

Analysis of Heavy Metal Pollution and Ecological Risk of Soils in Tirunelveli District, Tamil Nadu, India Using Energy Dispersive X-Ray Fluorescence (EDXRF) Technique

T. Krishnamoorthi¹, Satyanarayan Bramha², S. Sivakumar³, R. Ravichandran⁴, T. Kiruba¹ and R. Ravisankar^{1*}

¹Post Graduate and Research Department of Physics, Kalaingar Karunanidhi Government Arts College, Tiruvannamalai-606603, Tamil Nadu, India.

²HISD/SQRMG, Indira Gandhi Centre for Atomic Research, Kalpakkam-603102, Tamil Nadu, India.

³Department of Physics, Bharathidasan Government College for Women, Puducherry U.T- 605003, India.

⁴Department of Mechanical Engineering, Arunai Engineering College, Tiruvannamalai, 606603, Tamil Nadu, India.

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Abstract: Soil contamination with heavy metals led to a significant decline in quality of life and life expectancy. Polluted soil is now a prominent global concern due to rising industry, urbanization, and insufficient waste management practices. This study assessed heavy metal (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ba, As, Sr, and Cd) concentrations in soils of Tirunelveli District of Tamil Nadu using EDXRF technique. The mean concentrations of the eight metals are significantly elevated compared to the background values. The higher value of heavy metal concentration in this study may be ascribed to the influence of anthropogenic activities. The spatial map is drawn to better understand the distribution pattern of heavy metals in the study area. The ecological risk index (RI) for heavy metals is computed to assess the degree of soil contamination by different heavy metals. The Pollution Load Index (PLI) is utilized to assess the pollution degree in the research region. The distribution and correlation of heavy metals in soil along with possible remedial measures is discussed.

Keywords: Soil, Heavy Metals, Spatial Distribution, Ecological Risk Analysis.

1 Introduction

Soil is an essential element of an ecosystem. Soil has an ability to absorb and release substances, making it exposed to contamination from several sources. The continuous advancement of urbanization leads to development, agricultural practices, burial sites, and transportation emissions. The environment, which is our habitat and agricultural foundation, is contaminated by heavy metals. Heavy metals are found in soils originating from both source materials (lithosphere) and diverse anthropogenic activities. Multiple factors affect the distribution and segregation of these metals throughout the Earth, including the composition of source rocks, the extent of weathering, the chemical, physical, and biological properties of the soil, as well as climatic conditions. Human activities are the principal cause and are progressively intensifying, resulting in environmental degradation.

Heavy metals in soil originate from multiple sources, including atmospheric deposition, incorrect disposal of industrial solid and liquid waste, mining activities, sewage,

and the use of pesticides and fertilizers. These environmental metals are primarily released from gases, dirt, and dust produced by transportation, energy generation, metallurgy, and construction activities. Heavy metals predominantly enter the atmosphere as aerosols and later deposit into the soil through natural sedimentation and precipitation processes. Automobile mobility leads to considerable heavy metal poisoning. Heavy metals are introduced into the soil by irrigation sewage, sanitary sewage, chemical effluent, and industrial mining activities. Industries discharge several dangerous chemicals directly into rivers or open spaces. Moreover, human beings today routinely employ chemical pesticides and insecticides in agriculture. The continuous intensive usage has resulted in soil degradation.

The contamination of water and soil by heavy metals has become a significant global concern for both environmental integrity and public health [1]. The widespread presence of heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), and chromium (Cr) in the environment mostly results from anthropogenic

*Corresponding author e-mail: ravisankarphysics@gmail.com

activities, including industrial processes, agricultural practices, mining operations, and inadequate waste management. Research on soil heavy metal toxicity focuses on identifying areas with heightened pollution risk. The accurate conservation and restoration of ecosystems in soil contaminated by heavy metals require their characterization and remediation. A large number of studies on the degradation of urban soils due to heavy metals have been conducted in various cities during the past decade. Research indicates increased concentrations of heavy metal pollution in various places across India. Nonetheless, reliable data about heavy metal concentrations, pollution levels, and their specific impacts on human health have not been consistently obtained, accessed, or compared. An assessment of heavy metal exposure in urban areas of India is urgently needed. This research aimed to assess the pollution levels in the soils of Tirunelveli, Tamil Nadu.

The primary objectives of this research are to (1) assess the concentration of heavy metals in the study area; (2) examine the potential ecological concerns associated with heavy metal contamination in the soil; and (3) establish a database concerning the levels of heavy metal pollution for future reference.

2 Materials and Methods

2.1 Study Area

Tirunelveli district is located in the southern region of Tamil Nadu and covers an area of 6,823 km². The Tirunelveli district lies between 8°08' and 9°25' North latitude and 77°09' and 77°59' East longitude. This area is bounded by Virudhunagar district to the north, the Western Ghats to the west, Kanniyakumari district to the south, and Thoothukudi district to the east. Tirunelveli district consists of 11 taluks, 19 blocks, and 628 revenue villages, comprising an area of 681,065 hectares. A total area of 2509 km² has been allocated for irrigation purposes. The principal river water sources are the Thambarabarani, Nambiar, Chithar, and Karamaniyar rivers. The district's average rainfall is 880 mm, with the northeast monsoon producing greater rainfall than the southwest monsoon. The water requirements of this district's population are met by river water delivered by pipelines. In some parts of this district (northeast and southern regions), residents depend upon groundwater for potable use owing to insufficient river water in the summer months. This district utilizes dug wells, tube wells, tanks, and canals as sources of irrigation water. The principal geological formations in this district are fissible hornblende biotite gneiss and charnockite. The predominant soil types in this district include deep red soil (northwest region), black cotton soil (central part of the region), red sandy soil (central part of the region), saline coastal alluvium (southeast region), and river alluvium (river areas). A major portion of the district is characterised by plain topography. Red loam constitutes the

primary soil type in the district, at 48.21 percent, followed by black soil at 30.09 percent.

