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ASSESSMENT OF METAL CONTAMINATION USING SINGLE AND INTEGRATED POLLUTION INDICES IN SOIL SAMPLES OF NASHIK DISTRICT, INDIA

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ABSTRACT

Like water and air, soil is essential for growing vegetation and afforestation. Pollution of soil leads to contamination of vegetation and also of the nearby water reservoirs making it unhealthy for the human consumption. Heavy metal contamination of soil has been observed since years due to rapid industrialization, transportation and dumping of garbage at dumping sites. Pollution indices act as a powerful tool for assessing the extent of soil pollution. In this study, soil samples were collected from five different locations of Nashik district. These soil samples were then analyzed for 8 different elements such as Cu, Zn, Cd, Cr, Ni, As, Hg and Pb. To assess the soil quality, 9 pollution indices were evaluated in which 5 were single pollution and 4 were integrated pollution indices.

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INTRODUCTION

Soil is the dynamic body of natures and complex system in which all the times: chemical, biological, physical, geological, bio-geo-physicochemical reactions are taking place with characteristics that vary over time and space (Tamene, Seyoum 2015). Environmental pollution by heavy metals is due to many activities whereas in the soil system, pollution by heavy metals is mainly due to both natural processes such as weathering of minerals and anthropogenic activities related to industry, agriculture, burning of fossil fuels, vehicular emission, mining and metallurgical processes and their waste disposal (Alfred et al. 2013; Sapana et al. 2014). The biggest problem with heavy metals is the fact that they are persistent, and it is very difficult to eliminate them from the environment. Heavy metals can exert their toxicity via dermal, inhalation, and ingestion pathways, from urban soils, and influence human health with severe consequences (Boban et al. 2016).
Road dust originates from the interaction of solid, liquid and gaseous materials which are produced from different sources and deposited on a road. The composition and quantity of chemical matrix of road dust are indicators of environmental pollution. Road dust receives varying inputs of heavy metals from diversity of mobile or stationary sources such as vehicular emission, industrial plants, power generation plants, oil burning, waste incineration, construction and demolition activities as well as resuspension of surrounding contaminated soils. Lead (Pb), for example is known to come from the use of leaded gasoline whereas Cu, Zn and Cd from tyre abrasion, lubricants, industrial and incinerator emissions. The source of Ni and Cr in street dust is believed to be due to corrosion of vehicular parts and chrome plating of some motor vehicle parts

(Sana'a 2013).[1] Agriculture, which is the backbone of most economy, has also been adversely affected by upsurge in the indiscriminate dumping and disposal of wastes into land and water courses. The continuous pollution of both surface and underground water sources has reduced the quality and quantity of water needed for general agricultural requirements such as meeting crop water requirement during insufficient rainfall (Mohammed et al. 2015). Vegetables cultivated in soils polluted with toxic and heavy metals take up such metals and accumulate them in their edible and non-edible parts in quantities high enough to cause clinical problems both to animals and human beings consuming these metal-rich plants as there is no good mechanism for their elimination from the human body (Syed et al. 2012). With the rapid industrialization and economic development, heavy metals are continuing to be introduced to soils and sediments via several pathways, including fertilization, irrigation, rivers, runoff, atmospheric deposition, and point sources, where metals are produced as a result of metal mining, refining, and refinishing by products. Soils are usually regarded as the ultimate sink for heavy metals discharged into the environment, and sediments can be sensitive indicators for monitoring contaminants in aquatic environments. Therefore the environmental problem of soil and sediment pollution by heavy metals has received increasing attention in the last few decades in both developing and developed countries throughout the world.

Pollution index is a powerful tool for processing, analyzing, and conveying raw environmental information to decision makers, managers, technicians, and the public (Gong et al. 2008). In this study soil samples from five different locations of Nashik District were collected and analyzed for metal and heavy metal concentration. The data was then further analyzed using single and integrated pollution indices.The information derived from pollution indices help to assess the extent and degree of metals and also the intensity of anthropogenic contaminant deposition on surface soil.

