.	1.243	31.067	77.018	Mn	-0.533	0.223	0.656
				Zn	0.462	0.174	0.699
				Cu	0.600	0.556	-0.118

Table 6: The assessed results of principal component analysis and geoaccumulation index

Sampling site	Depth	Principal component analysis	I_{geo}			
			Fe	Mn	Zn	Cu
Site 1	0-20 cm	-0.42	-0.54	-0.59	-0.45	-0.16
	20-40 cm	+0.94	+0.05	+0.19	-0.13	+0.52
Site 2	0-20 cm	+2.9	-0.54	-0.39	-0.39	-0.39
	20-40 cm	+6.53	-0.43	+0.19	-0.36	-0.09
Site 3	0-20 cm	+0.02	-0.53	-0.51	-0.40	-0.17
	20-40 cm	+4.32	-0.49	-0.29	-0.36	+0.25
Site 4	0-20 cm	+0.07	-0.57	-0.40	-0.38	-0.22
	20-40 cm	+5.58	-0.48	+0.28	-0.53	-0.43
Site 5	0-20 cm	-1.4	-0.54	-0.50	-0.45	-0.17
	20-40 cm	+9.38	-0.46	+0.28	-0.47	-0.29
Site 6	0-20 cm	-0.98	-0.56	-0.47	-0.27	+0.14
	20-40 cm	+2.91	-0.31	0	-0.29	+0.10

in S_1 can be calculated, which is:

$$\mathbf{PCA(S_1) = Z_1S_1 \, x \, \frac{1.838}{1.838+1.243} + Z_2S_2 \, x \, \frac{1.243}{1.838+1.243}}$$

Similarly, the comprehensive contamination levels of heavy metals in other samples can be calculated by this same procedure and the results were shown in Table 5.

Multivariate analysis :

Two factors were extracted which reflect the major effective agents controlling the chemistry of soil samples at depth 0-20 cm (Table 6). Variance percentages mean showed that these two factors are enough for clarifying the approximate 46 per cent of the total variance observed in the data. Factor 1 explains 46 per cent of variance. High positive loading was present in factor 1 in sampling site 2 and sampling site 4. Factor 2 accounts for 31 per cent. Factor 2 showed high positive loadings in sampling site 5. From the factor analysis, it was understood that the sampling site 2, 4 and 5 were highly polluted. Eigen vector for the factor 1 and factor 2 showed the high positive leading F_1(Cu = 0.600) and F_2 (Cu = 0.556). It is obvious that these pattern have harmony with geo-accumulation index.

Factor analysis for the soil collected from different sites at depth 20 – 40 cm indicated approximately 70 per cent of the variance for the first factor alone. Factor 1 accounts for high positive loading at the sampling site 4 (Simmakal). Eigen vectors for the factor 1 indicate high positive loading of Zn (0.600) and Cu (0.607).

Assessment of principal component analysis result :

At depth 0 – 20 cm sampling site 2, 3 and 4 have high positive value. But sampling site 2 (Palaganatham) shows high positive principal component analysis (+2.9) which indicate it is highly polluted by heavy metals. It is in accordance with the results obtained from factor loading analysis. At depth 20 – 40 cm the comprehensive pollution levels of heavy metals in all the sampling sites were positive. In this depth soil geo accumulation index of Cu and Mn were found to relatively higher compared to other two heavy metals. Principal component analysis results show that the concentration of distribution of heavy metals in the soil. Although the Principal Component Analysis cannot identify the ecological risk levels of heavy metals in soil, the result of PCA can give the comprehensive information of heavy metal contamination in

Table 7 : Varimax related factor analysis result of soil samples at different sites at different depth (0-20 cm and 20-40 cm)

Sampling site	Depth		
	0 – 20 cm		20 – 40 cm
	F_1	F_2	F_1
Kalavasal	-0.650	0.000	-0.294
Palaganatham	1.495	1.463	-0.733
Periyar	-0.417	-0.580	-0.770
Simmakal	1.514	-1.524	2.207
Goripalayam	-0.720	0.957	0.372
Mattuthavani	-1.223	-0.315	-0.783

Table 8 : Pearson correlation matrix between elements Fe, Mn, Zn and Cu at different depths (0-20 cm and 20-40 cm)

	Depth (0 – 20 cm)				Depth (20 – 40 cm)			
Variables	Fe	Mn	Zn	Cu	Fe	Mn	Zn	Cu
Fe	1	-0.604	0.200	-0.162	1	-0.136	0.728	0.789
Mn		1	-0.328	-0.481		1	-0.620	-0.597
Zn			1	0.666			1	0.945
Cu				1				1

soil. The combination of results of principal component analysis and geo accumulation index can identify the comprehensive and single pollution levels of different elements in soils, which is very important for defining the extent of heavy metal pollution in soil.

