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Assessing Heavy Metal Contamination in Urban Soils - An Index Analysis Approach

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ABSTRACT

Traffic cum industrial site soil collected from Dindigul Town were analyzed for zinc, copper, lead, cadmium and chromium using Atomic Absorption Spectroscopy and assessed contamination levels of heavy metals on the basis of contamination factor, Enrichment factor and Ecological risk factor . Eight integrated indices were divided into two groups. One group is suitable for the normal distribution single indices, including the sum, average, weight average, vector modulus and Nemerow pollution indices and other for log-normal distribution including the product, root of product, and weighted power product pollution indices. The calculated results of contamination factor was found to be less than 1 in all the 18 sampling sites indicating that these sites have low contamination factor of these heavy metals. The Ecological risk factor for all the 18 sampling sites and for all the metals were found to be less than 40 indicating the low potential ecological risk. The Enrichment factor for Zn, Pb and Cd were found to be 2-5 which indicate that the soil is moderately enriched with Zn, Pb and Cd. The Cr enrichment factor is found to be greater than 5 indicating significant enrichment of Cr. The results of the pollution index show that the soil is enriched with Zn, Pb and Cd. The industrial site soil is much enriched with Cr. The urban soil Dindigul Town is found to be polluted.

Keywords: Ecological risk factor, Enrichment factor, Contamination factor, Heavy metals, Pollution indices, Atomic Absorption Spectroscopy.

INTRODUCTION

The pollution of soils by heavy metals from automobile source is a serious environmental issue. These metals are released during different operations of the road transport such as combustion, component wear. Fluid leakage and corrosion of metal. Lead, cadmium, copper and zinc are the major metal pollutants of the roadside environments and are released from fuel burning. Wear out of tyros, leakage of soils and corrosion of batteries and metallic parts such as radiators etc., [1]. The majority of the heavy metals are toxic to the living organisms and even those considered as essential can be toxic if present in excess. The heavy metals can impair important biochemical processes posing a threat to human health, plant growth and animal life [2-5]. Studies have shown that such pollutants can be harmful to the road side vegetation, wild life and then neighboring human settlements [6-13].The distribution of these metals in the roadside soil is strongly but inversely correlated with the increase in the distance from [14-16].This study constitutes a part of a broader research project on the ecology and conservation of the roadside vegetation in northern England [17-19].The present research was undertaken to study heavy metal (cadmium, copper, lead, zinc) contamination in the roadside soils in relation to their natural back ground levels. In addition, the spatial distribution of the four heavy metals in the roadside area was also investigated.

MATERIALS AND METHODS

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. 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: Samples were collected from Oct 2011 to Feb 2012. Five soil samples (the upper 2cm) 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 2mm sieve. About 5gm 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 ^{0} C for 72 hrs to constant weights [20]. Exactly 1g from each of these finely ground soil samples were weighed out using an electronic balance into properly cleaned 250ml glass beakers. Digestion was performed by adding 12ml of aqua regia (3:1,v/v, concentrated HCl to concentration HNO_3) in to the beaker covered with watch glasses on a hot plate for 3h at 110 ^{0}C. After evaporation to near dryness carefully, the sample was diluted with 20ml of 2% (v/v with water) Nitric acid and transferred into a 100ml volumetric flask after filtering through Whatman no:42 filter paper and diluted to 100ml with double distilled water [21,22] 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

Pollution Indices: Caeiro et al [23] analyzed the pollution indices to assess heavy metal contamination and classified them in to three types. (i) Contamination indices (ii) background enrichment indices, and (iii) ecological risk indices. In this Paper, it has been classified the commonly used pollution indices into two types (i) single indices and (ii) integrated indices in an algorithm point of view.

Single Indices: Single Indices are indicators used to calculate only one metal contamination, which include contamination factor, ecology risk factor and enrichment factor methods were illustrated as follows.

Contamination factor: A contamination factor (C^{i}`f) to describe the contamination of a given toxic substance in a lake or a sub basin suggested by Hakanson [24] is

$$C_f^i = \frac{\overline{C_{0-1}^i}}{C_n^i}$$

Where C_{0-1}^i is the mean content of the substance i from at least 5 samples sites and c^{i}_{n} is the pre-industrial reference level for the substance. The pre-industrial reference level given in table 1.