STUDY AREA

Nashik district is one part of Deccan Plateau. It is glorified by numerous biodiversity and forest. The prominent soils occurring in the district are black soil 65%, red soil 13%, lomy soil 18%, varkers soil 4%. Black soil is dominant in the area occurring particularly in Godavari river valley. Almost all soils are alkaline in nature (Collector 2007). The areas from where the soil samples were collected and analyzed further are called as stations. Soil samples were collected from five different stations as shown in the below figure 1. The climate of Nashik compares well with that of Pune and Bangalore. The climate is pleasant almost throughout the year. In winter, temperature as low as 2°C has been recorded in the city. The hottest month is May with temperature touching 43°C.

Figure 1. Four figures are included in this paper

Table 1. The coordinates and soil type of the soil samples collected from five different locations of Nashik district

Sr. no.	Areas from where the soil samples were collected	Coordinates	Soil type
1	Station 1	20°1'33.1644"N, 73°44'32.0928"E	Black soil and alkaline in nature
2	Station 2	20°1'30.6768"N, 73°44'31.542"E	
3	Station 3	20°1'29.3772"N, 73°44'32.3304"E	
4	Station 4	20°1'30.1764"N, 73°44'34.4436"E	
5	Station 5	20°1'32.7252"N, 73°44'34.7496"E	

Average rainfall is approx. 650 mm most of which is during the periods June-September. Evenings are cool even during summer as it is surrounded by hilly areas (Board 2005). The soil samples were collected in the month of February when the climate is cool and dry.

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SAMPLING OF SOIL SAMPLES

The sampling was conducted in the mid of the month of February, 2017. Soil samples were collected from five different stations. Sub-samples of approximately 100g from the depth of 0-20 cm at each station within 20cm x 20cm area were sampled for five times. These five sub-samples were further mixed thoroughly to form a homogenous bulk composite sample of approximately 500g. This bulk composite sample was sieved using 20 mesh size sieve to remove big stones and then grinded. For each sub-sample there were three replicates. Representative samples were dried and homogenized. These samples were then analyzed for 8 metals such as Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Mercury (Hg), Nickel (Ni) and Zinc (Zn).

Background samples from uncontaminated similar sediment layer

A crucial first step in evaluating the impact of sediment pollution and the level of contamination affecting a given area is to establish a reference background or baseline sample of known metal composition. Two methods are considered, firstly the use of average crustal values as reference concentrations, while the second method seeks to establish a local baseline by analyzing comparable local sediment unaffected by anthropogenic activity.

The main disadvantage of using average earth or crustal levels is that it ignores natural geochemical variability, and this may lead to false anomalies being recognized or anomalous concentrations above the pristine local background may not be recognized at all.

Another disadvantage is that the crustal values are bulk concentrations, and this undermines comparison with "fine fraction" sediment concentrations. The more recent approach to establishing reference values is to compare concentrations of the target metals in contaminated and uncontaminated sediments that are mineralogically and texturally similar or identical. This can best be done in cores by comparing the pollutant concentrations in the upper sediments layers with their preindustrial concentration in the deeper layers of the same core. Using this approach for a practical assessment of contamination, it is possible to establish a local "baseline" concentration for each core by taking the mean of several low concentration samples selected from the deep, least impacted levels of sediment cores. Since pollution effects may extend to a considerable variation in depth, the selection of the low concentration samples for baseline averaging is best done by inspection of the metal trends in the lower core (G.M.S 2008).

Background values: Natural contents of substance in the soil completely dependent on the compositional and mineralogical characteristic of the parent/source geological material (Maurizio 2016). The samples for estimation of background values were collected from the respective stations but from the deep cores so that the samples are identical with respect to mineralogy and texture.

The samples were collected from 500 - 600 cm deep from the surface. All the samples were sampled using stainless steel hand auger and hand spade and were placed in polyethylene bags so as to avoid contamination.

MATERIALS AND METHODS

All the reagents used were of analytical grade. Double distilled water was used for dilutions of all the standards and samples solutions.