2.2 Sampling methodology

The soil samples collected at different locations of Tirunelveli district, Tamilnadu is shown in Fig 1. The grid methodology is used to collect the soil samples in the study area. The samples were collected from the grid node points of the square grid. Each grid had a location chosen based on the sample site's accessibility. Thirty-one soil samples were taken from an undisturbed, uncultivated grass-covered area, located distant from man-made structures such as roads and buildings, in order to reduce any external influence on the sample results [15-16]. The soil samples were obtained with the only constraint that no sampling location should be located near a field boundary, road, tree, or other obstacle to sampling. The Garmin Oregon 550 handheld GPS device was used to measure the sampling points coordinates. Table 1 indicates the sampling locations for soil samples in Tirunelveli District, Tamil Nadu, India. Approximately 2 kilogramme of samples were obtained from each site. The top layer of soil (up to 2-3 cm) has been removed for removing the debris. The soil samples were collected at a depth of 3 to 5 centimetres. The collected soil samples were stored in polythene bags in the field and brought to the laboratory for initial processing and later analysis [17].

2.3 Sample preparation for EDXRF Techniques

Extraneous materials (shells, roots, stones, debris, etc.) were manually removed, and the soil samples were initially air-dried at ambient temperature. After being air-dried, the samples were subjected to oven drying at 110°C until a consistent weight was achieved; plant residues and stones were discarded. [18]. And then the samples were ground into a fine powder using an agate mortar. All of the soil samples were preserved in desiccators before chemical analysis. The oven-dried samples were passed through a 63µm test sieve to ensure homogeneity (fine particles) for analysis [19]. The primary benefit of utilising particles of approximately 63 µm is that heavy metals are predominantly associated with silt and clay. The dried soil samples were pulverized into a fine powder use an agate mortar. One gramme of powdered material was combined with one gramme of cellulose powder. The mixture was thoroughly crushed and compressed into pellets with a diameter of 20 mm using a 20-ton hydraulic press. The pellets have been investigated using an EDXRF spectrometer (Model: EX-6600 AF, manufactured by Xenometrix, Israel). The technical features of the EDXRF apparatus are presented in Table 2. The quantitative analysis was performed using the integrated nEXT software. A standard sediment sample (IAEA-433) was used as the reference material for equipment calibration.