Table 1. Pre-industrial reference level (μg/g) and toxic reponse factor by Hakanson (1980)

Elements	Hg	Cd	As	Cu	Pb	Cr	Zn
Pre-industrial reference level	**0.25**	**1.0**	**15**	**50**	**70**	**90**	**175**
Toxic response Factor	**40**	**30**	**10**	**5**	**5**	**2**	**1**

RESULTS AND DISCUSSION

The following terminologies are used to describe the contamination factor:C^i_f < 1, low contamination factor; $1 \leq C_f^i < 3$, Moderate contamination factor; $3 \leq C^i_f < 6$, Considerable contamination factors; $C^i_f \geq 6$, Very high contamination factor. Here, contamination factor (C^i_f) was expanded to be defined as

$$C_f^i = {C_i}/{C_n}$$

Which is also called contamination factors [25], where C_i is the content of metal i instead of mean content from at least 5 sample sites; C_{ri} is the reference value, baseline or national criteria of metal i. From the results of table (2 & 2a) the contamination factor of all the 18 sampling sites range as Zn; 0.006-0.168, Cu; 0.0544-0.1842, Pb; 0.006-0.0141 Cd; 0.016-0.22 and Cr; 0.009-0.0526. It is understood from the contamination factor all the control area site ranging from S_1-S_6 have lowest contamination factor and traffic cum industrial site S_7-S_8 have maximum contamination factor. Considering the contamination factor of metals such as Zn, Cu, Pb, Cd and Cr shows that the contamination factor is found to be below one which shows the sites are said to be low contaminated.

Table 2. Contamination factor of Heavy metals at Selected Sites

Heavy metals	S1	S2	S3	S4	S5	S6	S7	S8	S9
Zn	0.011	0.011	0.011	0.007	0.006	0.0074	0.014	0.014	0.0146
Cu	0.065	0.065	0.067	0.054	0.055	0.0538	0.168	0.1692	0.1664
Pb	0.010	0.01	0.0114	0.007	0.007	0.006	0.0135	0.0125	0.014
Cd	0.016	0.030	0.038	0.017	0.018	0.013	0.15	0.12	0.22
Cr	0.012	0.012	0.013	0.01	0.0108	0.0097	0.015	0.0151	0.014

Table2a. Contamination factor of Heavy metals at Selected Sites

Heavy metals	S10	S11	S12	S13	S14	S15	S16	S17	S18
Zn	0.0117	0.0121	0.0115	0.168	0.0172	0.0166	0.0141	0.01405	0.0146
Cu	0.01632	0.1638	0.1618	0.1824	0.182	0.1842	0.1746	0.1748	0.1728
Pb	0.0129	0.0135	0.0117	0.0139	0.0127	0.0141	0.012	0.0131	0.0117
Cd	0.055	0.133	0.033	0.135	0.054	0.154	0.105	0.124	0.024
Cr	0.0102	0.011	0.0098	0.052	0.0526	0.0520	0.0515	0.028	0.0291

Table 3. Ecological Risk factor of heavy metals at selected sites.

Heavy metals	S1	S2	S3	S4	S5	S6	S7	S8	S9
Zn	0.011	0.111	0.011	0.007	0.006	0.007	0.014	0.014	0.0146
Cu	0.328	0.325	0.35	0.272	0.279	0.269	0.84	0.846	0.832
Pb	0.0535	0.05	0.057	0.035	0.037	0.03	0.067	0.062	0.07
Cd	0.48	0.9	1.14	0.51	0.054	0.39	4.5	3.6	6.6
Cr	0.024	0.0248	0.026	0.02	0.021	0.019	0.03	0.030	0.028

Table 3 a Ecological Risk factor of heavy metals at Selected Sites

Heavy metals	S10	S11	S12	S13	S14	S15	S16	S17	S18
Zn	S10	S11	S12	S13	S14	S15	S16	S17	S18
Cu	0.0117	0.0121	0.0115	0.168	0.0172	0.0166	0.0141	0.0140	0.0146
Pb	0.816	0.819	0.809	0.912	0.911	0.921	0.873	0.8741	0.864
Cd	0.0645	0.0675	0.585	0.0695	0.0635	0.0705	0.06	0.0655	0.0585
Cr	1.65	`3.99	0.99	4.05	1.62	4.62	3.5	3.720	0.72