A 0.25g soil sample from bulk composite sample was placed in the clean Teflon digestion vessel with concentrate acid mixture of 5ml HNO_3, 1ml HCl and 2ml H_2O_2. The vessels were tightly closed, placed into the microwave digestor and then digestion was carried out for 30 mins. After digestion was completed, the vessels were allowed to cool at room temperature and each digest was transferred quantitatively with distilled water to 50ml volumetric flask. These solutions were analyzed by Thermo Electron corporation make ICP-MS. Optimization of instrumental conditions was done after the completion of mass and detector cross calibration. This was done by following the manual tuning procedure using manufacturer's Thermo tuning solution A which contained Li, Be, Co, Ni, In, Ba, Ce, Pb, Bi, and U at 10 μg/L. For data acquisition, the ICP-MS was operated in peak jump mode, with dwell time 20 ms, 100 sweeps and a forward RF power of 1400W. Five point calibration curve was plotted prior the sample analysis and the calibration standards used were CertiPUR ICP multi-element standard solution XXI for MS (Merck) in 2% HNO3 with National Institute of Standards and Technology (NIST) Tracebility.

Pollution indices used for assessment of metal contamination

Pollution indices help in assessing the metal contamination. Pollution indices are mainly classified as simple pollution indices and integrated pollution indices. Single indices are indicators used to calculate only one metal contamination, which include contamination factor, ecological risk factor, enrichment factor, and index of geo-accumulation etc. 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 (Gong et al. 2008). In this study, to assess the metal contamination in the soil samples four single indices and five integrated indices were estimated. Hence a total of nine pollution indices were estimated to understand the pollution level of the soil.

Single Indices

Contamination factor (Cf):- The level of contamination of soil by metal is expressed in terms of contamination factor as follows:-

Contamination factor (Cf) = Concentration of soil sample (Ci)/ Concentration of background sample (Cb)

The different contamination factor level is shown in table 2.

Table 2 terminologies used to describe the different contamination factor level in soil [7, 8, 13]

Sr. no.	Contamination factor (Cf)	Contamination level
1	Cf < 1	Low contamination
2	1 < Cf < 3	Moderate contamination factor
3	3 < Cf < 6	Considerable contamination
4	Cf > 6	Very high contamination

Ecological risk index (Er):- According to Hankanson, the Ecological risk index (Er) can be quantified using following equation 1:

Er = Tf x Cf (equation 1)

Where, Er = ecological risk index
Tf = toxic-response factor of the element
Cf = contamination factor of element

The Hankanson terminologies used to describe the Ecological risk index and Potential ecological risk index (RI) are stated in table 3.

Table 3 different grades of ecological risk index and potential ecological risk index [8, 14]

Sr. no.	Ecological risk index (Er)	Grades of ecological risk of metal
1	Er < 40	Low
2	40 < Er > 80	Moderate
3	80 < Er > 160	Considerable
4	160 < Er > 320	High
5	320 < Er	Very high

According to Hankanson and Xu et al, the toxic-response factor for the metals As, Cd, Cr, Cu, Pb, Hg, Ni and Zn are as per table 4.

Table 4. Toxic-response factor by Hankanson and Xu et al [15]

Parameter	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
Toxic-response factor	10	30	2	5	5	40	5	1

Enrichment factor (EF):- The Enrichment factor is an indicator used to assess the presence and intensity of anthropogenic contaminant deposition on surface soil. These indexes of potential contamination are calculated by the normalization of one metal concentration in the topsoil respect to the concentration of a reference element. A reference element is an element particularly stable in the soil, which is characterized by absence of vertical mobility and/or degradation phenomena. Aluminium is a conservative element and a major constituent of clay minerals, and it has been used successfully by several scientists (Maurizio 2016). Hence in this study also Al was used as a reference element.

The Enrichment factor can be calculated by using the below equation:-

EF = (Metal/RE) soil/ (Metal/RE) background (equation 2)

Where, EF = Enrichment factor

RE = reference element

According to Sutherland, five enrichment factor categories are recognized on the basis enrichment factor values and these different categories are tabulated as per table 5.