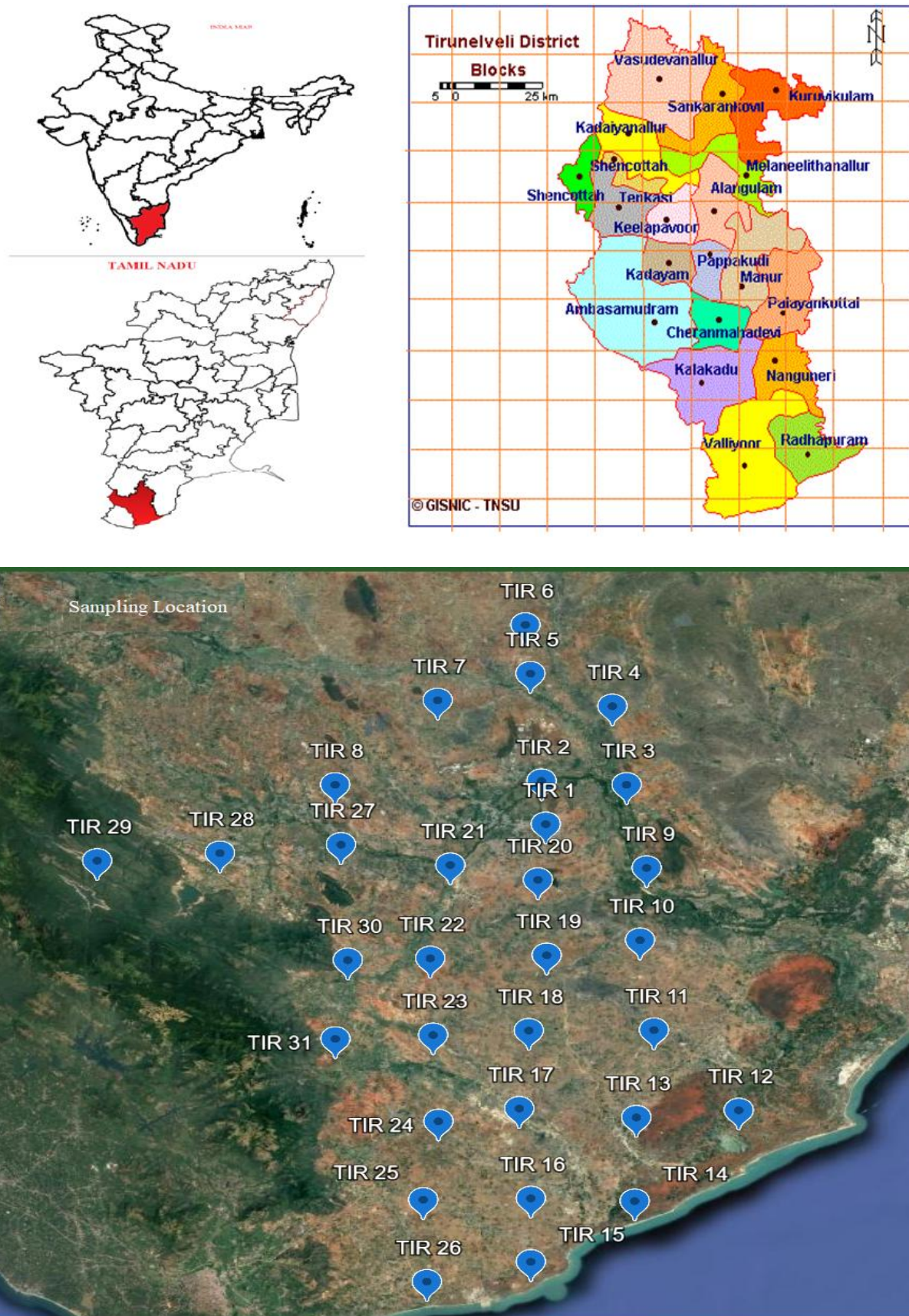


Fig. 1: Study Area of Interest and grids Map Sampling locations in Tirunelveli district.

Table1: Sampling location for soil samples of Tirunelveli District, Tamil Nadu, India.

Sample ID	Location Name	Latitude	Longitude
TIR-1	Tirunelveli	8°42'02"	77°45'43"
TIR-2	Melapattam	8°45'06"	77°45'28"
TIR-3	Vadavallanadu	8°44'50"	77°50'31"
TIR-4	Kodiankulam	8°50'25"	77°49'41"
TIR-5	Kannansannatti	8°52'44"	77°44'49"
TIR-6	Terkuilandaikulam	8°56'12"	77°44'31"
TIR-7	Manur	8°50'50"	77°39'18"
TIR-8	VadakkuAriyanayakipuram	8°44'50"	77°33'13"
TIR-9	Thiruchandur Patti	8°38'56"	77°51'42"
TIR-10	Mashinpalleri	8°33'49"	77°51'18"
TIR-11	Kulngvelli	8°27'27"	77°52'07"
TIR-12	Kommadikottai	8°21'46"	77°57'08"
TIR-13	Keeraikaranthattu	8°21'16"	77°51'04"
TIR-14	Kaalikumarapuram	8°15'21"	77°50'58"
TIR-15	Idinthakarai	8°11'04"	77°44'49"
TIR-16	Chidambarapuram	8°15'33"	77°44'49"
TIR-17	Kottaikarungulam	8°21'54"	77°44'08"
TIR-18	Kathanadappu	8°27'25"	77°44'42"
TIR-19	Moolakaraipatti	8°32'45"	77°45'46"
TIR-20	Itteri	8°38'05"	77°45'15"
TIR-21	Keelaomanallur	8°39'08"	77°40'03"
TIR-22	Srivaramangaipuram	8°32'32"	77°38'52"
TIR-23	Vaigaikulam	8°27'06"	77°39'02"
TIR-24	ThirumalaPuram	8°21'00"	77°39'21"
TIR-25	Dhanakkarkulam	8°15'27"	77°38'27"
TIR-26	Perumanal	8°09'40"	77°38'40"
TIR-27	Cheranmahadevi	8°40'35"	77°33'34"
TIR-28	Singampatti	8°39'59"	77°26'23"
TIR-29	Karaiyar	8°39'26"	77°19'07"
TIR-30	Kaisanri	8°32'24"	77°33'59"
TIR-31	Malayadipudur	8°26'50"	77°33'15"

Table 2: Technical specification of EDXRF.

X-ray Source	3-60 kV, 370W, 10-5833 μ A, Rh Target
Detector	Silicon drift detector (25mm ²)
Resolution	136 eV $\pm$ 5eV @ 5.9 KeV (Mn X-ray)
Auto sampler	10 sample holder

2.5 Multivariate Statistical Analysis

The widely available SPSS (Statistical Package for Social Sciences, version 16.0) software was used to examine the correlation among the examined heavy metals in soil by Pearson correlation, factor analysis, and cluster analysis. This study aimed to find the natural and anthropogenic sources of heavy metals.[18].