Ecological risk factor: An ecological risk factor (E_r^i) to quantitatively express the potential ecological risk of a given contaminant also suggested by Hakanson [24] is

$$E_r^i = T_r^i . C^i_f$$

Where T_r^i is the toxic –response factor for a given substance, and C^i_f is the contamination factor. The T_r^i values of heavy metals (including as) by Hakanson [24] are also given in Table I. The following terminologies are used to describe the risk factor: $Er^i < 40$, low potential ecological risk; $40 <= Er^i < 80$, moderate potential ecological risk; $80 <= Er^i < 160$, considerable potential ecological risk; $160 <= Er^i < 320$, high potential ecological risk; and $Er^i >= 320$, very high ecological risk. From the table (III & IIIa) the Ecological risk Factor of heavy metal ranges in between for Zn 0.006-0.172, Cu 0.269-0.921, Pb 0.03-0.0705, Cd 0.39-6.6 and Cr 0.018-0.2044. The Ecological risk factor for all the heavy metals were found to be minimum as Zn (S_5), Cu(S_6), Pb(S_6), Cd(S_6) and Cr(S_6)and were found to be maximum Zn (S_{14}), Cu(S_{15}), Pb(S_{15}), Cd(S_9) and Cr(S_{10}). The Ecological risk index was found to be less than 40 describing the studied area as low potential Ecological risk environment.

Enrichment factor: An element enrichment factor (EF) was calculated by the following formula

$$EF = (C_i / C_{ie})_S / (C_i / C_{ie})_{RS}$$

Where C_i is the content of element i in the sample of interest or the selected reference sample. So $(C_{i/} C_{ie})$ s is the heavy metal to immobile element ratio in the samples of interest, and $(C_{i/} C_{ie})_{Rs}$ is the heavy metal to immobile element ratio in the selected reference sample. According to Sutherland [26], five contamination categories are generally recognized on the basis of the enrichment factor: EF < 2, depletion to mineral enrichment; 2 <= EF < 5, moderate enrichment; 5 <= EF < 20, significant enrichment; 20 <= EF < 40, very high enrichment; and EF > 40, extremely high enrichment. Enrichment Factor (EF) of an element in the studied sample was based on the standardization of a measured element against a reference element. It is understood from the table (3 & 3a) above enrichment factor analysis; Cr is more enriched in the sampling sites of Dindigul Town because Dindigul Town experiences more of Leather industries.

Table 4. Enrichment Factor of heavy metals at different selected sites

Heavy metals	S1	S2	S3	S4	S5	S6	S7	S8	S9
Zn	2.2179	2.270	2.1639	1.7733	1.690	1.456	1.112	1.102	1.136
Cu	0.9097	0.887	0.9173	0.9503	0.952	0.920	0.764	0.771	0.755
Pb	2.2583	2.076	0.0219	1.8593	1.925	1.560	0.822	0.769	0.848
Cd	2.5714	4.085	6.2857	3.6	3.714	2.571	3.165	2.6	4.733
Cr	0.8587	0.873	0.7975	0.8977	0.954	0.860	1.803	0.073	0.067

Table 4a. Enrichment Factor of heavy metals at different selected sites

Heavy metals	S10	S11	S12	S13	S14	S15	S16	S17	S18
Zn	1.063	1.089	1.0409	0.9422	0.941	0.8745	0.938	0.930	0.978
Cu	0.865	0.861	0.8603	0.7202	0.701	0.6819	0.816	0.816	0.816
Pb	0.918	0.928	0.8372	0.8255	0.738	0.7887	0.853	0.923	0.832
Cd	1.377	3.111	0.8222	1.6209	0.631	1.75	1.513	1.776	0.348
Cr	0.057	0.061	0.0560	8.7197	8.616	8.1041	5.586	5.558	5.842

Integrated Indices: Integrated Indices are indicators used to calculate more than one metal contamination which were based on the single indices. Each kind of integrated index might be composed by the above single indices separately. According to algorithm, eight integrated methods were illustrated as following.