Table 5 different categories of EF values which describes the enrichment of the element in soil [8, 12, 13]

Sr. no.	EF values	EF categories
1	EF < 2	Deficiency to minimal enrichment
2	2 < EF > 5	Moderate enrichment
3	5 < EF > 20	Significant enrichment
4	20 < EF > 40	Very high enrichment
5	EF < 40	Extremely high enrichment

Index of Geo-accumulation (Igeo):- Geo-accumulation index was originally stated by Muller in 1969 in order to determine and define metal contamination in sediments by comparing current concentrations with pre-industrial levels (Mohsen and Alireza 2014). It can be calculated by following equation (Mohsen and Alireza 2014; Adel 2011):-

Igeo = $\log_2$ Cn/1.5xBn (equation 3)

Where, Cn = concentration of metal in soil

Bn = background concentration of metal

1.5 = is a factor used to minimize the effect of possible variations in the background values which may be due to lithologic variations in the sediments or lithogenic effect

According to Muller, seven different classes of Index of geo-accumulation values are classified as following table 6.

Table 6 different classes of index of geo-accumulation values [8, 16, 17, 18]

Sr. no.	Class	Igeo values	Sediment quality
1	0	Igeo ≤ 0	Uncontaminated
2	1	0 < Igeo < 1	Uncontaminated to moderately contaminated
3	2	1 < Igeo < 2	Moderately contaminated
4	3	2 < Igeo < 3	Moderately to heavily contaminated
5	4	3 < Igeo < 4	Heavily contaminated
6	5	4 < Igeo < 5	Heavily to extremely contaminated
7	6	Igeo ≥ 5	Extremely contaminated

Integrated indices

Contamination degree (Cdeg):- Hankanson proposed contamination degree as a measure of the degree of overall contamination in surface layers of soil at respective sites. Contamination degree is the sum of contamination factor of all the elements and is given by following equation:-

Cdeg = $\sum_{i=1}^{n} Cf$ (equation 4)

Modified contamination degree (mCd):- Abrahim presented a modified and generalized form of the Hankanson equation for the calculation of the overall degree of contamination at a given sampling or coring site as follows: (a) The modified formula is generalized by defining the degree of contamination (mCd) as the sum of all the contamination factors (Cf) for a given set of estuarine pollutants divided by the number of analyzed pollutants; (b) The mean concentration of a pollutant element is based on the analysis of at least three samples; and (c) The baseline concentrations are determined from standard earth materials (Syed et al. 2012). The modified equation for calculating the contamination factor is given as follows:-

mCd = Σ Cf / n (equation 5)

Where, mCd = contamination degree
Cf = contamination factor
n = number of elements analyzed

The description of modified contamination degree is given in table 7.

Table 7 terminologies used to describe modified contamination degree values [7, 8]

Sr. no.	Modified contamination degree mCd	Modified degree of contamination level
1	mCd < 1.5	Nil to very low degree of contamination
2	1.5 ≤ mCd < 2	Low degree of contamination
3	2 ≤ mCd < 4	Moderate degree of contamination
4	4 ≤ mCd < 8	High degree of contamination
5	8 ≤ mCd < 16	Very high degree of contamination
6	16 ≤ mCd < 32	Extremely high degree of contamination
7	mCd ≥ 32	Ultra high degree of contamination

Pollution load index (PLI):- Pollution load index is a potent tool in heavy metal evaluation (Andem 2015). It was developed by Tomlinson et al (1980) and is calculated as follows:-

$PLI = \sqrt[n]{Cf1 \times Cf2 \times Cf3 \times \ldots\ldots\ldots Cfn}$ (equation 6)

Where, PLI = Pollution load index

Cf = contamination factor

n = number of elements analyzed

The pollution index levels are categorized in three levels as per table 8.

Table 8. Terminologies used to describe different pollution load index levels [18, 19]

Sr. no.	Pollution load index category	Soil quality
1	PLI < 1	Perfect
2	PLI = 1	Only baseline levels of pollutants are present
3	PLI > 1	Deterioration of soil quality

Potential ecological risk index (PERI):- This method comprehensively considers the synergy, toxic level, concentration of the heavy metals and ecological sensitivity of heavy metals. PERI is formed by three basic modules: degree of contamination (Cd), toxic-response factor (Tr) and ecological risk factor (Er) (X. Jiang 2014). According to this method, the potential ecological risk index of a single element (Er) and comprehensive potential ecological risk index (RI) can be calculated by using following equation:-

$RI = \sum Er$ (equation 7)

Where, RI = Potential ecological risk index

Er = Ecological risk index

The 4 different grades of potential ecological risk index are as given in table 9.