Correlation analysis :

Correlation analysis is carried out the extent of relationship between heavy metals investigated. It is shown in Table 8.

For the six sampling sites at depth 0-20 cm, the related correlation matrix showed that highest correlation was between Fe and Mn and Zn and Cu. It was found that there was a positive and significant correlation between Zn and Cu (+0.66) and negative significant correlation was found between Fe and Mn (-0.604). The lowest correlation was found between Fe and Zn (+0.200). At depth 20-40 cm for all the sampling sites, the Pearson correlation matrix showed the positive and significant relation between Fe and Zn (+0.728), Fe and Cu (+0.789), Zn and Cu (+0.945). The significant correlation was found between Mn and Zn (-0.620) and Mn and Cu (-0.597) (Table 8).

Conclusion :

The mean heavy metal value in six different sampling sites at two different depth were compared with critical heavy metal value. The concentration of heavy metals at all the six sampling sites were found to be below the critical heavy metal values. The critical heavy metal values (mg/kg) in soil (Fergusson, 1990; Romheld and Marshcner, 1991; Baumbach, 1996) was as follows Fe (50), Mn (300), Zn (300) and Cu (50-125). The concentration of Fe at a depth of 0 – 20cm and 20 – 40cm at different sites were found to be site 4 > site 3 > site 6 > site 1 > site 2 > site5 and site 4 > site 3 > site 2 > site 5 > site 6 > site 1. The concentration of Mn at different depth soil is in the following order site 5 > site 1 > site 6 > site 3 > site 4 > site 2 and site 3 > site 1 > site 6 > site 5 > site 2 > site 4. The heavy metal concentration of Zn at different depth were found to be site 2 > site 3 > site 4 > site 5 > site 6 > site 1 and site 4 > site 5 > site 2 > site 6 > site 1 > site 3. Similarly the concentration of Cu was to be site 2 > site 4 > site 5 > site 3 > site 1 > site 6 and site 4 > site 5 > site 2 > site 6 > site 3 > site 1. The Enrichment Index for sampling site 2 was found to be greater than 2 which indicate the sampling site 2 (Palaganatham) was enriched with heavy metals. The geo accumulation index for six sampling site at depth 0-20cm shows the geo accumulation index for all the heavy metals were found to be less than 1 except Cu. In sampling site six (Mattuthavani) the concentration of Cu was found to be higher. At depth 20-40 cm the geo accumulation index for all the heavy metals except Mn and Cu was found to be less than 1. It is well established that at S_1 (I_{geo} Mn, I_{geo} > 1), S_2 (I_{geo}Mn > 1), S_3 (I_{geo} Cu > 1), S_4 (I_{geo} Mn > 1), S_5 (I_{geo} Mn > 1), S_6 (I_{geo} Mn > 1). It is well understood that at the depth of soil Cu and Mn are heavily polluted. The reason behind this is 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 and Tainsho, 2004). Copper is generally used in brake to control heat transport (De-Miquel *et al.*, 1997). Site with heaviest road traffic (site 2) had highest values of Mn and Cu. This is attributable to deposition of fume from exhaust of moving vehicles. However the values for the heavy metals were below the critical values (WHO standard). The finding above is consistent with recent observation of Moses (2006) that heavy metals concentration in soil are increasing due to dumping of industrial and municipal wastes in top soil and emission from motor vehicles. Moses (2006) reported that addition of heavy metals to soil resulted to their accumulation in top soil. The Principal Component Analysis result show the comprehensive pollution level. The sampling site 2 (Palaganatham), site 4 (Simmakal) are heavily polluted. From the geo accumulation index Mn and Cu are the two important contamination elements of the soil in the studied area. Combination of the Principal Component Analysis and Geo accumulation index can determine both the comprehensive and single factor pollution levels of different elements in soil, thus being particular important to soil contamination assessment.

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