Sum of pollution index: A sum of pollution index (PI_{sum}) can be defined as

$$PI_{sum} = \sum_{i=1}^{m} P_i$$

Where P_i is the single pollution index of heavy metal i, and m is the count of the heavy metal species. The sum of pollution index was widely used in soil and sediment quality assessment by heavy metals such as the degree of contamination and the potential ecological risk [27, 24].

The degree of contamination factor (C_d) was originally defined as the sum of all contamination factors

$$C_d = \sum_{i=1}^{m} C_f^i$$

Where C^i_f is the single index of contamination factor and m is the count of the heavy metal species.

The degree of contamination of all the heavy metals for all the sampling sites was found to be less than one. The sampling site had the degree of contamination of heavy metals in the range of 0.0899-0.5513. It was found to be very low (Cd<m) indicating low degree of contamination.

The potential ecological risk index (RI) was in the same manner as degree of contamination defined as the sum of risk factors.

$$RI = \sum_{i=1}^{m} Er^{i}$$

Where E^{ri} is the single index of ecological risk factor, and m is the count of the metal species. The following terminology was used for the potential ecological risk index: RI <150, low ecological risk; 150<=RI<300, moderate ecological risk; 300<=RI < 600 considerable ecological risk and RI>600, very high ecological risk when the toxic –response factors were used for the eight elements in table1 by Hakanson [24]. The potential ecological risk Index of heavy metals at all the sampling sites ranged between 0.3976 to 7.544. The ecological risk was found to be very low (RI < 50) which indicates the sampling site was found to be low ecological risk.

Average of pollution index: Average of pollution index (PI_{AVG}) can be defined as

$$PI_{Avg} = \frac{1}{m}\sum_{i=1}^{m} P_i$$

Where P_i is the single pollution index of heavy metal i, and m is the count of the heavy metal species. This kind of pollution index was used by Bhattacharya et al. [28] to assess the quality of abandoned–mine–tailings environment. A PI_{AVG} value of >1 indicates low quality soil because of contamination. Average pollution index using contamination factor (CF_PI_{Avg}) was found to be less than one for the entire sampling site indicating that the sites are not contaminated by heavy metals very severely. Considering average pollution index using ecological risk (ERI_PI_{Avg}) shows that sampling sites S_7, S_9, S_{13} and S_{15} were found to have more than one which indicate low quality soil because of contamination. It is also understood that traffic cum industrial site were found to have low quality soil. Average pollution using enrichment factor (EF_PI_{Avg}) was found to be greater than one for all the sampling sites.

Weighted average of pollution index: Weighted average of pollution index ($PI_{W\ AVG}$) can be defined as

$$PI_{wAvg} = \sum_{i=1}^{m} w_i P_i$$

Where P_i is the single pollution index of heavy metal i, and m is the count of the heavy metal species, and $W_i$is the weight of the $P_{i.}$ Here the conditions =1 was not necessary, so the "average" was just for the sake of meaning in terminology [23], which was defined as Where Pi is the concentration factor (CF) single pollution index of heavy metal; m is the count of the heavy metal i, whose value varies from 1 to 5 on the basis of classified pollution classes. In other words, the potential ecological risk index (RI) by Hakanson [24] was the weighted average pollution index on the basis of contamination factor with the toxic – response factor weightsfrom figures the weighted average pollution index considering contamination factor (CF_PI_{WAvg}) is found to be less than one in all the sampling sites it is ranged in between 0.018-0.110 the sampling sites were least contaminated with heavy metals and found to be low polluted. The sampling sites S_7, S_9, S_{13} and S_{15} are said to have more than one that is (Er_PT_{WAvg}>1) indicating it is low polluted soil. The weighted average pollution index considering Enrichment Factor (EF_PI_{WAvg}) was found to be in the range in between 0.857-2.572. The sampling sites such as S_2, S_3, S_{13}, S_{14}, S_{15}, S_{16}, S_{17} and S_{18} are have been EF_PI_{WAvg}>2 which indicates these sampling sites are low polluted and comes under class 2 low polluted soil.

Product of pollution index: A product of pollution index (PI_{prod}) can be defined as

$$PI_{\mathrm{Prod}} = \prod_{i=1}^{m} P_i$$

Where P_i is the single pollution index of heavy metal i and m is the count of the heavy metal species. Product of pollution index using contamination factor (CF_PI_{prod}) and ecological risk factor (ER_PI_{prod}) were found to be less than one in all the 18 sampling sites. From the figures product of pollution index of enrichment factor of heavy metal at 18 sampling sites ranged between 0.067-17.756. Sampling sites are enriched with heavy metals such as Zn, Cu, Pb, Cd and Cr.