3 Results and discussions

3.1 Heavy metal distribution in soil

The determined heavy metal concentration for 31 soil samples collected from Tirunelveli District of Tamil Nadu using Energy dispersive X-ray fluorescence (EDXRF) is given in Table 3 illustrates the mean concentrations of metals that exist in the following order of

Fe>Ba>Mn>V>Sr>Cr>Zn>Ni>Cu>Co>As>Cd. The heavy metal concentration varies from 48.2-1770.9 mg kg⁻¹ for V; from 59.2- 155.9 mg kg⁻¹ for Cr; from 114.4-2342.7 mg kg⁻¹ for Mn; from 7017-69546 mg kg⁻¹ for Fe; from 2.8-25.9mg kg⁻¹ for Co; from 2.0-61.8 mg kg⁻¹ for Ni; from 26.4-40.9mg kg⁻¹ for Cu; from 16.4-85.8 mg kg⁻¹ for Zn; from 73.0-1799.3 mg kg⁻¹ for Ba; from 4.1-13.7 mg kg⁻¹ for As; from 23.4 - 651.0 mg kg⁻¹ for Sr and from 0.3-0.4 mg kg⁻¹ for Cd. Fig. 3 shows the variation of locations and concentrations of the elements. The higher concentration of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ba, As, Sr & Cd noticed in TIR19, TIR20, TIR13, TIR11, TIR12, TIR13, TIR14, TIR17, TIR2, TIR27, TIR6 may be due to anthropogenic inputs. This is because to rapid global industrialization and inadequate urbanization, which have notably heightened the risk of environmental pollution by heavy metals [20]. A comparison of the observed elemental concentrations from this study with regional, national, and international levels is presented in Table 4.

Table 3: Heavy Metal Concentration (ppm) in soil samples From Tirunelveli District.

SAMPLE ID	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ba	As	Sr	Cd	PLI
TIR-1	107.1	102.3	527.9	40182.0	15.6	31.7	33.2	69.9	875.2	9.9	174.8	0.3	0.8
TIR-2	513.5	59.2	155.8	19135.0	7.5	24.0	31.5	47.1	902.4	13.7	141.7	0.3	0.7
TIR-3	136.1	88.1	414.5	29864.0	11.5	29.6	30.5	63.5	761.9	9.2	289.5	0.4	0.8
TIR-4	168.3	107.8	467.2	31829.0	12.2	33.5	30.3	54.0	981.6	9.0	283.8	0.4	0.8
TIR-5	120.3	95.6	348.0	25524.0	9.9	38.3	32.3	64.1	809.0	10.8	221.6	0.3	0.8
TIR-6	154.3	135.5	1481.6	65445.0	24.9	25.4	35.2	68.6	824.2	8.1	86.9	0.4	0.8
TIR-7	269.7	109.5	582.3	40191.0	15.5	37.9	34.2	73.8	1115.3	7.7	228.2	0.4	0.9
TIR-8	247.1	112.9	613.8	48295.0	18.5	31.6	34.5	83.7	1239.6	7.9	254.2	0.4	0.9
TIR-9	245.5	122.4	607.3	50480.0	19.1	31.4	35.4	73.8	845.5	8.9	198.0	0.4	0.9
TIR-10	146.7	139.2	722.8	35725.0	13.4	37.2	34.0	44.8	746.1	7.2	208.8	0.4	0.8
TIR-11	790.9	133.8	1091.4	69546.0	25.9	2.0	28.8	84.6	290.7	11.0	52.3	0.3	0.7
TIR-12	290.3	143.0	572.1	33509.0	12.7	61.8	32.8	48.5	939.6	7.3	247.0	0.3	0.9
TIR-13	237.1	126.3	2342.7	59746.0	22.4	36.9	40.9	59.3	1046.6	8.6	187.5	0.3	1.0
TIR-14	186.7	118.8	1037.3	50229.0	19.0	38.8	38.6	85.8	818.3	8.5	224.9	0.3	0.9
TIR-15	184.2	137.4	589.6	31207.0	11.9	41.7	32.5	44.7	714.2	7.8	286.3	0.3	0.8
TIR-16	205.6	115.2	861.5	47323.0	18.0	47.1	40.3	76.3	932.7	8.0	245.1	0.3	0.9
TIR-17	304.6	104.9	582.6	28029.0	10.8	29.7	31.6	48.7	1799.3	8.0	536.0	0.3	0.9
TIR-18	171.1	99.9	654.4	34063.0	12.9	34.5	35.5	62.3	1536.9	9.1	455.1	0.4	0.9
TIR-19	1770.9	126.4	709.5	52418.0	19.8	2.0	32.6	80.7	107.4	11.8	24.3	0.3	0.6
TIR-20	156.3	155.9	291.6	22109.0	8.4	51.7	34.5	45.0	535.5	6.2	132.7	0.4	0.7
TIR-21	236.8	129.7	218.6	14223.0	5.5	31.3	28.8	28.8	208.1	6.3	382.7	0.3	0.6
TIR-22	1213.7	115.2	437.2	34577.0	13.4	6.8	33.4	57.4	73.0	13.1	23.4	0.3	0.6
TIR-23	217.5	122.2	950.1	49975.0	18.9	43.8	36.6	68.1	846.4	8.6	186.1	0.4	0.9
TIR-24	162.0	107.7	366.1	28437.0	11.0	30.6	31.8	74.9	743.5	10.5	198.0	0.4	0.8
TIR-25	198.9	115.7	346.4	42147.0	16.0	42.2	33.3	60.2	392.6	10.5	63.2	0.4	0.7
TIR-26	192.9	144.6	410.3	58873.0	22.4	45.9	36.9	71.2	367.0	10.8	56.7	0.4	0.8
TIR-27	144.3	78.8	233.4	20576.0	7.9	37.2	31.2	44.2	1316.5	8.0	651.0	0.4	0.8
TIR-28	278.8	104.3	232.7	15458.0	6.0	25.6	26.4	28.3	145.3	5.3	333.8	0.3	0.6
TIR-29	185.0	120.5	313.5	46664.0	17.6	45.7	32.6	62.1	426.6	8.6	54.9	0.3	0.7

