STUDY ON ENRICHMENT AND GEO-ACCUMULATION OF SOME TOXIC METALS IN SOILS OF INDUSTRIAL VICINITY, CHHATTISGARH, INDIA

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ABSTRACT

This study aimed to identify the potential risk of soil samples of those areas which are in the near vicinity of industrial activities. For this purpose, the Geo-accumulation index, enrichment factor, contamination factor and pollution load indexes were calculated to evaluate Pb, Cr, Co and Ni in soils of industrial areas near Raipur district, Chhattisgarh state. The obtained results were calculated for contamination evaluation by comparing the data with background metal concentration to assess the actual risk of assessment. The EF values for Pb and Ni were moderately contaminated ($EF > 4$) with moderate human intervention (> 1.5) rather than natural. These values were further supported by negative kurtosis and a significant positive correlation with other studied metals. A study of Igeo and PLI indicated that the soil is not highly contaminated ($I_{geo} \leq 0$). The results suggest that the area in the near vicinity of industrial activities area under threat of toxic metal enrichment, though the values are not seen as alarming but indicate the need for rapid precautionary actions to avoid any future threat. Hence the areas which are in the vicinity of industries should be taken care of properly even if the concentration values are under the threshold limit.

Keywords: Contamination Factor, Enrichment Factor, Correlation, Pollution Load Index, Geoaccumulation Index etc.

RASĀYAN J. Chem., Vol. 14, No.2, 2021

INTRODUCTION

Air water and soil are vital parts of the environment. Soil provides the substratum for the support and nutrients for plant growth. The Soil plays important role in the cycling of nutrients, water and gaseous components between the atmosphere and earth and act as a source and reservoir also. Soils not only supply the nutrients but also serve as dumping yards for many human activity wastes. The modification of soils for agriculture and the burial of archaeological remains are some examples of this. Soils are formed as a result of the disintegration process of rocks present in the earth bed. Hence soil contains many trace and toxic metals in different concentrations. Nevertheless, human activities add many pollutants to this soil and contaminate it. One of the universal problems is Soil pollution due to highly predisposed heavy metals by human-induced activities.¹⁻² Worldwide both developed and developing countries are dealing with the environmental issue of soil pollution by heavy metals.² An assessment study of soil nutrients and physicochemical parameters in the region of Hiwarkhed village of Amravati district (Maharashtra state), India suggests that there was a marked variation in physicochemical parameters of various soil samples in different farmer's field of the same area.³

The US Environment Protection Agency (EPA) has declared some metals as the most toxic elements in the environment such as nickel (Ni), chromium (Cr), copper (Cu), arsenic (As), cadmium (Cd), and lead (Pb).⁴⁻⁶ Most of the developing countries are facing the severe environmental issue of soil pollution by heavy metals due to increased industrialization and urbanization.^{2,7-9} Due to their toxicity, non-biodegradable properties and accumulative behavior, the heavy metals acquire great concern.^{2,8} Soil toxicity by heavy metals may have different origin like industrial activities, power generation, manufacturing, waste spills, or fossil fuel burning and waste disposal^{2,10-14} but the harmful effect of accumulated heavy metals in soil and their potential environmental risk on soil ecosystem is disquiet.^{2,14-16}

Enrichment factors (EF), Contamination factor (Cf) and geoaccumulation load index (Igeo) are widely used methods to assess the ecological risks of heavy metals in soil.^{2, 17}

The enrichment factor of an area indicates the relative enrichment of any pollutant as compared to pre-industrial soils from the same environment.^{2, 18-20} The environment is facing serious pollution threats originated from the rapid development, congestion and activities from industries, which has raised attention due to heavy metal contamination.^{2, 8}

Several studies reported the high concentration of heavy metals in the industrial area soils in Bangladesh.^{2, 21, 22} The present study focused on the variations of heavy metals in soils of the study area. The objective of this study was to assess the contamination evaluation of heavy metals in soil in the industrial vicinity of Raipur district and Bhatapara.

