CHAPTER - V

A STUDY OF HEAVY METAL POLLUTION IN INDUSTRIAL SOIL

Atmospheric deposition of anthropogenic derived chemicals is an important source of environmental pollution. It contributes to the load of pollutants in urban runoff\(^1\). In some areas, the atmospheric deposition of pollutant has reached levels which are toxic to human and organisms. Soil constitutes part of vital environmental, ecological and agricultural resources that have to be protected from further degradation as an adequate supply of healthy food needed for the world’s increasing population. Heavy metals can affect both the yield of crops and their composition. Thus determination of the elemental status of a cultivated land has to be made in order to identify yield limiting deficiencies of essential micronutrients of plants grown in polluted soils\(^2\). Although heavy metals are naturally present in soils, contamination comes from many local sources such as industry, agriculture, combustion of fossil fuels and road traffic\(^3\).

Studies have shown that urban soils can receive large inputs of trace metals from different anthropogenic sources but especially from automobile emission\(^4\). Plants growing in contaminated environments can accumulate trace elements at high concentrations causing a serious health risk to consumers\(^5\). Trace metals may enter the human body through inhalation of dust, consumption of contaminated drinking water, direct ingestion of soil and consumption of food plants grown in metals contaminated soil\(^6\). Among other sources, lead (Pb) particles in the environment may come from vehicle emissions where leaded gasoline is used, flaking lead paints, incinerators and waste disposal. Studies have found that the lead burden in the urban environment is strongly related to the vehicular traffic density\(^7\). Due to the environmental persistence heavy metals can be accumulated in soil, which will increase potential risk to environment and population. Uncontrolled emission from fast growing factories, mining and over uses of agricultural chemicals fertilizers and pesticides had lead to the heavy metal contamination of the agricultural soils.

The unprecedented economic development in India in recent years has been accompanied by unprecedented environmental changes. Particulate matter in the air is one of the fastest growing types of environmental pollution\(^8\). The fall out of atmospheric particles is an important factor when considering the atmospheric particles is an important factor when considering the fate and effects of air pollution\(^9\). This matter
contains heavy metals and other elements that can exhibit adverse effects on human health (eg. cancer and cardio vascular disease) and the environment\textsuperscript{10}.

Studies have shown that in urban areas, atmospheric particles primly originate from gasoline and diesel powered vehicles, which both stir up existing road dust and discharge additional particulates into the environment\textsuperscript{11}.

Pb, Cr, Cu,Ni and Zn were included for study because they might be expected to be present at enhanced levels along roadsides. They have been investigated in recent years in a number of studies\textsuperscript{12,13}. Therefore, heavy metals elements such as Iron (Fe),Manganese (Mn),Zinc (Zn), Copper(Cu), Lead(Pb), Cadmium (Cd) and Chromium (Cr) were selected for study. The study is also important that it can be used as basis for planning management strategy to achieve better environment quality and substantial development of the Dindigul town.

\textbf{5.1 RESOURCES AND RESEARCH METHODS}

\textbf{5.1a THE STUDY AREA DESCRIPTION AND SAMPLE COLLECTION}

The study area is located in the southern part of India, close to Kodaganar river basin, 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. A total of 18 samples are collected for the study from three different samplings sites include residential area(Lakshmana puram),traffic cum commercial area(Bus stand)and industrial area(Tannery). Selections of sampling locations are listed in table 5.1.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{Site No.} & \textbf{Site} & \textbf{Location Description} & \textbf{Category} \\
\hline
1. & Thomaiyarpuram bypass & Tanneries, Small scale industries & Industrial (Tannery area) \\
\hline
2. & Dindigul Bus stand & Traffic, hotels, shopping complex, theatre, commercial complex, market & Commercial cum Traffic \\
\hline
3. & Lakshmanapuram & Residential areas of lower and middle classes, small shops & Residential \\
\hline
\end{tabular}
\caption{Table 5.1 Sampling Sites}
\end{table}
Eighteen samples were collected from each site at random to cover the entire sampling area. Large stone and plant materials were removed. To determine the mobility of heavy metals, 18 core samples were collected between 0-20cm, 20-40 cm and 40-60cm depth using a core extractor of 2.5 cm diameter. Composite samples of respective depths were prepared, air dried for 3 days and sieved through a 1-mm nylon mesh. The samples were stored in polyethylene bags and analyzed separately.

5.1b HEAVY METAL ANALYSIS

500g of each air dried composite sample was ground separately to pass through a 2mm sieve. About 5g 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. 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 aquaregia (3:1, v/v, concentrated HCl to concentrated HNO₃) into the beaker covered with watch glasses on a hot plate for 3h at 110°C. After evaporation to near dryness carefully, the sample was diluted with 20ml 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 100ml with double distilled water and used for chemical analyses. Heavy metal analysis was carried for Fe, Mn, Zn, Cu, Pb, Cd and Cr using flame Atomic Absorption Spectroscopy(AAS) (air-C₂H₂background correction mode)(Perkins-Elmer Analyst 300). Analytical wavelength were 372 for Fe, 403 for Mn, 213 for Zn, 324 for Cu, 405 for Pb, 326 for Cd and 425 for Cr. Reagents blanks for soil were also prepared by carrying out the whole extraction procedure, but without samples.

5.1c SEM AND EDAX

Sample collection and analysis

The morphology and chemical composition of the individual heavy metals were examined by scanning electron microscopy (SEM) and X-ray micro- analysis with energy dispersion spectroscopy (EDS). The X-ray microanalysis data about particles were analyzed using multivariate techniques (Hierarchical cluster analysis, Principal factor analysis) to determine the principal components of metals. The analysis was performed using JSM-6390 Scanning microscope (JOEL) equipped with a thin window oxford instruments (UK) system for X-ray microanalysis by energy dispersion spectrometry (EDS) and XRD (Shimadzu-6000). The collected samples were randomly selected and
analyzed. The chemical composition was found by X-ray microanalysis. The X-ray spectrum was accumulated for 50 seconds with a beam current of 0.6 nA and acceleration voltage of 20 kV. The intensities of the characteristic X-ray lines were converted into corresponding atomic concentration by standard less ZAF correction method.