TIR-30	48.2	99.0	114.4	7017.0	2.8	49.0	29.6	16.4	128.5	4.1	476.5	0.3	0.5
TIR-31	586.1	107.0	219.0	23805.0	9.2	32.5	34.5	57.5	216.3	9.1	47.3	0.3	0.6
MINIMUM	48.2	59.2	114.4	7017.0	2.8	2.0	26.4	16.4	73.0	4.1	23.4	0.3	0.5
MAXIMUM	1770.9	155.9	2342.7	69546.0	25.9	61.8	40.9	85.8	1799.3	13.7	651.0	0.4	1.0
AVERAGE	318.4	115.4	596.6	37309.7	14.2	34.1	33.4	59.6	731.8	8.8	224.3	0.3	0.8
Shale Value [21]	130	90	850	47200	19	68	45	95	580	13	300	0.3	-
SGV Value (2011) [22]	-	120	-	-	30	35	100	350	-	15	-	0.4	-

Table 4: Comparison of present study with National and International works.

S. NO	LOCATION	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	REFERENCE
1	Changhua County, Taiwan	-	4.9	-	-	-	8.5	14.9	27.4	5.2	0.3	[3]
2	Sanandaj,, Kurdistan, Iran	-	28.7	-	-	14.8	47.9	42.6	77.2	3.8	0.1	[5]
3	Three Industrial Cities of South Korea	-	0.6	-	-	-	1.1	2.3	1.7	4	.0	[7]
4	Ulaanbaatar, Mongolia	38.8	1986.9	-	-	-	13.6	53.3	11.0	16.4	-	[11]
5	Tianjin, china	-	70.7	-	-	-	29.4	27.5	94.13	3	0.2	[12]
6	Northwest Nile Delta, Egypt	171.0	-	-	-	17.4	70.3	37.8	14.9	25.5	-	[13]
7	Munshiganj, Munshiganj District, Bangladesh	-	-	498.0	359.42.0	-	-	49.5	44.4.0	-	-	[14]
8	Granitic terrain of southern India	116.3	45.6	-	-	14.9	33.4	24.4	44.3	-	-	[4]
9	Indian cities, India	-	412.3	-	-	-	7	15.9.8	43.7.4	38.6	-	[8]
10	South India	-	43.2	-	-	16.5	7.6	40.6	34.7	-	-	[9]
11	Cuddalore District, Tamil Nadu	-	54.4	-	281.97.0	-	28.0	20.3	67.6	-	-	[6]
12	Ranipet, Tamil Nadu, India	115.0	501.2	-	-	-	-	47.8	32.9.6	-	-	[10]
13	Average conc. In shale (Background Value)	-	100.0	850.0	47.0	-	68.0	50.0	90.0	-	0.3	[23]
14	Threshold limit	-	64.0	-	-	-	50.0	63.0	20.12.	0	-	[24]
15	Average conc. In world soil	-	125.0	-	3.8	-	23.0	28.0	75.	0	0.1	[25]
16	World soil average levels	-	59.5	488.0	-	-	29.0	38.9	70.0	-	-	[26]
17	Tirunelveli, Tamil Nadu, India	318.4	115.4	596.6	373.10.0	14.2	34.1	33.4	59.6	8.8	0.3	Present study