EXPERIMENTAL

Study Area

The Raipur city is the capital of Chhattisgarh state of India with fast-developing urbanization and industrialization purposes. The various industries like a power plant, steel, paint, chemical, wire and others are situated in this city. The industrial area situated on the agricultural surface of Raipur i.e., power plant, steel, paint, chemical, wire, agro-food and others are continuing in the region. The Siltara, Urla, Gogaon, Rawabhatha villages are the industrial area of the city.

General Procedure

A total 120 soil samples were collected in 2018- 2019 with proper guidelines of the sampling Procedure. After sampling the soil samples were kept for dry and grind well for apply to mesh filter. The prepared soil samples were applied for analysis in laboratory.^{23, 24} Before taking soil samples, the study area was divided into four zodiacs i.e., North, South, East and West industrial areas, after that five soil samples of soil were taken from each area in the year 2018- 2019. The proper guidelines of the sampling procedure were followed during sampling and analysis. All the soil samples were transported to the laboratory for physical and chemical analysis. All the samples in the laboratory were dried filtered with proper mesh size digested and analyzed following the standard process.^{25, 26}

Detection Method

The ultra-pure water and analytical grade fine chemicals were used for the preparation of samples and analysis of samples. The selective analytical method, chemicals and instruments were used for the soil analysis. The selective analytical methods i.e., UV-Visible spectrophotometer, pH meter, conductivity meter, atomic absorption spectrophotometer was used for the analysis of soil parameters of all the soil samples. Soils were air-dried, crushed and sieved for various physicochemical parameters through 2-mm stainless sieve to remove debris.²⁷

Analytical Discussion

For the assessment of contamination level in soils of the study area the data obtained were statistically analyzed first and then calculated for enrichment factor, Contamination factor, Pollution load Index and Geo-accumulation Index.

Enrichment Factor (EF)

Enrichment factor is assumed as an impressive tool and used for determining hazardous element magnitude of environment.²⁸ Enrichment factor (EF) can be used to differentiate between whether the contamination of metal is due to anthropogenic activities and or from natural sources. The enrichment factor of the metals was calculated as the ratio of elemental concentration of soil normalized to a reference Fe. The reference element is often the one characterized by low occurrence variabilities, such as the most commonly used elements; Aluminum (Al), Zirconium (Zr), Titanium (Ti), Iron (Fe) and Scandium (Sc).^{29, 30} The enrichment factor was calculated using the formula originally introduced by Buat-Menard.³¹

$$\text{Enrichment Factor} = (\text{Cx/Fe})_{\text{Sample}} / (\text{Cx/Fe})_{\text{World Soil}}$$

Where, Cx stands for concentration of metal 'x', (Cx/Fe) sample is the metal to Fe ratio in the sample of interest, (Cx/Fe) world soil is the natural background value of metal x to Fe ratio. Five contamination categories of EF were used in the study to evaluate the enrichment status of the soil. The higher EF value indicates the anthropogenic origin of contamination.³²

- EF < 2 is a deficiency to minimal enrichment
- EF 2-5 is moderate enrichment
- EF 5-20 is a significant enrichment
- EF 20-40 is very high enrichment
- EF > 40 is extremely high enrichment

EF was employed to assess the degree of contamination and to understand the distribution of the elements of anthropogenic factors. This is also an impressive tool used for determining the hazardous magnitude of elements on the environment.²⁸ If the calculated value of EF is higher than 1.5 from the lower value of the range it indicates enrichment is due to human interference. Enrichment factor effects of metals known as minor, moderate, severe, and very severe modification when enrichment factor values are 1.5–3, 3–5, 5–10 and >10 respectively.³³

Contamination Factor (C_{if})

The contamination factor can be calculated by dividing the heavy metal concentration in soil by the baseline or the background value of that metal in soil.

$$(C_{if}) = C_{\text{HeavyMetal}} / C_{\text{Background}}$$

The extent of contamination may be evaluated into four classes based on the CF value ranged from 1 to 6 which are: low degree (C_{if}<1), moderate degree (1 ≤ C_{if}< 3), considerable degree (3 ≤ C_{if}< 6) and very high degree (C_{if} ≥ 6).^{2,4}

Geo-accumulation Index (I_{geo})

To determine the contamination degree of soil from toxic metals the Geoaccumulation index (I_{geo}) is considered a remarkable tool. Worldwide geo accumulation index is used to assess the degree of soil pollution.³⁴ To categories, the soil based on its pollution level the most effective objective is a geo-accumulation index (I_{geo}). Geo-accumulation index (I_{geo}) may be assessed by applying the equation given hereby,

$$I_{\text{geo}} = \log_2 (C_n / 1.5B_n)$$

Where, C_n is the determining element (n) concentration assessed from the soil, B_n is the geochemical baseline value of element n in the background sample.¹⁵ For decreasing possible variation in background values of element n, factor 1.5 is used to ascribe lithogenic effects.