Root of the product of pollution index: A root of the product of pollution index ($PI_{r\ prod}$) can be defined as

$$PI_{r\,\mathrm{Prod}} = \left(\prod_{i=1}^{m} P_i\right)^{\frac{1}{m}}$$

Where P_i is the single pollution index of heavy metal i, and m is the count of the heavy metal species. An example of this type index is the pollution load index (PLI), which is based on the concentration factor (CF) of each metal in the soil [29,25]. PLI was calculated as the m^{th} root of the product of the m single indices. The pollution load index (PLI) provides a simple and comparative means for assessing the level of heavy metal pollution. Values of PLI=1 indicate heavy metal loads close to the back ground level, and values above 1 indicate pollution .The metal pollution index (MPI) used by Usero et al., [30] is also consistent with the form equation, but the concentration of metal i was used rather than the pollution index (P_i). Figures clearly explain the root of product of pollution index of contamination factor (CF_PLI) and ecological risk factor (Er_PLI) were found to be less than. It indicates that the heavy metal load is close to the back ground level. It is inferred that these sites are not contaminated severely by these metals. But the root of product of pollution index of enrichment factor of heavy metals at sampling sites S_1-S_7 and S_{13}-S_{18} were found to be greater than one which indicates the sampling sites are enriched with heavy metals.

Weighted power product of pollution index: A weighted power product of pollution index (PI_{wprod}) can be defined as

$$PI_{wp\,\mathrm{Prod}} = \prod_{i=1}^{m} P_i^{wi}$$

where P_i is the single pollution index of heavy metal i; m is the count of the heavy metal species and W_i is the weight of the P_i Weighted power product of pollution index considering contamination factor (CF_PI_{WProd}) and ecological risk factor (Er_PI_{WProd}) for all the sampling sites are found to be less than 1 indicating the soil is not contaminated (i.e) zero ecological risk factor of heavy metals. The weighted power product of pollution index of Enrichment factor (EF_PI_{WProd}) for S_1-S_7, and S_{13}- S_{18} are greater than 1 indicating the soil is polluted which is given in the figures.

Vector modulus of pollution index: Vector modulus of pollution index (PI_{vector}) can be defined as

$$PI_{vectorM} = \sqrt{\frac{1}{m}\sum_{i=1}^{m} {p_i}^2}$$

Where P_i is the single pollution index of heavy metal i; m is the count of the heavy metal species. Vector modulus of pollution index considering contamination factor, (PI_{vector} _CF) was found to be less than one which indicate the soil is not contaminated with heavy metals. Vector modulus of pollution index of Ecological risk factor($PI_{vector_}$EF) of heavy metals for sampling sites S_7-S_{11}, S_{13} - S_{17} are greater than one and range between 1.215 – 3.374 indicating the soil is polluted considering ecological risk factor. The vector modulus of pollution index of Enrichment factor for all the 18 sampling sites ranged between 1.63-5.751. It is inferred that all the sampling sites are enriched with heavy metals Shown in figures.

Nemerow pollution index: A Nemerow pollution index ($PI_{Nemerow}$) was applied to assess the quality of soil environment widely [31] and was defined as

$$PI_{Nemerow} = \sqrt{\frac{(\frac{1}{m}\sum_{i=1}^{m} p_i)^2 + p_{i\max}{}^2}{2}}$$

Where P_i is the single pollution index of heavy metal P_{imax} is the maximum value of the single pollution indices of all heavy metals, and m is the count of the heavy metal species. The quality of soil environment was classified into 5 grades from Nemerow pollution index ;$PI_{Nemerow}$<07,safety domain :0.7<= $PI_{Nemerow}$<1.0, precaution domain ;1.0<=$PI_{Nemerow}$<2.0, slightly polluted domain ;2.0<=$PI_{Nemerow}$<3.0, moderately polluted domain ; and $PI_{Nemerow}$ >3.0,seriously polluted domain by Cheng et al., [31].The reference values used to calculate single index by Cheng et al., [31] were the pollution threshold values rather than the base lines. A Nemerow pollution index ($PI_{Nemerow}$) considering contamination factor,($PI_{Nemerow}$_CF) was found to be less than one which indicates the soil is not contaminated with heavy metals . Pollution index of Ecological risk factor ($PI_{Nemerow}$_Er) for all the sampling sites are found to be greater than 1 indicating more polluted due to heavy metals .The Nemerow pollution index of pollution of enrichment factor ($PI_{Nemerow}$_EF) for all the sampling sites ranged between 9.0910-11.007 it is inferred that all the sampling sites are enriched with heavy metals. It is found in the figures.