5.2 QUANTIFICATION OF SOIL POLLUTION

5.2a ENRICHMENT FACTOR (EF)

To search for the most likely sources of elements in soil, Enrichment Factors were calculated for individual elements. In order to assess the variations in the heavy metal accumulations in the soils, the calculated measures that are Enrichment Factor and Normalized scatter coefficient were used. The Enrichment Factor (EF) is a ratio of the concentrations of the heavy metals in the soil samples to the corresponding concentration of natural local background concentration. Enrichment Factor (EF) is a useful tool in differentiating the trace elements originating from human activities and those from natural processes and in determining the degree of anthropogenic pollution\(^{17}\). Normalization of the atmospheric deposition to a reference (conservative) element not associated with anthropogenic is an available approach to determine the degree of atmospheric contamination. Enrichment Factor is calculated with the help of the formula given by Subramanian\(^{18}\).

\[
EF = \frac{\text{Value of a given metal Concentration found on soil (mg/kg)}}{\text{Natural local background concentration of the metal (mg/kg)}} \quad (1)
\]

The Enrichment Factor values close to unity indicate crusted origin, those less than to suggest a possible mobilization or depletion of metals\(^{19}\), whereas EF >1.0 indicates that the element is anthropogenic origin. Enrichment Factors greater than 10 are considered to be non-crusted source.

Also, five contamination categories are recognized on the basis of the Enrichment Factor:

- EF < 2  Depletion to minimal Enrichment,
- EF = 2-5  Moderate Enrichment
- EF = 5-20  Significant Enrichment,
- EF = 20-40  Very high Enrichment,
- EF = >40  Extremely high Enrichment.

Despite certain shortcomings, the Enrichment Factor\(^{20}\), due to its universal formula is a relatively simple and easy tool for assessing Enrichment degree and comparing the contamination of different environmental media. Anthropogenic activities,
specifically the mining of metals from ores have increased the prevalence and occurrence of heavy metal contamination at the Earth’s surface.

5.2b ENRICHMENT INDEX

Generally, the extent of anthropogenic contamination can be expressed using the enrichment index\(^{21}\). The EI is based on the average ratio of the actual and median concentrations of the given contaminants.

\[
EI = \frac{\left( \frac{Fe}{Fe_{med}} + \frac{Mn}{Mn_{med}} + \frac{Zn}{Zn_{med}} + \frac{Pb}{Pb_{med}} + \frac{Cu}{Cu_{med}} + \frac{Cd}{Cd_{med}} + \frac{Cr}{Cr_{med}} \right)}{7}
\]

Where \(M_{med}\) 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.

5.2c NORMALIZED SCATTER COEFFICIENT (NSC)

Normalized scatter coefficient (NSC) has been calculated to assess the temporal variability of the heavy metals in the soils. It help us to understand the increasing or decreasing concentration of heavy metals in the soils with the passage of time which is independent of the past focusing only at the period of study. The Normalized scatter coefficient (NSC) for heavy element is calculated with the following formula\(^{22}\).

\[
NSC = \frac{\text{Concentration in the last sampling} - \text{Concentration in the first sampling}}{\text{Concentration in the last sampling} + \text{Concentration in the first sampling}} \times 100 \quad ------ (3)
\]

The NSC values +100% indicates absolute increase while -100% means absolute decrease. The value of 0% can be regarded for no change in the parameters under consideration.

5.3 GEO ACCUMULATION INDEX

The assessment of soil or sediment enrichment can be carried out in many ways. The most common one is the index of geo accumulation\(^{23}\). In this work, the geo
accumulation index ($I_{\text{geo}}$) have been applied to assess heavy metals (Fe, Mn, Zn, Cu, Pb, Cd and Cr) distribution and contamination in the soil samples in the Dindigul town.

The index of geo accumulation index ($I_{\text{geo}}$) was originally used with bottom sediment by Muller. It is computed by the following equation.

$$I_{\text{geo}} = \log_2 \left( \frac{C_n}{1.5 B_n} \right) \quad (4)$$

Where, $C_n$ is the measured concentration of the element in the tested sediment (soil) and $B_n$ is the geochemical background value of the element in fossil argillaceous sediment (average shale). The constant 1.5 is introduced to minimize the effect of possible variation in the background values which may be attributed to lithogenic variations in the sediment gave the following interpretation for the geo accumulation index:

$I_{\text{geo}} < 0 =$ practically unpolluted; $0 < I_{\text{geo}} < 1 =$ unpolluted to moderately polluted; $1 < I_{\text{geo}} < 2 =$ moderately polluted; $2 < I_{\text{geo}} < 3 =$ moderately to strongly polluted; $3 < I_{\text{geo}} < 4 =$ strongly polluted; $4 < I_{\text{geo}} < 5 =$ strongly to extremely polluted and $I_{\text{geo}} > 5 =$ extremely polluted.

**5.4 CONTAMINATION FACTOR**

To assess the extent of contamination of heavy metals in soil and also provide a measure of the degree of overall contamination along a particular soil, contamination factor and pollution load Index has been applied. The contamination factor (CF) parameter is expressed as:

$$CF = \frac{C_{\text{metal}}}{C_{\text{background}}} \quad (5)$$

Where CF is the contamination factor, $C_{\text{metal}}$ is the concentration of pollutant in sediment, $C_{\text{background}}$ is the background value for the metal and $n$ is the number of metals. The CF reflects the metal enrichment in the sediment. The geochemical background values in continental crust averages of the trace metals under consideration reported by Taylor and McLennan was used as back ground values for the metal. The CF was classified into four groups, where the contamination factor $CF < 1$ refers to low contamination;

- $1 \leq CF < 3$ means moderate contamination;
- $3 \leq CF \leq 6$ indicates considerable contamination and
- $CF > 6$ indicates very high contamination.
5.4a POLLUTION LOAD INDEX (PLI)

Each soil sample was evaluated for the extent of metal pollution by employing the method based on the pollution load index (PLI) developed by Thomilson as follows:

\[
\text{PLI} = \frac{n}{\sqrt{\left(\text{CF}_1 \times \text{CF}_2 \times \text{CF}_3 \ldots \times \text{CF}_n\right)}} \quad (6)
\]

Where \( n \) is the number of metals studied and \( \text{CF} \) is the contamination factor calculated as described in an earlier equation. The PLI provides simple but comparative means for assessing a site quality, where a value of PLI < 1 denotes perfection, PLI = 1 present that only baseline levels of pollutants are present and PLI > 1 would indicate deterioration of site quality.

5.5 INTEGRATED POLLUTION INDEX (IPI)

To further assess the contamination levels of the metals in the Dindigul Town an integrated pollution index (IPI) of the metals was calculated in this study. The IPI is defined as the mean value of the pollution index (PI) of an element. In this study, the PI of each element is defined as the ratio of the metal concentration of the corresponding metal as the following formulation.

\[
\text{PI}_i = \frac{\text{C}_i}{\text{B}_i} \quad (7)
\]

Where \( \text{C}_n \) is the concentration of element in environment, \( \text{B}_n \) is the background value. The IPI is classified as IPI < 1 low level of pollution; 1 < IPI < 2 moderate level of pollution; 2 < IPI < 5 high level of pollution and IPI > 5 extreme high level of pollution. In this study IPIs of the metals in soils are calculated.