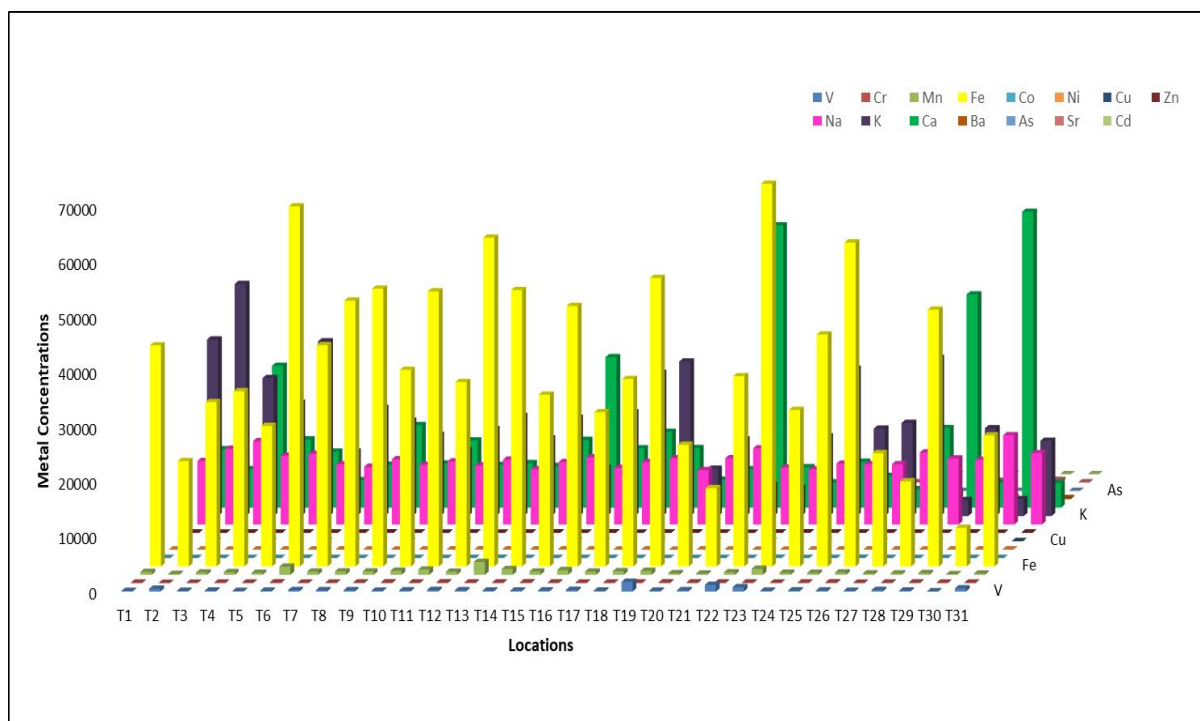


Fig.2: Heavy metal concentration in the soil with different locations.

3.2 Metal Discussions

3.2.1 Barium

Barium is emitted into the atmosphere during the production of barium compounds [27]. Barium levels in the study area varied from 73.0 to 1799.3 mg/kg, with a mean of 731.8 mg/kg. Seventy seven percent of the samples exceed the value of 300 mg/kg [28]. Barium readily displaces other sorbed alkaline earth metals from certain oxides, such as MnO_2 and TiO_2 , but is displaced from Al_2O_3 by alkaline earth metals like Be and Sr. In temperate humid climatic zones, Ba is likely to be sequestered by Fe-oxides, rendering it immobile. Barium in soil can be readily mobilized under various physicochemical conditions. The barium distribution is illustrated in figure 3.

3.2.2 Chromium

Chromium exhibits modest mobility, particularly under mildly oxidizing and reducing circumstances and at near-neutral pH levels. The adsorption of Cr^{6+} diminishes as pH rises, but the adsorption of Cr^{3+} escalates with rising pH. Conversely, Cr (VI) is detrimental to biological systems [29]. Chromium levels in the study area from 59.2 to 155.9 mg/kg, with a mean of 115.4 mg/kg. Eighty percent of the samples exceed the value of 100 mg/kg [23]. In this study most of the samples are exceeded than the normal value which may be due to the source of Cr appears to be anthropogenic from the existing tannery industries, where

they are using Cr and its compounds. The chromium distribution in the study area is given in figure 4.

3.2.3 Copper

Copper typically accumulates in the surface horizons, a phenomenon attributed to the bioaccumulation of the metal and contemporary anthropogenic sources [30]. The copper level in soil samples is varied from 26.44 to 40.87 mg/kg with a mean value of 33.36 mg/kg. The normal threshold value prescribed in soil is 30 mg/kg and eighty percentage of the sample is exceeding the threshold value. This indicated that copper values were found to be high in the study area. These higher values may be due to copper accumulation in the soil attributable to sectors such as steel production, blast furnace operations, and the utilization of agrochemicals in the aerated industry. The Cu level is characterized by point sources of contamination, notably uncontrolled, active, or unattended garbage dumps, which are numerous in the research region. The distribution of copper in the study area is given in figure 5.

3.2.4 Strontium

Strontium is closely linked to calcium and serves as an indicator of calcareous rocks, particularly in conjunction with Sr, Mg, and Ba. Where Ca and additional components signify calcareous rocks, together with other elements (e.g., REEs) indicate felsic intrusive. Bedrock geology may be conducive to skarn mineralization. Sr is readily mobilized during weathering, particularly in oxidizing acidic

conditions, and is integrated into clay minerals and strongly rectified by organic matter [29,31]. The mean Sr content in the research area is 224.3 mg/kg with a range of 23.4 to 651.0 mg/kg. The concentration of Sr in soil is within reasonable limits, indicating its typical levels and reflecting the baseline value in the soil. This indicates that its source seems to be the geogenic contribution of Sr in the soil. The distribution of strontium in the study area is given in figure 6

3.2.5 Vanadium

Vanadium commonly possesses extensive and diverse

industrial applications in dyes, textiles, metallurgy, and electronics. Vanadium levels ranged from 48.2 to

1770.9mg/kg in the study area with a soil mean of 318.4mg/kg (Fig. 7). Normal threshold value for vanadium in soils is 100 mg/kg [32]. Ninety six percentage of samples showed higher than threshold value indicating that bearing on V content in soil samples. The vanadium level in soil is reliant upon the parent material and the pedogenic processes involved in its formation and also majority of the industries are textile and petroleum products, are the source is anthropogenic activities in the study area. The distribution of vanadium in the study area is given in figure 7.