Müller 1969³⁵ has defined seven classes of Geoaccumulation Index ranging from Class 0 (I_{geo}=0, unpolluted) to Class 6 (I_{geo}>5, extremely polluted). The highest class (Class 6) reflects at least a 100-fold enrichment factor above background values.

The Pollution Load Index (PLI)

Pollution load index is a compound system for determining the quality of the soil. The pollution load index can be determined for six toxic metals like chromium, nickel, copper, arsenic, cadmium, and lead.³⁶ Pollution load index may be measured from a formula given hereby:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \quad (4)$$

The pollution load index is the result of the total toxicity level of hazardous metals in soil. Where n is the number of metals (n = 4 in this study). PLI<1 implies that the site is free from contamination whilst, PLI=1 implies baseline level of pollution and PLI> 1 = deterioration of site quality.

RESULTS AND DISCUSSION

Of all the samples collected from the industrial area of the region, the result obtained was compared with the values described for assessing the ecological risk. Moreover, the background values taken for calculating the contamination evaluation were the higher value of the guideline value range prescribed for the metals (Table-1). Hence the contamination evaluation results obtained from the study are of more significant importance as the background values are taken are higher than the normal soil background concentration of the metals. The purpose of this comparison was to assess the actual risk of contamination.

Table-1: Guideline Values of Metals

Metals	Concentration in mg/kg	Reference
Pb	250 - 500	Indian Standard 1983, Awashthi,2000
Cr	200 - 300	Finland, 2007
Co	100 - 250	Finland, 2007
Ni	75 - 150	Indian Standard 1983, Awashthi,2000

The guideline values for metals defined on ecological grounds are derived by adding the average natural concentration of the mineral soil to the calculatory concentration describing the acceptable ecological risk of the substance.

Heavy Metal Contamination in Soil

Descriptive statistics of the Raipur soil samples show that the concentration of Pb, Cr, Co and Ni found in the range 91.96-114.44 mg/kg, 6.93 – 46.69 mg/kg, 13.91-27.93 mg/kg, 20.22-43.4 mg/kg respectively. A negative value of Kurtosis supports that more numbers of sample values are closer to the mean value suggesting the less extreme tail values than the tails of normal distribution. The skewness values suggest that the Cr and Co values are moderately skewed while Pb, Ni and Fe values are less skewed or show more symmetrical distribution (Table-2). Table-3 shows the descriptive statistics of the Bhatapara soil samples, Where the concentration of Pb, Cr, Co and Ni in soil was found in the range 99.88- 120.79 mg/kg, 14.86-45.69 mg/kg, 11.89-25.73 mg/kg, and 19.55-39.38 mg/kg respectively. A negative kurtosis value was found for Cr and Ni while Pb and Co show a low positive value of kurtosis. Negative skewness values for Pb and Cr suggest that a large number of samples having concentration near to mean value while positive skewness for Co and Ni suggest the extreme tail distribution of concentration values from the mean value.

Table-2: Basic Statistical Parameters for the Distribution of Metals at Bhatapara(units are mg/kg)

Bhatapara	Pb	Cr	Co	Ni	Fe
Mean	103.20	26.81	20.92	31.81	16.17
Standard Error	2.51	4.45	1.57	2.59	1.79
Median	100.20	15.85	21.50	33.10	14.50
Standard Deviation	11.24	19.88	7.01	11.59	8.03
Sample Variance	126.42	395.37	49.13	134.41	64.41
Kurtosis	-0.60	-1.01	-0.01	-0.44	-1.20
Skewness	0.15	0.54	0.58	0.27	0.28
Range	40.00	65.50	26.30	41.40	24.50
Minimum	81.20	2.40	11.70	14.40	5.50
Maximum	121.20	67.90	38.00	55.80	30.00

Tables-4 and 5 presents the correlation matrix of the studied heavy metals and results reveal that in Raipur soil samples the Pb in the soil is significantly positively correlated with Cr and Ni concentration while in Bhatapara soil samples significant positive correlation is found between Ni and Co.