5.6 HEAVY METAL INDEX (HMI)

For the surface soil, heavy metal index (HMI) was determined, which is the mathematical function for indicating total heavy metal pollution of each site, according to the summation equation proposed by Herzig. Heavy metal index (HMI) Categories, Pictographs and predicates are given in table 5.2.

\[
\text{Heavy metal index} = \sum_{i=1}^{n} \text{Lc}_i \quad (8)
\]

Where \( \text{Lc}_i \) represents load class that is the load category value of the \( i^{th} \) heavy metal and ‘n’ is the number of heavy metals used for computing HMI.
Table 5.2

Heavy metal index (HMI) Categories, Pictographs and predicates

<table>
<thead>
<tr>
<th>HMI load categories</th>
<th>Pictographs</th>
<th>Predicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 7.0</td>
<td>.</td>
<td>Very Low</td>
</tr>
<tr>
<td>7.01 – 14.00</td>
<td>.</td>
<td>Low</td>
</tr>
<tr>
<td>14.01 – 21.00</td>
<td>.</td>
<td>Medium</td>
</tr>
<tr>
<td>21.01 – 28.00</td>
<td>.</td>
<td>High</td>
</tr>
<tr>
<td>28.01 – 35.00</td>
<td>.</td>
<td>Very high</td>
</tr>
<tr>
<td>&gt; 35.00</td>
<td>.</td>
<td>Critically High</td>
</tr>
</tbody>
</table>

The numerical load class is hard to pick up at a glance and hence converted into dots representing proportionally increasing load representative supply (LRS). The LRS values for each metal were obtained by dividing their range values into six equidistant categories. This graphic conversion of heavy metal pollution into a pictograph enables a quick overview and allows simple direct comparisons of elements amongst the study sites. Similarly, a six levels verbal evaluation called the “predicate” of the load representative supply (LRSP) is used to facilitate the verbal evaluation. Furthermore, HMI is divided into six equidistant load categories and provided with pictographs and predicates which assist in the characterization of study sites from least to the heaviest pollution levels.

5.7 POLLUTION INDICES

Caeiro\(^3^2\) analyzed the pollution indices to assess heavy metal contamination.

i) 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.

ii) 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\(^{33} \).

\[
C_{i}^f = \frac{C_{i}^{i}}{C_{n}^{i}} \quad (9)
\]

Where \( C_{i}^{i} \) is the mean content of the substance \( i \) from at least 5 samples sites and \( c_{i}^{i} \) is the pre-industrial reference level for the substance. The pre-industrial reference level given in table 5.3

<table>
<thead>
<tr>
<th>Elements</th>
<th>Hg</th>
<th>Cd</th>
<th>As</th>
<th>Cu</th>
<th>Pb</th>
<th>Cr</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-industrial reference level</td>
<td>0.25</td>
<td>1.0</td>
<td>15</td>
<td>50</td>
<td>70</td>
<td>90</td>
<td>175</td>
</tr>
<tr>
<td>Toxic response Factor</td>
<td>40</td>
<td>30</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

The following terminologies are used to describe the contamination factor:

\( C_{i}^f \leq 1 \), low contamination factor

\( 1 \leq C_{i}^f < 3 \), 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

\[
C_{i}^f = \frac{C_{i}}{C_{n}} \quad \text{(10)}
\]

Which is also called contamination factors\(^{34,35} \), where \( C_{i} \) is the content of metal \( i \) instead of mean content from at least 5 sample sites; \( C_{n} \) is the reference value, baseline or national criteria of metal \( i \).

5.7 a 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\(^{33}\). \[E_r^i = T_r^i, C_i^f ------ (11)\]

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\(^{33}\) are also given in table 5.3. The following terminologies are used to describe the risk factor: \(E_r^i<40\), low potential ecological risk; \(40< = E_r^i<80\), moderate potential ecological risk; \(80< = E_r^i<160\), considerable potential ecological risk; \(160< = E_r^i<320\), high potential ecological risk; and \(E_r^i>= 320\) very high ecological risk. Although the risk factor was originally used as a diagnostic tool for the purpose of controlling pollution, it was successfully used for assessing the quality of sediments and soils in environment by heavy metals. Ecological risk factor for each metal is calculated by multiplying toxic response factor and the contamination factor value of heavy metal.

**5.7b ENRICHMENT FACTOR**

An element enrichment factor (EF) was initially developed to speculate on the origin of elements in the atmosphere, precipitation or seawater\(^{36}\), but it was progressively extended to the study of soils, lake sediments, peat, tailings and other environmental materials. The formula to calculate EF is \[EF = (C_i / C_{ie})_S / (C_i / C_{ie})_{RS} \quad (12)\]

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\(^{37}\). The selected reference sample is usually an average crust or a local back ground sample. The immobile element is often taken to be \(Al^{38}\), \(Li\), \(Sc\), \(Zr^{39}\) or \(Ti\) and sometimes \(Fe^{40}\) or \(Mn^{41}\) has been used. \(Al\) (for terrestrial sources) and \(Na\) (for Oceanic sources) have been used for the purpose of comparing the chemical composition of atmospheric particulate material collected at the South Pole to the composition of the crust or the ocean. According to Sutherland\(^{42}\), 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. A reference element is often the one characterized by low occurrence variability, such as the most commonly used elements: Al, Fe, Ti, Si, Sr and K.

5.7c POTENTIAL ECOLOGICAL RISK INDEX (RI)

Concentration of heavy metal toxic response and ecological risk factor are put forward by Hakanson33.

\[
RI = \sum_{i=1}^{m} E_{ri}^{i}
\]

Where \(E_{ri}^{i}\) 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): \(RI <150\), 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 table 5.3.

5.8 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.

5.8 a 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 risk43.
5.8b AVERAGE OF POLLUTION INDEX

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

$$PI_{Avg} = \frac{1}{m} \sum_{i=1}^{m} P_i$$  \hspace{1cm} (15)

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 to assess the quality of abandoned–mine–tailings environment. API_{Avg} value of >1 indicates low quality soil because of contamination.

5.8c WEIGHTED AVERAGE OF POLLUTION INDEX

Weighted average of pollution index (PI_{W Avg}) can be defined as

$$PI_{W Avg} = \sum_{i=1}^{m} w_i P_i$$  \hspace{1cm} (16)

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 \( P_i \).

5.8d PRODUCT OF POLLUTION INDEX

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

$$PI_{prod} = \prod_{i=1}^{m} P_i$$  \hspace{1cm} (17)

Where \( P_i \) is the single pollution index of heavy metal i and m is the count of the heavy metal species.