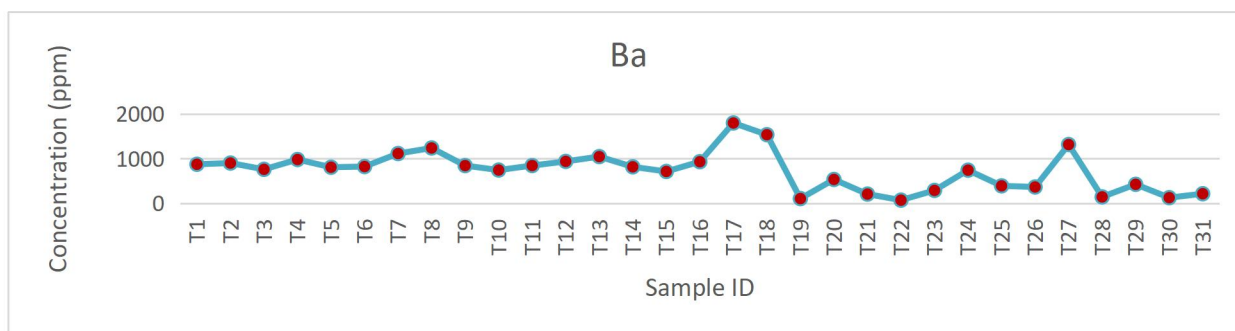


Fig. 3: Sample ID Vs Barium metal concentration (Ba).

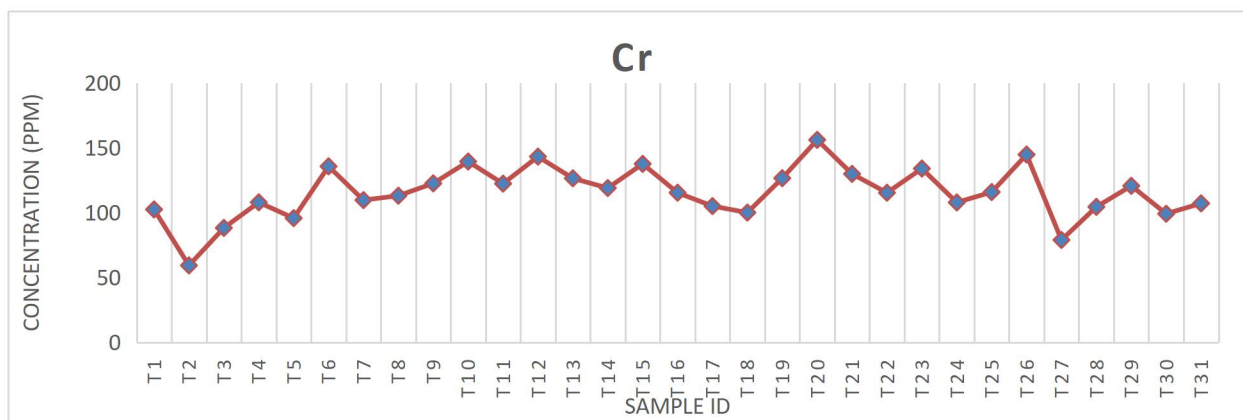


Fig. 4: Sample ID Vs Chromium metal concentration (Cr).

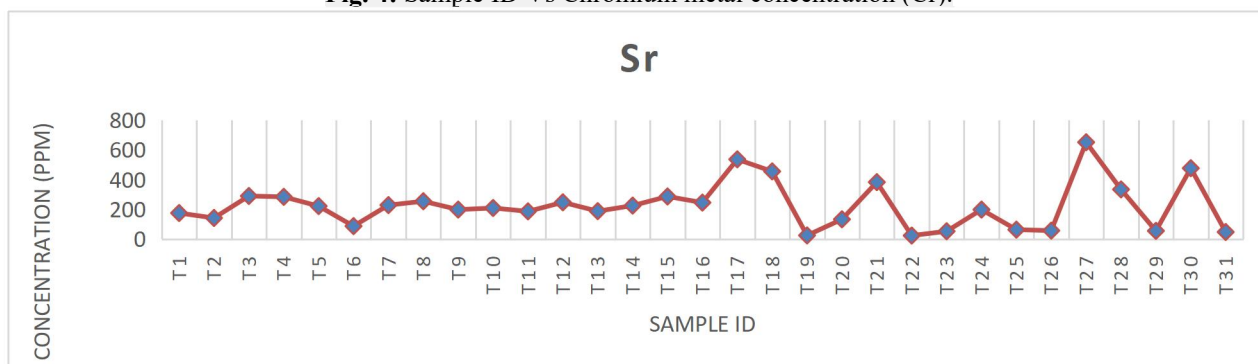


Fig. 6: Sample ID Vs Strontium metal concentrations (Sr).