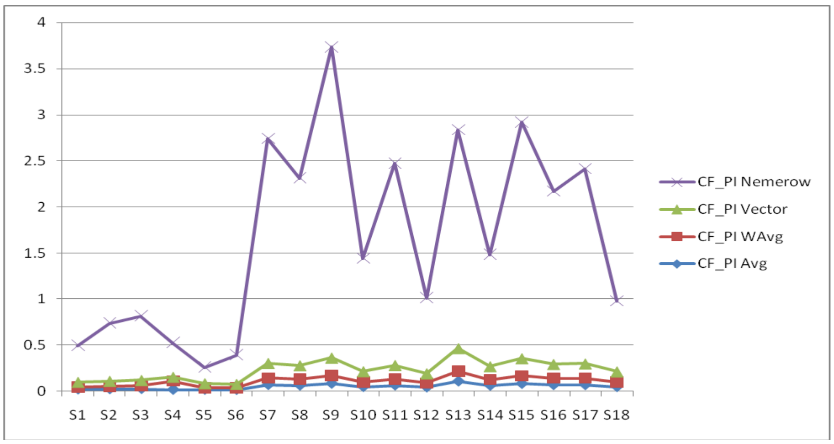

Fig (a): Integrated pollution indices based on Contamination Factor

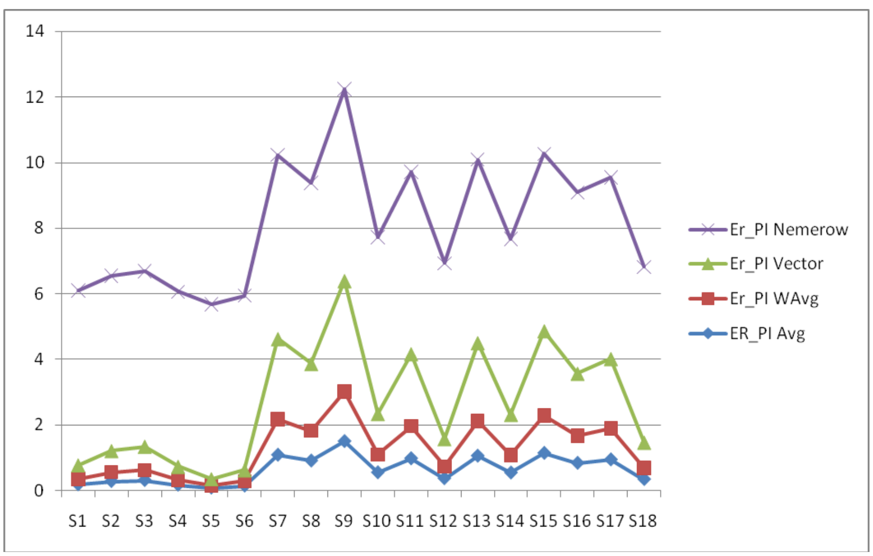

Fig (b): Index of PI Sum based on Ecological Risk Factor

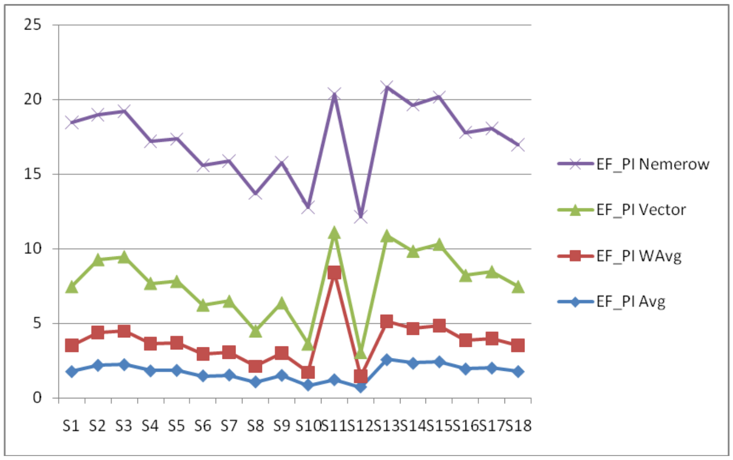

Fig (c): Indices based on Enrichment Factor

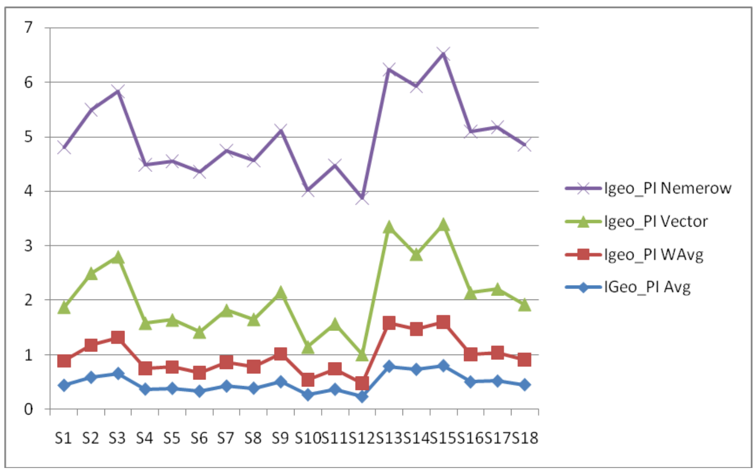

Fig (d): Indices based on Geo accumulation indices for Soil Assessment in Dindigul Town

APPLICATIONS

The Pollution of contamination levels of heavy metals can be assessed on the basis of Contamination factor, Enrichment factor and Ecological risk factor.

CONCLUSIONS

The concentration of heavy metals Zn, Cu, Pb, Cd and Cr and the concentration levels in eighteen sampling sites from Dindigul Town have been studied in this work. The concentration of Zn ranged between 1.21-3.02, Cu ranged between2.69-9.21, Pb ranged between 0.42-0.992, Cd ranged between 0.013-0.154 and Cr ranged between 0.90-4.74.The traffic and industrial sites have the maximum concentration of heavy metals that is S14(Zn-3.02),S15(Cu-9.21), S15(Pb-0.992),S15(Cd-0.154) and Cr S14(Cr-4.74). The calculated contamination factor of heavy metals reveal that the order of contamination factor is Cu(0.1374)>Cd(0.0799)>Cr(0.02278)>Zn(0.0209)> Pb(0.011).The calculated results of enrichment factor heavy metals reveal that Cr(2.0776)>Cd(2.6139)>Zn(1.3179)>Pb(1.1530)>Cu(0.8317). The calculated results ecological risk factor of heavy metals indicates that Cd (2.3711) > Cu (0.6710) >Cr(0.0556)>Pb(0.0553)>Zn(0.0209). It was inferred that contamination factor for all the sampling sites were found to be less than 1 indicating the sampling sites are low contaminated .Ecological risk factor for all the eighteen sampling sites were found to be less than 40 describing that the soil is at low potential ecological risk. Enrichment factor for Zn, Pb and Cd were found to be greater than 2-5 which are recognized as the soil is moderately enriched with Zn, Cd and Pb enrichment. Cr have the enrichment factor>5 which indicates that Cr is significantly enriched with the sampling sites. Cu have low enrichment factor indicating that Cu is not enriched in the soil. The geoaccumulation index for Zn, Cu and Pb are said to be less than one for all the sampling sites and classified into zero class. Average pollution index, weight average pollution index, product average index, root pollution index, weighted power pollution index, vector pollution index and Nemerow pollution index using contamination factor ,Enrichment factor ,ecological risk factor and showed the similar results. Contamination factor, enrichment factor and ecological risk factor assessment results indicate low pollution of heavy metals. The assessment results of enrichment index indicate there is considerable contamination Zn, Cu, Pb, Cd and Cr pollution which is mainly originate from traffic and industrial activities. These findings indicate that more attention should to be paid heavy metal pollution.

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