5.8e ROOT OF THE PRODUCT OF POLLUTION INDEX

A root of the product of pollution index (PI_{r prod}) can be defined as Where \( P_i \) is the single pollution index of heavy metal i and m is the count of the heavy metal species.

$$PI_{r Prod} = \left( \prod_{i=1}^{m} P_i \right)^{\frac{1}{m}}$$  \hspace{1cm} (18)

An example of this type index is the pollution load index (PLI), which is based on the Contamination factor (CF) of each metal in the soil.
5.8f WEIGHTED POWER PRODUCT OF POLLUTION INDEX

A weighted power product of pollution index (PI\textsubscript{wpprod}) can be defined as

\[
PI\textsubscript{wpprod} = \prod_{i=1}^{m} P_i^{w_i}  
\]

Where \( P_i \) is the single pollution index of heavy metal \( i \) and \( m \) is the count of the heavy metal species and \( pW_i \) is the weighted power product of pollution index. Considering contamination factor (CF\_PI\textsubscript{WPprod}) and Potential ecological risk Inedx (RI\_PI\textsubscript{WPprod}).

5.8g VECTOR MODULUS OF POLLUTION INDEX

Vector modulus of pollution index (PI\textsubscript{vector}) can be defined as

\[
PI\textsubscript{vectorM} = \sqrt{\frac{1}{m} \sum_{i=1}^{m} P_i^2}  
\]

Where \( P_i \) is the single pollution index of heavy metal \( i \) and \( m \) is the count of the heavy metal species.

5.8h NEMEROV POLLUTION INDEX

A Nemerow pollution index (PI\textsubscript{Nemerow}) was applied to assess the quality of soil environment widely and was defined as

\[
PI\textsubscript{Nemerow} = \sqrt{\frac{1}{m} \sum_{i=1}^{m} P_i^2 + P_{i_{\text{max}}}^2}  
\]

Where \( P_i \) is the single pollution index of heavy metal \( P_{i_{\text{max}}} \) 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 :\( PI\textsubscript{Nemerow} < 0.7 \), safety domain; \( 0.7 \leq PI\textsubscript{Nemerow} < 1.0 \), precaution domain; \( 1.0 \leq PI\textsubscript{Nemerow} < 2.0 \), slightly polluted domain; \( 2.0 \leq PI\textsubscript{Nemerow} < 3.0 \), moderately polluted domain; and \( PI\textsubscript{Nemerow} > 3.0 \), seriously polluted domain by Cheng\textsuperscript{45}. 
5.9 POLLUTION SOURCE IDENTIFICATION

5.9a 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\textsuperscript{46}.

5.9b 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. Many researchers 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.

5.9c 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 can readily be seen.

5.9d 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.
5.10 RESEARCH FINDINGS AND DISCUSSION

5.10a Quantification of soil pollution

Back ground metal concentration in the analyzed composite samples are presented in table 5.4.

Table 5.4

<table>
<thead>
<tr>
<th>Sampling Stations</th>
<th>Fe</th>
<th>Mn</th>
<th>Zn</th>
<th>Cu</th>
<th>Pb</th>
<th>Cd</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>5.11</td>
<td>15.84</td>
<td>0.53</td>
<td>2.17</td>
<td>0.2</td>
<td>0.001</td>
<td>0.76</td>
</tr>
<tr>
<td>S2</td>
<td>7.42</td>
<td>7.76</td>
<td>1.62</td>
<td>7.92</td>
<td>0.83</td>
<td>0.074</td>
<td>0.54</td>
</tr>
<tr>
<td>S3</td>
<td>9.07</td>
<td>6.47</td>
<td>2.04</td>
<td>8.25</td>
<td>0.85</td>
<td>0.054</td>
<td>0.35</td>
</tr>
<tr>
<td>Mean</td>
<td>7.2</td>
<td>10.023</td>
<td>1.396</td>
<td>6.113</td>
<td>0.626</td>
<td>0.043</td>
<td>0.55</td>
</tr>
</tbody>
</table>


Concentration of Fe, Mn, Zn, Cu, Pb, Cd and Cr are analyzed at different sampling sites such as control, traffic and tannery at different depths 0-20 cm and 20-40 cm are presented in table 5.5 with its percent of variation.
Iron (Fe)

Iron is important in plant nutrition as they are essential crop micronutrients Fe can be in insoluble forms in calcareous soils causing deficiencies (ferric chlorosis). In spite of elevated soil content, total Fe or Mn are not a good indicator of their plant availability. For example Fe is mainly present in precipitated forms such as oxides and hydroxides in the soils. At depth (0-20cm) the Iron concentration in the soil varied from 8.57mg/kg to 11.15 mg/kg. The major source identified for Fe was due to stacking of over burden dump and fugitive emission. At depth (20-40cm) Fe content of the soil varies from 6.84mg/kg to 9.10mg/kg. The percent of variation of Fe at traffic site and at tannery site compared to control was found to be 19.95% and 30.1% respectively and at depth 20-40 cm traffic and tannery site showed the variation 29.39% and 33.04% respectively. The critical limits used for classify site as toxic is Fe>50 kg. In all the three sampling sites Fe is found to be in the higher level compared to the critical limits.

Manganese (Mn)

Manganese is also an essential element for plants and animal. Its uptake is being controlled metabolically. Soil derives manganese from the parent material and its contents in the rocks are higher than the concentration of other micronutrients apart from iron. Manganese found in the range of 11.52 mg/kg to 19.20 mg/kg at depth (0-20cm) and 9.64 mg/kg to 39.73 mg/kg at depth (20-40 cm). Critical Manganese concentration in soil is rather high 1500-3000 mg/kg. At depth 0-20 cm and at depth 20-40 cm, Mn showed decrease of variation 40%, 23.69%, 44.98% and 39.73% respectively. The critical limit for Mn used for classifying site as toxic was 5 mg/kg. In all the three sampling sites, Mn is found to be in the higher level compared to the critical limits.

Zinc (Zn)

Since no major industry exists in the study areas such as smelting operations, we may assume that the primary sources of Zn are probably from the motor vehicle tire rubber exacerbated by poor road surfaces and the lubricating oils in which Zn is found as part of many additives such as Zinc dithiophosphates. It may also be noticed that in many of the urban sites examined, the Zn content was below the maximum permissible zinc concentration limit prescribed (of 200 mg/kg) by European commission and in many sites the concentration exceeded the general phyto-toxicity level of 250 mg/kg. The Zinc content in the soil varied from 1.97 mg/kg to 2.96 mg/kg at depth (0-20cm) and 1.25
mg/kg to 2.50 mg/kg at depth (20-40 cm) respectively. The Zn soil level falls in the range of 1.25 mg/kg to 2.96 mg/kg. At two different depths it showed the maximum variation 28.93%, 50.25%, 64.8% and 100% respectively. The critical limit for Zn used to classify site as toxic was 300 mg/kg. In all the three sampling sites, Zn is found to be higher in industrial site (2.96) mg/kg compared to other two sites. This value is small compared with many other studies. In this study, Pb/Zn ratio for control, traffic and industrial sites were found to be 0.381, 0.464 and 0.341 respectively. The ratio was less than one (<1) which may indicate soil, Zn pollution which was related to the local condition.