Table 9 terminologies used to describe different grades of potential ecological risk levels [8, 14, 21, 22]

Sr. no.	Potential ecological risk index (RI)	Grades of overall risk of contamination
1	RI < 150	Low
2	150 < RI > 300	Moderate
3	300 < RI > 600	Considerable
4	600 < RI	Very High

Nemerow Pollution Index:- Cheng et al developed a comprehensive pollution index equation based on single pollution index. Nemerow composite index method not only takes account all the individual evaluation factor which also highlights the importance of the most contaminated elements (Jintao 2011). In this study the single pollution index used to calculate Nemerow pollution index is contamination factor.
It is calculated by the following equation:-

$P_{nemerow} = \sqrt{[(1/n\,\Sigma\,P)2 + (Pmax)\,2] / 2}$ (equation 8)

Where, $P_{nemerow}$ = Nemerow pollution index
P = single pollution index, in this study contamination factor was used as single pollution index
n = number of elements analyzed

The Nemerow pollution index is categorized into 5 different classes as mentioned in table 10.

Table 10. Terminologies used to understand different grades of Nemerow pollution index [8, 20, 24]

Sr. no.	Grades of Nemerow pollution index	Terminology for pollution grade
1	$P_{nemerow} \leq 0.7$	Clean
2	$0.7 < P_{nemerow} \leq 1$	Warning limit
3	$1 < P_{nemerow} \leq 2$	Slight pollution
4	$2 < P_{nemerow} \leq 3$	Moderate pollution
5	$P_{nemerow} > 3$	High pollution

RESULTS AND DISCUSSIONS

Concentration of soil samples under study: - Soil sample solutions prepared for five different stations were run on ICP in triplicates for all the elements under study as shown in Table 11. The mean values were calculated and used to evaluate the pollution indices further.

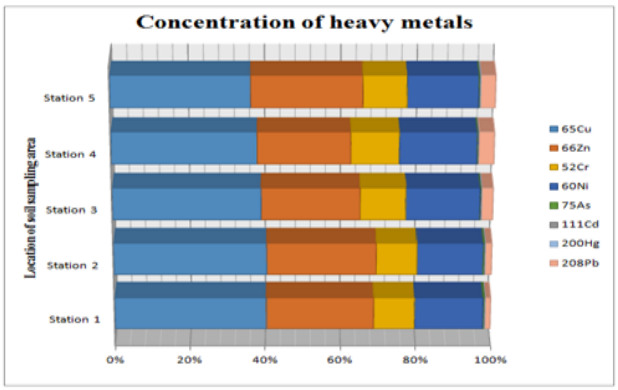

Figure 2. Represents the concentration of heavy metal at respective sampling stations

The Figure 2 and table 11 depicts that the stations 4 and 5 have higher concentrations of heavy metals such as Pb, Hg. While the other stations 1, 2 and 3 were found to be rich in elements like Cu, Zn, Cr and Ni. Cd was found in more or less same concentration at all the stations. Al contributed as a major element at station 1. For station 1 and 2, As concentration was found on higher side as compared to other three stations. The concentrations of Cr and Ni were found to be stable for all five stations. Stations 1 and 2 were found to be rich in Cu as compared to stations 3, 4 and 5.