Contamination Evaluation

For evaluation of the contamination level of soil samples, the following factor was calculated. The Enrichment Factor (EF), Contamination Factor (CF), Pollution Load Index (PLI) and Geo- accumulation Index (Igeo) were calculated and results are shown in Figs.-1 to 4.

Table-3: Basic Statistical Parameters for the Distribution of Metals at Raipur (units are mg/kg).

Raipur	Pb	Cr	Co	Ni
Mean	110.335	30.28	18.805	29.465
Standard Error	2.337895	3.446841	1.547366	2.217114
Median	110.5	37.15	19.05	30.1
Standard Deviation	10.45538	15.41474	6.92003	9.915234
Sample Variance	109.315	237.6143	47.88682	98.31187
Kurtosis	0.176107	-1.38229	1.037028	-0.18091
Skewness	-0.49201	-0.27169	0.933771	0.393582
Range	42	49.4	26.5	37.3
Minimum	88.2	4.6	10.5	14.9
Maximum	130.2	54	37	52.2

Table-4 and 5: Correlation Matrix for the Distribution of Metals

Raipur	Pb	Cr	Co	Ni	Fe
Pb	1.00				
Cr	0.68	1.00			
Co	0.45	0.25	1.00		
Ni	0.56	0.12	0.42	1.00	
Fe	0.28	0.38	0.07	0.02	1.00

Bhatapara	Pb	Cr	Co	Ni
Pb	1.00			
Cr	0.36	1.00		
Co	0.37	0.19	1.00	
Ni	-0.005	0.003	0.56	1.00

Fig.-1: Enrichment Factor of Raipur and Bhatapara Soil Samples

Fig.-2: Contamination Factor of Raipur and Bhatapara Soil Samples

The study of the enrichment factor of soil samples in Raipur and Bhatapara reveals the moderate enrichment of soil with Pb and Ni which Cr and Co show minimal enrichment (Fig.-1). Enrichment values of Pb and Ni are closer to the upper end of the range with moderate enrichment i.e., moderate

enrichment with moderate modification, while Cr and Co show minimal enrichment with values closer to the upper end of the range i. e. minimal enrichment with moderate modification.³³ The EF study also reveals the presence of these metals in soil is anthropogenic rather than natural.³²

The study of the contamination factor of soil samples in Raipur and Bhatapara reveals the soil samples have a low degree of contamination with the studied parameters (Fig.-2). Figures-3 and 4 show the PLI and Igeo values of metals in Raipur and Bhatapara soil samples and $PLI < 1$ implies that the site is free from contamination in both the sites while negative values of Igeo of both sites suggest the uncontaminated status.

Fig.-3: PLI of Raipur and Bhatapara Soil.

Fig.-4: Igeo of Raipur and Bhatapara Soil

CONCLUSION

The analysis of heavy metals and statistical analysis of the data reveals that the negative value of kurtosis and skewness suggests the more even distribution of metals in soil and also confirms that their presence is not occasional but rather accumulation is gradual. The metal concentration values are not disquieting and show moderate to minimal enrichment with poor contamination factor value which was further supported by the low value of PLI and Igeo. Nevertheless, the study reveals the metal contamination in soil is anthropogenic rather than natural with minor to moderate human modification. The negative kurtosis with a significant positive correlation value of metals studied signifies the gradual and steady contamination and a future threat. Proper care and step should be taken by the authorities in this area to prevent any further deterioration of the soil quality. Comparing the results for Raipur and Bhatapara soils, both the sites are in the same condition concerning contamination evaluation. This study necessitates the future monitoring of the site for any further anthropogenic enrichment with toxic metals and necessitating the need of drawing attention by authorities

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[RJC-6266/2020]