**Copper (Cu)**

Cu is derived from engine wear from thrust bearings, bushing and bearing metals. Copper found in the range of 3.29 mg/kg to 9.15 mg/kg at depth (0-20 cm) and 2.73 to 8.76 mg/kg at depth (20-40 cm) respectively. The mean concentration of Cu at different sampling site and at 0-20 cm and 20-40 cm varied 2.73 mg/kg to 9.15 mg/kg. It also showed increase of variation to the maximum that is traffic and tannery sites more than 100% respectively. The critical heavy metal value in soil for copper is 50-125 mg/kg. The normal Cu content of agricultural soils is 5 to 50 mg/kg concentrations below 8 mg/kg could indicate a deficiency for some crops as Cu is an essential micronutrients. In this study, all the samples were the normal range and none is exceeded.

**Lead (Pb)**

In the last decades, much attention has been directed towards lead in the roadside environments as a result of its wide spread use as an anti knocking agent in gasoline. In the recent years the lead content in gasoline was markedly decreased in the world. This decrease has reduced the addition of lead to the environment by motor vehicles. However, the previously deposited Lead remains a major contaminant of the road side environments. Although the Lead content in gasoline is minimized these days the increased traffic has caused an increase in the lead emission in the road side environment. The Lead found in the range of 0.76 mg/kg to 0.952 mg/kg at depth (0-20 cm) and 0.48 mg/kg to 0.860 mg/kg at depth (20-40 cm) respectively. The presence of Pb coming from the emission of vehicles as well as its presence in the soils polluted with wastes from different operations. The concentrations of Lead at different sites and at different depths are control (0.760 mg/kg), traffic (0.94 mg/kg) and tannery (0.952 mg/kg) at (0-20 cm). Control (0.48 mg/kg), traffic (0.885 mg/kg) and at tannery (0.860 mg/kg) at (20-40 cm). It showed the maximum of percent of variation traffic (76%) and tannery (25.26%) at (0-
20cm) and for traffic (84.38%) and tannery (79.17%) at (20-40cm) respectively. The critical limit for Pb 100mg/kg in soil. The Pb content in the traffic site was found to be higher compared to the other two sampling sites. In India the most probable source of contamination is the Lead particulate matter emitted from gasoline vehicles which settles not for from the highway.\textsuperscript{50}

**Cadmium (Cd)**

The sources of cadmium in the urban areas are much less well defined than those of Pb but metal plating and tire rubber were considered the likely sources of Cd.\textsuperscript{54} Cadmium and Zinc are found in lubricating oils as part of many additives. It was reported that the cadmium level in car tires is in the range of 20 to 90mg/kg as associated Cd contamination in the process of vulcanization.\textsuperscript{55} In the absence of any major industry in the sampling sites, the levels of Cd could be due to lubricating oils and/or old tires, that are frequently used and the rough surfaces of the roads which increase the wearing of tires. The Cadmium concentration found in the soil at the depth (0-20cm) was found to be 0.028 mg/kg to 0.16 mg/kg and at the depth (20-40 cm) 0.016 mg/kg to 0.084 mg/kg respectively. The mean concentration of Cd varied from 0.016 mg/kg to 0.16 mg/kg respectively. At traffic and tannery and at different depths it showed the maximum of variation more than 100. The critical limit for Cd is 3mg/kg in soil. The Cd content in all the three sites was found to be less compared with critical value. The ratio Cd/Pb for control, traffic and industrial are 0.028, 0.099 and 0.085 respectively. In the entire sampling sites Cd/Pb ratio was found to be less than 1 which indicates the lead content is found to higher concentration compared to Cd.

**Chromium (Cr)**

Chromium is one of the known environmental toxic pollutants in the world.\textsuperscript{56} Besides these chromium plating and alloys in motor vehicles is considered to be a more probable source of Cr.\textsuperscript{57} An elevated concentration between 5-30 mg/kg is considered critical for plants and could cause yield reduction.\textsuperscript{58} The toxic effects of chromium in take in skin rash, nose irritations, bleeds, upset stomach, ulcers, weakened immune system, kidney and liver damage, nasal itch and lungs cancer.\textsuperscript{59} Chromium is found in soil in the range of 1.08 mg/kg to 4.68 mg/kg at depth (0-20 cm) and 0.92 mg/kg to 2.56 mg/kg at the depth (20-40 cm) respectively. The mean concentration of Cr varied from 0.92 mg/kg to 4.68 mg/kg and it showed more than 100% variation at tannery site but less variation at
traffic site. The critical limits for Cr 50-200 mg/kg. In this work all sampled sites showed within the normal range of chromium concentration.

The quality guidelines for soil heavy metal contaminations developed in certain countries indicate wide variations. In France, the soil threshold levels of heavy metals are Pb, 100; Zn, 300; Cd, 0.07; Ni, 50 and Cu, 100 mg /kg. The mean and range of total heavy metal concentrations in normal soils reported by London were Pb, 35(2 to 300); Zn, 90(1 to 900); Cd, 0.35(0.01 to 2); Ni, 50(2 to 750); Cu, 30(2 to 250); Cr, 70(5 to 1500) and Mn, 1000(20 to 10,000) mg kg⁻¹. Furthermore, limits for total concentrations of heavy metals in soil according to EEC were Cd, 3; Cu, 200; Pb,200 and Zn,300 mg kg⁻¹ while, the Dutch reference values are 0.8,36,35 and 140 mg kg⁻¹, respectively. Singh in their all India coordinated research project reported Pb,4.2 to 60; Zn,0.8 to 119.6; Cd,0.04 to 0.96; Ni,0.88 to 6.78; Cu,1.18 to 70.2; Cr,2.1 to 9.16 and Mn 56.6 to 59.3mg/kg soil. The critical limits used for classify sites are toxic were Pb >1, Zn >2, Cd>1, Ni >3, Cu>1, Cr >5, Mn >5 and Fe >5 mg/ kg.