Table 11. The result data of soil samples collected from Nashik district

SAMPLES UNDER STUDY									
STATION 1									
Elements	65Cu	66Zn	27Al	52Cr	60Ni	75As	111Cd	200Hg	208Pb
Unit	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
R1	781.7	496.7	105200	215.1	355.7	7.9	0.7	0.8	26.5
R2	772.8	496.6	103800	210.8	353.9	8.0	0.7	0.7	26.9
R3	801.7	676.5	101900	212.2	353.5	11.4	0.9	0.9	30.8
Mean	785.4	556.6	103633.3	212.7	354.4	9.1	0.8	0.8	28.1
STATION 2									
Elements	65Cu	66Zn	27Al	52Cr	60Ni	75As	111Cd	200Hg	208Pb
Unit	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
R1	795.6	672.1	99310	206.6	344.5	10.8	1.0	0.8	32.2
R2	790.9	522.2	98970	210.9	343.2	6.6	0.5	0.8	33.0
R3	756.9	485.1	95730	204.2	328.7	5.9	0.5	0.9	36.0
Mean	781.1	559.8	98003.3	207.2	338.8	7.8	0.7	0.8	33.7
STATION 3									
Elements	65Cu	66Zn	27Al	52Cr	60Ni	75As	111Cd	200Hg	208Pb
Unit	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
R1	698.8	496.3	92730	199.0	337.2	5.6	0.5	0.8	45.8
R2	691.8	446.4	92490	196.7	325.2	5.1	0.5	0.8	40.5
R3	663.7	426.4	102600	232.2	362.4	5.2	1.0	2.1	71.7
Mean	684.8	456.4	95940.0	209.3	341.6	5.3	0.7	1.2	52.7
STATION 4									
Elements	65Cu	66Zn	27Al	52Cr	60Ni	75As	111Cd	200Hg	208Pb
Unit	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
R1	659.9	436.1	99990	223.6	358.6	5.0	0.9	1.8	72.5
R2	657.3	408.7	91890	218.4	345.0	6.5	1.0	1.6	65.3
R3	654.2	416.8	92270	216.0	342.7	6.3	1.0	1.4	67.3
Mean	657.1	420.5	94716.7	219.3	348.8	5.9	1.0	1.6	68.4
STATION 5									
Elements	65Cu	66Zn	27Al	52Cr	60Ni	75As	111Cd	200Hg	208Pb
Unit	Ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
R1	682.9	545.4	92960	215.1	347.1	5.8	1.2	1.8	71.2
R2	678.0	549.1	93090	210.9	344.6	5.5	1.1	1.8	72.3
R3	634.4	499.5	88920	200.9	322.2	4.4	1.0	1.4	69.7
Mean	665.1	531.3	91656.7	209.0	338.0	5.2	1.1	1.7	71.1

R1, R2 and R3 represent the triplicates 1, 2 and 3 for that particular station.

Table 12 provides the result data for background samples from respective stations.

BACKGROUND VALUES									
STATION 1									
Elements	65Cu	66Zn	27Al	52Cr	60Ni	75As	111Cd	200Hg	208Pb
Units	Ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
R1	678.4	546.1	97456.1	181.4	247.9	4.2	0.7	0.5	10.1
R2	715.6	499.2	96854.7	152.4	238.7	6.9	0.6	0.5	14.2
R3	703.9	485	95315.5	161.8	252.9	5.1	0.3	0.4	12.9
Mean	699.3	510.1	96542.1	165.2	246.5	5.4	0.5	0.5	12.4
STATION 2									
Elements	65Cu	66Zn	27Al	52Cr	60Ni	75As	111Cd	200Hg	208Pb
Units	Ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
R1	725.4	500.6	89452.3	131.6	222.4	3.1	0.5	0.6	9.9
R2	689.4	487.2	88514.2	119.4	208.7	5.7	0.2	0.4	12.9
R3	700.5	481.3	88287.4	111.1	206.1	5.0	0.3	0.5	10.8
Mean	705.1	489.7	88751.3	120.7	212.4	4.6	0.3	0.5	11.2
STATION 3									
Elements	65Cu	66Zn	27Al	52Cr	60Ni	75As	111Cd	200Hg	208Pb
Units	Ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
R1	565.3	339.1	80987.5	104.3	246.8	3.9	0.5	0.9	22.3
R2	582.6	314.8	81004.3	116.7	260.1	5.6	0.5	1.1	18.4
R3	586.4	322.9	78652.0	101.2	252.1	2.5	0.5	0.5	18.7
Mean	578.1	325.6	80214.6	107.4	253.0	4.0	0.5	0.8	19.8
STATION 4									
Elements	65Cu	66Zn	27Al	52Cr	60Ni	75As	111Cd	200Hg	208Pb
Units	Ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
R1	567.4	366.8	89741.1	194.1	197.5	4.7	0.2	0.5	16.3
R2	548.2	356.9	90481.3	180.4	214.8	5.5	0.3	0.6	18.4
R3	539.2	406.6	90515.0	182.3	197.9	5.4	0.2	0.7	16.7
Mean	551.6	376.8	90245.8	185.6	203.4	5.2	0.2	0.6	17.1
STATION 5									
Elements	65Cu	66Zn	27Al	52Cr	60Ni	75As	111Cd	200Hg	208Pb
Units	Ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
R1	600.4	501.4	90485.6	128.9	209.8	4.2	1.0	1.1	21.5
R2	587.2	500.7	89745.1	137.8	221.3	3.5	0.9	0.9	25.6
R3	559.3	497.0	90195.6	130.5	226.8	4.0	0.6	0.9	25.8
Mean	582.3	499.7	90142.1	132.4	219.3	3.9	0.8	1.0	24.3