The results from our studies for Fe, Mn, Zn, Cu, Pb, Cd and Cr reflect values less than the critical limits value which shows the soil is not contaminated one while assessing the effect of individual heavy metal in the soil. Concentration of heavy metals at different depths and at different sampling sites are represented in figures 5.1- 5.7.
Fig 5.1 Concentration of Fe (µg/g) at different depths and at sampling sites

Fig 5.2 Concentration of Mn (µg/g) at different depths and at sampling sites
Fig 5.3 Concentration of Zn (μg/g) at different depths and at sampling sites

Fig 5.4 Concentration of Cu (μg/g) at different depths and at sampling sites
Fig 5.5 Concentration of Pb (µg/g) at different depths and at sampling sites

Fig 5.6 Concentration of Cd (µg/g) at different depths and at sampling sites
Fig 5.7 Concentration of Cr (µg/g) at different depths and at sampling sites
Scheme-II Contamination of Soil by Heavy Metals
5.11 ENRICHMENT FACTOR

In order to evaluate the rate of accumulation of heavy metals in the soils the mean values for all heavy metals during the study period were considered, along with the EF values of all seven elements and it is given in table 5.6. The Enrichment Factor (EF), due to its universal formula, is a relatively simple and easy tool for assessing enrichment degree and comparing the contamination of different environmental media. Table 5.7 shows the Enrichment Factor (EF) between the studied metals in soil. Cr and Cd shows highest enrichment average value (4.58 and 3.6 respectively). The order of average metal Enrichment Factor (EF) is Cr (4.58) > Cd (3.61) > Zn (1.93) > Pb (1.78) > Mn (1.49) > Fe (1.41) > Cu (1.17). As it can be observed the Enrichment Factor (EF) trends are comparable and show a similar behavior. Fe and Cu have the less than 2 Enrichment Factor in all the 18 Sampling Sites. The Enrichment Factor Cd, Pb, Zn was found to be more than 2 for 6 sampling sites. Sampling sites 7 and 8 show more than 2 Enrichment Factor in Cr and Cd. Sampling sites 10 and 12 showed less than 2 Enrichment Factor for all the seven metals. Sampling sites 13 and 15 showed more than 2 Enrichment Factor in Cr, Cd and Mn. Cr and Cd showed more than 2 Enrichment Factor in the sampling sites 16 and 17. In the industrial site that is sampling sites 13, 14, 15, 16, 17 and 18 showed the highest Enrichment Factor in Cr that is Enrichment Factor is equal to more than 5. It indicates that Cr is highly enriched in the industrial sites. It also indicated Cr and Cd have high degree of metal enrichment in the industrial sampling sites.

The mean concentration heavy metals were plotted against Enrichment Factor. It is given in the figure 5.8. The scatter plot is obtained (Fig 5.9). From the Fig 5.9 it is found out that Cr is having the highest Enrichment followed Cd, Zn, Pb, Fe, Mn and Cu. It is inferred that Cr have high rate of accumulation in this soil followed by other metals. Though Cr, Cd, and Pb have lesser concentration but have higher Enrichment. Enrichment Factor normally reveals the addition and / or removal of metal under consideration which is a result of cumulative activity in the region. Hence the Enrichment Factor should denote the total Enrichment and / or depletion of an element and cannot evaluate the trend for the short term accumulation.
Table 5.6

Enrichment factor for heavy metals in the soils of study area

<table>
<thead>
<tr>
<th>Sampling stations</th>
<th>Fe</th>
<th>Mn</th>
<th>Zn</th>
<th>Cu</th>
<th>Pb</th>
<th>Cd</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁</td>
<td>1.661</td>
<td>1.212</td>
<td>3.698</td>
<td>1.511</td>
<td>3.75</td>
<td>4</td>
<td>1.427</td>
</tr>
<tr>
<td>S₂</td>
<td>1.686</td>
<td>1.215</td>
<td>3.830</td>
<td>1.497</td>
<td>3.5</td>
<td>7.5</td>
<td>1.427</td>
</tr>
<tr>
<td>S₃</td>
<td>1.682</td>
<td>1.209</td>
<td>3.641</td>
<td>1.543</td>
<td>4</td>
<td>9.5</td>
<td>1.342</td>
</tr>
<tr>
<td>S₄</td>
<td>1.318</td>
<td>1.105</td>
<td>2.339</td>
<td>1.253</td>
<td>2.45</td>
<td>4.25</td>
<td>1.184</td>
</tr>
<tr>
<td>S₅</td>
<td>1.350</td>
<td>1.103</td>
<td>2.283</td>
<td>1.285</td>
<td>2.6</td>
<td>4.55</td>
<td>1.289</td>
</tr>
<tr>
<td>S₆</td>
<td>1.346</td>
<td>1.109</td>
<td>2.471</td>
<td>1.239</td>
<td>2.1</td>
<td>3.25</td>
<td>1.157</td>
</tr>
<tr>
<td>S₇</td>
<td>1.386</td>
<td>1.488</td>
<td>1.543</td>
<td>1.060</td>
<td>1.144</td>
<td>4.411</td>
<td>2.5</td>
</tr>
<tr>
<td>S₈</td>
<td>1.377</td>
<td>1.489</td>
<td>1.518</td>
<td>1.063</td>
<td>1.060</td>
<td>3.529</td>
<td>2.518</td>
</tr>
<tr>
<td>S₉</td>
<td>1.390</td>
<td>1.476</td>
<td>1.580</td>
<td>1.050</td>
<td>1.180</td>
<td>6.470</td>
<td>2.333</td>
</tr>
<tr>
<td>S₁₀</td>
<td>1.190</td>
<td>1.243</td>
<td>1.265</td>
<td>1.030</td>
<td>1.092</td>
<td>1.617</td>
<td>1.703</td>
</tr>
<tr>
<td>S₁₁</td>
<td>1.200</td>
<td>1.247</td>
<td>1.308</td>
<td>1.034</td>
<td>1.114</td>
<td>3.911</td>
<td>1.833</td>
</tr>
<tr>
<td>S₁₂</td>
<td>1.187</td>
<td>1.269</td>
<td>1.246</td>
<td>1.021</td>
<td>0.993</td>
<td>0.970</td>
<td>1.648</td>
</tr>
<tr>
<td>S₁₃</td>
<td>1.534</td>
<td>2.275</td>
<td>1.446</td>
<td>1.105</td>
<td>1.266</td>
<td>2.5</td>
<td>13.371</td>
</tr>
<tr>
<td>S₁₄</td>
<td>1.573</td>
<td>2.273</td>
<td>1.480</td>
<td>1.104</td>
<td>1.161</td>
<td>1</td>
<td>13.542</td>
</tr>
<tr>
<td>S₁₅</td>
<td>1.636</td>
<td>2.244</td>
<td>1.431</td>
<td>1.116</td>
<td>1.291</td>
<td>2.851</td>
<td>13.257</td>
</tr>
<tr>
<td>S₁₆</td>
<td>1.295</td>
<td>1.635</td>
<td>1.215</td>
<td>1.058</td>
<td>1.106</td>
<td>2.002</td>
<td>7.228</td>
</tr>
<tr>
<td>S₁₇</td>
<td>1.296</td>
<td>1.638</td>
<td>1.205</td>
<td>1.059</td>
<td>1.197</td>
<td>2.296</td>
<td>7.2</td>
</tr>
<tr>
<td>S₁₈</td>
<td>1.282</td>
<td>1.622</td>
<td>1.254</td>
<td>1.047</td>
<td>1.067</td>
<td>0.444</td>
<td>7.485</td>
</tr>
</tbody>
</table>
Fig 5.8 Mean concentrations and Enrichment Factors for the heavy metals

Fig 5.9 Bivariate plot of the mean concentrations and enrichment factors of the heavy metals

5.11a 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\textsuperscript{65}. 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 such as 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 geochemical character of the soil. For this reason only areas with EI > 2 are considered for being seriously affected by contamination.

The results of the table 5.7 showed that Enrichment index ranged between 0.609 to 2.015. The minimum enrichment index was assessed for the sampling sites S₁ to S₆. Since the EI value for these sampling sites (S₁ to S₆) lie below one indicated that these sampling sites are not affected by industrial activity. But the sampling site S₇ to S₁₈ have the enrichment index greater than 1 indicating these sites are contaminated and affected by industrial activity. It is very obvious from the table 5.8 that sampling site S₉, S₁₃, S₁₄ and S₁₅ have enrichment index (EI >=2) greater than or equal to two indicating these sampling soils are seriously affected by contamination. The order of enrichment index in the various sampling sites is S₁₀(2.02) > S₁₅(1.81) > S₁₃(1.75) > S₁₄(1.54) > S₁₆(1.44) > S₁₇ (1.35) > S₇(1.30) > S₈ (1.22) > S₁₁(1.11) > S₁₈ (1.00) > S₁₀(0.911) > S₂ (0.85) > S₁₂(0.84) > S₁(0.82) > S₃(0.788) > S₅(0.676) > S₆(0.631) > S₄(0.609).

**Table 5.7**

<table>
<thead>
<tr>
<th>Sampling Sites</th>
<th>EI</th>
<th>Fe</th>
<th>Mn</th>
<th>Zn</th>
<th>Cu</th>
<th>Pb</th>
<th>Cd</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁</td>
<td>0.823</td>
<td>0.333</td>
<td>0.243</td>
<td>0.742</td>
<td>0.303</td>
<td>0.075</td>
<td>0.803</td>
<td>0.286</td>
</tr>
<tr>
<td>S₂</td>
<td>0.851</td>
<td>0.339</td>
<td>0.244</td>
<td>0.769</td>
<td>0.301</td>
<td>0.070</td>
<td>1.51</td>
<td>0.296</td>
</tr>
<tr>
<td>S₃</td>
<td>0.788</td>
<td>0.338</td>
<td>0.243</td>
<td>0.731</td>
<td>0.301</td>
<td>0.080</td>
<td>1.906</td>
<td>0.261</td>
</tr>
<tr>
<td>S₄</td>
<td>0.609</td>
<td>0.265</td>
<td>0.222</td>
<td>0.469</td>
<td>0.252</td>
<td>0.049</td>
<td>0.853</td>
<td>0.238</td>
</tr>
<tr>
<td>S₅</td>
<td>0.676</td>
<td>0.271</td>
<td>0.221</td>
<td>0.458</td>
<td>0.258</td>
<td>0.052</td>
<td>0.903</td>
<td>0.259</td>
</tr>
<tr>
<td>S₆</td>
<td>0.631</td>
<td>0.270</td>
<td>0.223</td>
<td>0.496</td>
<td>0.249</td>
<td>0.042</td>
<td>0.652</td>
<td>0.232</td>
</tr>
<tr>
<td>S₇</td>
<td>1.304</td>
<td>0.278</td>
<td>0.297</td>
<td>0.301</td>
<td>0.213</td>
<td>0.221</td>
<td>0.886</td>
<td>0.502</td>
</tr>
</tbody>
</table>
5.11b NORMALIZED SCATTER COEFFICIENT (NSC)

The Normalized scatter coefficient (NSC) for heavy element is calculated and given in table 5.8. The order of mean metal Normalized Scatter coefficient (NSC) is Cr (11.52) > Cd (10.77) > Mn (8.86) > Zn (7.60) > Fe (3.65) > Pb (3.56) > Cu (2.55). The positive NSC values indicate that all the heavy metals are accumulated in the soil. Cr and Cd are more accumulated compared to other heavy metals. The sampling sites 1 to 10, Pb is accumulated in a faster rate. In the industrial sites 13 to 15 all the heavy metals are accumulated in the faster rate. The scatter plot of mean concentration of heavy metals was plotted against the Enrichment Factors (Fig 5.10) which shows the Cr have high Enrichment Factor followed by Cd, Zn, Pb, Mn, Fe and Cu. Mn is having higher mean concentration followed by Fe, Cu, Zn, Pb, Cr and Cd. Cr is having less mean concentration but having highest enrichment. Similarly Cd is having less mean concentration but having highest enrichment. Similarly Pb and Zn are having lesser mean concentration but higher enrichment factor. But the metals such as Cu, Fe and Zn are having higher mean concentration but lesser Enrichment Factor. It is much evident from the Fig 5.10 that Cr,
Cd, Pb and Zn are having lesser mean concentration but higher Enrichment Factor, on contrary Mn, Fe and Cu having higher mean concentration but lesser Enrichment Factor.
Table 5.8
Normalized scatter coefficient (%) of the heavy metals in the soils of the study area