R1, R2 and R3 represent the triplicates 1, 2 and 3 for that particular station.

The Zn concentration for stations 3 and 4 were comparatively lesser than that of stations 1, 2 and 5 with almost 100 ppb lower in concentration. For assessment of the pollution indices, the background samples were also analyzed in the fashion similar to the unknown soil samples.

The results of the pollution indices for five stations are tabulated from table 13 to 17. The contamination factor for Pb at station 5 was found at the level of very high contamination according to Hankanson terminology. This projects that the station 5 soil samples is very highly contaminated with Pb metal.

Table 13 contamination factor (Cf), degree of contamination (Cdeg), modified contamination degree (mCd) and pollution load index (PLI) of soil samples from Nashik district

	Contamination factor (Cf)								Degree of contamination (Cdeg)	Pollution load index (PLI)
Elements	Cu	Zn	Cr	Ni	As	Cd	Hg	Pb		
Station 1	1.1	1.1	1.3	1.4	1.7	1.6	1.6	2.3	12.1	1.47
Station 2	1.1	1.1	1.7	1.6	1.7	2.3	1.6	3.0	14.1	1.67
Station 3	1.2	1.4	1.8	1.4	1.3	1.4	1.5	2.7	12.7	1.54
Station 4	1.2	1.1	1.2	1.7	1.1	5.0	2.7	4.0	18.0	1.89
Station 5	1.1	1.2	1.6	1.6	1.3	1.4	2.8	6.8	17.8	1.81
								Mean	74.7	NA
								mCd	9.3	NA

Table 14. Ecological risk index and potential ecological risk index of soil samples from Nashik district

	Ecological risk index (Er)								
Elements	Cu	Zn	Cr	Ni	As	Cd	Hg	Pb	Potential ecological risk index (PERI)
Station 1	5.5	1.1	2.6	7.0	17.0	48.0	64.0	11.5	156.7
Station 2	5.5	1.1	3.4	8.0	17.0	69.0	64.0	15.0	183.0
Station 3	6.0	1.4	3.6	7.0	13.0	42.0	60.0	13.5	146.5
Station 4	6.0	1.1	2.4	8.5	11.0	150.0	108.0	20.0	307.0
Station 5	5.5	1.2	3.2	8.0	13.0	42.0	112.0	34.0	218.9

Table 15 enrichment factor of soil samples from Nashik district

Enrichment factor (EF)								
Elements	Cu	Zn	Cr	Ni	As	Cd	Hg	Pb
Station 1	1.05	1.02	1.20	1.34	1.57	1.49	1.49	2.11
Station 2	1.00	1.04	1.55	1.44	1.53	2.11	1.45	2.72
Station 3	0.99	1.17	1.49	1.13	1.11	1.17	1.25	2.23
Station 4	1.14	1.06	1.13	1.63	1.08	4.76	2.54	3.81
Station 5	1.10	1.18	1.55	1.60	1.31	1.35	2.79	6.72

Table 16. Index of geoaccumulation of soil samples collected from five different locations of Nashik district