<table>
<thead>
<tr>
<th>Sampling Sites</th>
<th>Fe</th>
<th>Mn</th>
<th>Zn</th>
<th>Cu</th>
<th>Pb</th>
<th>Cd</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_1</td>
<td>-0.759</td>
<td>-0.129</td>
<td>-1.754</td>
<td>0.459</td>
<td>3.448</td>
<td>-30.43</td>
<td>-1.587</td>
</tr>
<tr>
<td>S_2</td>
<td>-0.64</td>
<td>0.130</td>
<td>0.771</td>
<td>-1.055</td>
<td>3.225</td>
<td>-40.74</td>
<td>3.087</td>
</tr>
<tr>
<td>S_4</td>
<td>10.33</td>
<td>4.715</td>
<td>20.215</td>
<td>8.072</td>
<td>18.110</td>
<td>-5.8823</td>
<td>5.084</td>
</tr>
<tr>
<td>S_5</td>
<td>10.474</td>
<td>4.430</td>
<td>19.877</td>
<td>9.882</td>
<td>0.282</td>
<td>10.3448</td>
<td>10.432</td>
</tr>
<tr>
<td>S_6</td>
<td>0.341</td>
<td>-0.0432</td>
<td>0.806</td>
<td>-0.118</td>
<td>3.825</td>
<td>11.111</td>
<td>-0.369</td>
</tr>
<tr>
<td>S_7</td>
<td>-0.145</td>
<td>0.391</td>
<td>-1.185</td>
<td>0.478</td>
<td>-1.554</td>
<td>-18.918</td>
<td>3.488</td>
</tr>
<tr>
<td>S_8</td>
<td>7.635</td>
<td>8.962</td>
<td>9.890</td>
<td>1.449</td>
<td>2.315</td>
<td>46.341</td>
<td>18.942</td>
</tr>
<tr>
<td>S_9</td>
<td>0.718</td>
<td>8.808</td>
<td>8.225</td>
<td>1.265</td>
<td>1.333</td>
<td>6.007</td>
<td>15.384</td>
</tr>
<tr>
<td>S_11</td>
<td>-1.232</td>
<td>0.033</td>
<td>-1.172</td>
<td>0.054</td>
<td>4.343</td>
<td>42.857</td>
<td>-0.636</td>
</tr>
<tr>
<td>S_12</td>
<td>-3.220</td>
<td>0.683</td>
<td>0.511</td>
<td>-0.490</td>
<td>-0.966</td>
<td>-6.574</td>
<td>0.4291</td>
</tr>
</tbody>
</table>
The Normalized scatter coefficient plot is obtained (Fig 5.11). Cr, Cd, Mn, Zn and Pb were found to have higher Normalized scatter coefficient compared to other metals. Cu and Fe having higher concentration but lesser Normalized scatter coefficient. It is observed that Cr, Cd, Mn, Zn, and Pb have the highest Normalized scatter coefficient value even with the small mean concentration which is indicating high rate of accumulation. The Normalized scatter coefficient can evaluate the enrichment and/or depletion of a particular element in the period of time with respect to the last sampling. The mean values of Enrichment Factor and Normalized scatter coefficient for all the seven heavy metals are studied together from the Fig 5.11. It is found out that Cr have the highest Enrichment Factor followed by Cd, Mn, Zn, Fe, Pb and Cu on the other hand the Normalized scatter coefficient values indicate that Cr is getting enriched with faster rate followed by Cd, Zn, Pb, Mn, Fe and Cu. It is obvious from the Fig 5.11 that Cr and Cd are having both higher Normalized scatter coefficient.
Fig 5.11 Bivariate plot of the mean concentrations and normalized scatter coefficients of the heavy metals

5.12 GEO ACCUMULATION INDEX

Geo accumulation index for Fe, Mn, Zn, Cu, Pb, Cd and Cr at different depth and at different sampling sites are given in table 5.9. The geo accumulation index varies from 0.161 to 0.541, -0.697 to 1.325, 1.309 to 1.896, 0.015 to 1.49, 1.341 to 1.647, 2.222 to 4.737 and -0.078 to 2.037 for Fe, Mn, Zn, Cu, Pb, Cd and Cr at depth (0-20cm) and similarly geo accumulation index varies from -0.164 to 0.247, -0.441 to -1.1700, 0.653 to 1.653, -0.254 to 1.418, 0.678 to 1.56, 1.415 to 3.807 and -0.2937 to 2.681 for Fe, Mn, Zn, Cu, Pb, Cd and Cr at depth (20-40 cm) respectively.

The geo accumulation index for Fe, Mn and Cr was found to be 0< Igeo <=1 belongs class 1 that is from unpolluted to moderately polluted at depth (0-20cm) and (20-40cm) respectively. The geo accumulation index for Zn, Cu and Pb was found to be 1< Igeo <=2 belongs to class 2 that is moderately polluted. The geo accumulation index for Cd was found to be 3< Igeo <=4 belongs to class 4 that is strongly polluted.
5.13 CONTAMINATION FACTOR

The contamination factor of environmental concern range as Fe : (1.187 – 1.686), Mn : (1.103 – 2.275), Zn : (1.206 – 3.830), Cu : (1.021 – 1.543), Pb : (0.993 – 4), Cd : (0.444 – 9.5), and Cr : (1.157 – 13.543). The heavy metals such as Fe, Mn, Zn, Cu and Pb have average contamination factor $1 \leq C_f < 3$ which shows these metals are moderately contaminated in the soil. The metals such as Cd and Cr have the contamination factor greater than 3 that is $3 \leq C_f \leq 6$, which indicate considerable contamination factor. From contamination factor, it has been found out Fe, Mn, Zn, Cu and Pb are moderately contaminated and Cd and Cr are considerably contaminated in the soil. It is given in table 5.10.

Table 5.10

Descriptive statistics of the Contamination factor of heavy metals in analyzed soils

<table>
<thead>
<tr>
<th>Metals</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Std. deviation</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.187</td>
<td>1.686</td>
<td>1.411</td>
<td>0.173</td>
<td>1.363</td>
</tr>
<tr>
<td>Mn</td>
<td>1.103</td>
<td>2.275</td>
<td>1.490</td>
<td>0.399</td>
<td>1.362</td>
</tr>
<tr>
<td>Zn</td>
<td>1.205</td>
<td>3.830</td>
<td>1.949</td>
<td>0.906</td>
<td>1.530</td>
</tr>
<tr>
<td>Cu</td>
<td>1.021</td>
<td>1.543</td>
<td>1.171</td>
<td>0.177</td>
<td>1.083</td>
</tr>
<tr>
<td>Pb</td>
<td>0.993</td>
<td>4</td>
<td>1.782</td>
<td>1.028</td>
<td>1.189</td>
</tr>
<tr>
<td>Cd</td>
<td>0.444</td>
<td>9.5</td>
<td>3.607</td>
<td>2.355</td>
<td>3.389</td>
</tr>
<tr>
<td>Cr</td>
<td>1.157</td>
<td>13.542</td>
<td>4.583</td>
<td>4.585</td>
<td>2.083</td>
</tr>
</tbody>
</table>
5.14 POLLUTION LOAD INDEX AND INTEGRATED POLLUTION INDEX

To effectively compare whether the 18 sampling sites suffer contamination or not, the pollution load Index (PL1) was applied. The PL1 is aimed at providing a measure of the degree of the overall contamination at the sampling sites. The PL1 is calculated from CF values and showed that the soil is deteriorated soil. Sampling sites $S_1$ to $S_{18}$ shows the more pollution load Index values. From PL1, it is inferred that Dindigul soil is more polluted. Table 5.11 and fig 5.12 show the distribution of the Pollution Load Index in urban soil in Dindigul Town. The result show that Dindigul Town not only rapidly developing Town but vehicle population and number of industries are increasing to a larger extent.

![Fig 5.12 Pollution load index for heavy metals at different sampling sites](image)

Fig 5.12 Pollution load index for heavy metals at different sampling sites

Fig 5.13 shows integrated pollution Index for all the eighteen sampling sites are found nearly equal to two and more than two. It is significant that Dindigul town is in the high level of pollution. This indicates that urban soil in the Dindigul town has been significantly influenced by heavy metals.
Fig 5.13 Integrated pollution Index for heavy metals at different sampling sites

5.15 POTENTIAL ECOLOGICAL RISK

Potential ecological risk for multiple metals (RI) is found to be more than 110 to 220 which shows moderate ecological risk grade. It is given in table 5.12.