Geoaccumulation index								
Elements	Cu	Cd	As	Pb	Hg	Zn	Ni	Cr
Station 1	-0.42	0.09	0.17	0.60	0.09	-0.46	-0.06	-0.22
Station 2	-0.44	0.64	0.18	1.00	0.09	-0.39	0.09	0.19
Station 3	-0.34	-0.10	-0.18	0.83	0.00	-0.10	-0.15	0.25
Station 4	-0.33	1.74	-0.40	1.42	0.83	-0.43	0.19	-0.34
Station 5	-0.39	-0.13	-0.17	2.19	0.92	-0.32	0.12	0.07

Table 17. Nemerow pollution index data for soil samples collected from Nashik district

Nemerow Pollution indices											
Elements	Cu	Cd	As	Pb	Hg	Zn	Ni	Cr	PI	mean	PI nemerow
Station 1	1.1	1.6	1.7	2.3	1.6	1.1	1.4	1.3	12.1	1.51	1.95
Station 2	1.1	2.3	1.7	3.0	1.6	1.1	1.6	1.7	14.1	1.76	2.46
Station 3	1.2	1.4	1.3	2.7	1.5	1.4	1.4	1.8	12.7	1.59	2.22
Station 4	1.2	5.0	1.1	4.0	2.7	1.1	1.7	1.2	18.0	2.25	3.88
Station 5	1.1	1.4	1.3	6.8	2.8	1.2	1.6	1.6	17.8	2.23	5.06

The background samples were also analyzed in triplicate and the mean value was considered for the calculation of that particular element. The results of the background samples for all the samples are tabulated in Table 12.

Assessment of soil quality using pollution indices:- To understand the quality of soil, nine pollution indices were evaluated including single and integrated.

Second heavy metal Cd was found in considerable contaminated level at station 4 soil samples. Rest all the elements fall under the moderate contamination level for all the stations. The stations 4 and 5 were found on the verge of considerable degree of contamination as per the Hankanson terminologies for contamination degree. As compared to the stations 4 and 5, other stations were moderately contaminated as per the values of contamination degree. The ecological risk index for Cd was found in the level for high potential

ecological risk for station 4 followed by 108 and 120 ecological risk index for Hg metal falling under the category of considerable potential ecological risk. The other metals such as Cu, Zn, Cr, Ni, As and Pb were present in low ecological risk. The values of PERI for stations 1, 2, 3 and 5 soil samples were found in the range of low ecological risk. For station 4, the PERI value on the verge of considerable ecological risk value. The enrichment factor values were found to be high for Pb for station 5 making it significantly enriched and for station 4 Cd was found to be moderately enriched. The elements Cu, Zn, Cr, Ni and As were found in the depleted level at all the stations according to Sutherland terminology for enrichment factor. The index of geoaccumulation value for Pb for station 5 soil sample fall under the class of moderately to strongly polluted as per Muller's classification. For station 4 the elements Cd and Pb fall under the class of moderately polluted. The other stations were found in the range from unpolluted to moderately pollute. As per the Cheng et al classification of Nemerow pollution index reference values described the station 5 soil sample as seriously polluted soil. The station 4 was on the verge of serious soil pollution. Station 2 and 3 fall under moderately polluted domain whereas station 1 soil sample fall on the border of slightly polluted to moderately polluted domain.

Conclusion

The comparative figures 2 and 3 were drawn which depicted that the overall pollution indices values are higher for stations 4 and 5. From the assessment of single and integrated pollution indices it is observed that the soil samples from stations 4 and 5 are polluted with heavy metals like Pb and Cd. These stations were found to be moderately contaminated with Hg metal. The soil samples from stations 1, 2 and 3 were slightly polluted with the heavy metals. Since the enrichment factor provides estimate of the anthropogenic impact on sediments by using normalization method, all the stations were found to be at depletion to mineral enrichment level for elements like Cu, Zn, Ni and Cr. The higher amount of heavy metals at stations 4 and 5 may be attributed to the vehicles passing on to the nearby road. The higher values of pollution indices may be due to the presence of small scale industries nearby the sampling sites. Since the climate was cool at the time of sampling, the pollutants may have settled down on the surface soil.

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