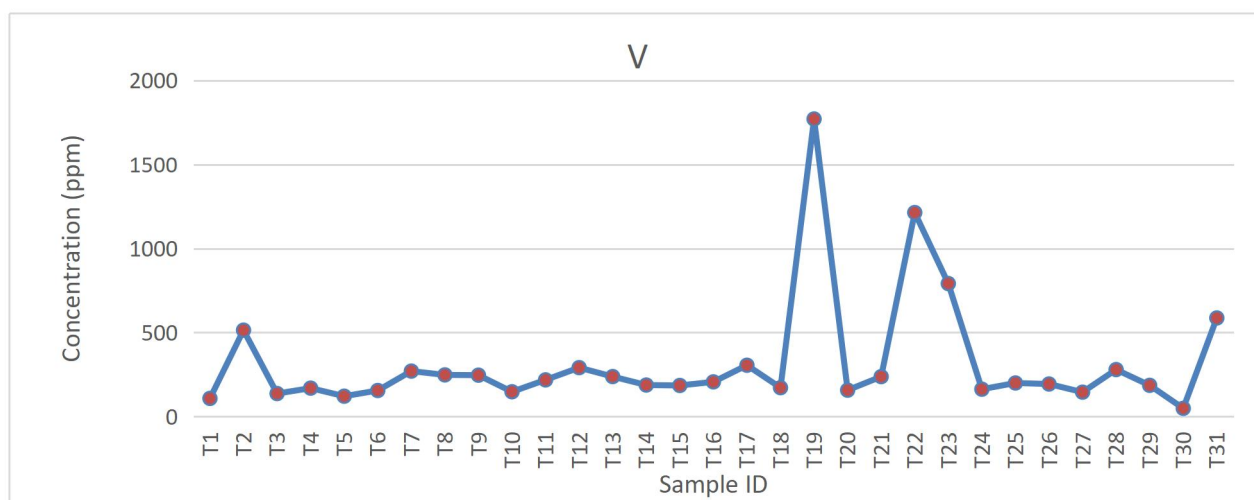


Fig.7: Sample ID Vs Vanadium metal concentration (V).

3.2.6 Zinc

Zinc is a trace metal that is vital for the growth of peoples, animals, and plants, although it can pose a risk to the biosphere at raised quantities. The primary causes of pollution are factories and the application of liquid manure, composted materials, and agrochemicals, including fertilizers and insecticides, in farmland [33]. The mean zinc concentration is 59.63mg/kg, ranges from 16.43 to 85.80mg/kg in the study area. The normal threshold value prescribed in soil is 200 mg/kg [34]. None of the samples are not exceed the threshold value and indicating that the study area is free of Zn metal. However, zinc are found in the nearby industrial areas which may clearly indicate the source to be anthropogenic and not natural [35]. The distribution of zinc in the study area is given in figure 8.

3.2.7 Arsenic

Arsenic is a metalloid belong to group VA and period 4 of the periodic table, occurs in many minerals, mainly as As₂O₃, and can be extracted from the processing of ores predominantly containing Cu, Pb, Zn, Ag, and Au. It is also found in the residues of coal combustion [36]. Arsenic is a significant heavy element that raises concerns about both natural and human health perspectives [37]. Arsenic produces many inorganic and organic compounds with varying toxicity, which reflects the physicochemical features of arsenicals of differing valency. Arsenic was detected in soil samples within the range of 4.090–13.743mg/kg with an average of 8.822 mg/kg. The soil sample contains arsenic are probably the result of discharge from industrial waste or by leaching from sewage [38]. The distribution of arsenic in the study area is given in figure 9.

3.2.8 Cadmium

Cadmium is highly hazardous, causing symptoms including nausea, vomiting, respiratory distress, cramps, and loss of consciousness at raised dosages. The values of cadmium concentration in soil varied from 0.305 to 0.397 mg/kg with an average of 0.347 mg/kg. All soil tests exhibit elevated cadmium concentrations beyond the thresholds established by the Swedish soil guideline values. This may result from effluents of industrial waste or leaching from polluted landfills [39]. High cadmium concentration in some locations (TIR-6, TIR-18, TIR-20, TIR-10) may be attributed to large use of PVC plastics, nickel cadmium batteries, insecticides, motor oil, and disposal of sludge in dump sites [40]. The cadmium distribution in the study area is given in figure 10.

3.2.9 Iron

Iron is the main metal of the lithosphere, containing around 5%, predominantly found in magmatic rocks. Iron is released as corrosion by products in aquatic and land-based settings [41]. The values of iron concentration in soil varied from 7017 to 69546 mg/kg with a mean of 37310 mg/kg. The high concentration of Iron is noticed in TIR-23, TIR-6, TIR-13, TIR-26 may be due industrial and municipal discharges. The distribution of iron in the study area is given in figure 11.

3.2.10 Cobalt

Cobalt concentration in soil, it varied from 2.75 to 25.88 mg/kg with a mean of 14.20 mg/kg. The cobalt concentration in this study is beyond the limit as prescribed by the Swedish soil guideline values for soils. This indicated that soil is free from cobalt sources. The distribution of cobalt in the study area is given in fig 12.

3.2.11 Nickel

Nickel is a silvery-white metal that achieves a high luster; it is a transition metal, characterized by its hardness and ductility. It typically occurs in conjunction with sulfur and iron in pentlandite, with sulfur in millerite, with arsenic in the mineral nickeline, and with arsenic and sulfur in nickel glance [42]. Common sources of nickel comprise contamination from municipal sewage sludge, effluent from sewage treatment facilities, and groundwater next to

landfill sites. Industries such as ceramics, steel and alloys, electroplating, and refractory materials contribute to nickel manufacturing. Anthropogenic sources encompass the combustion of fuel or trash emitted by enterprises. The concentration of nickel in soil, it varied from 2.00 to 61.84 mg/kg with an average of 34.10 mg/kg. The nickel value, according to Swedish guidelines, must be below 50 mg/kg. The soil sample from Tirunelveli does not exceed the limits of the Swedish soil quality guidelines. The distribution of nickel in the study area is given in figure 13.

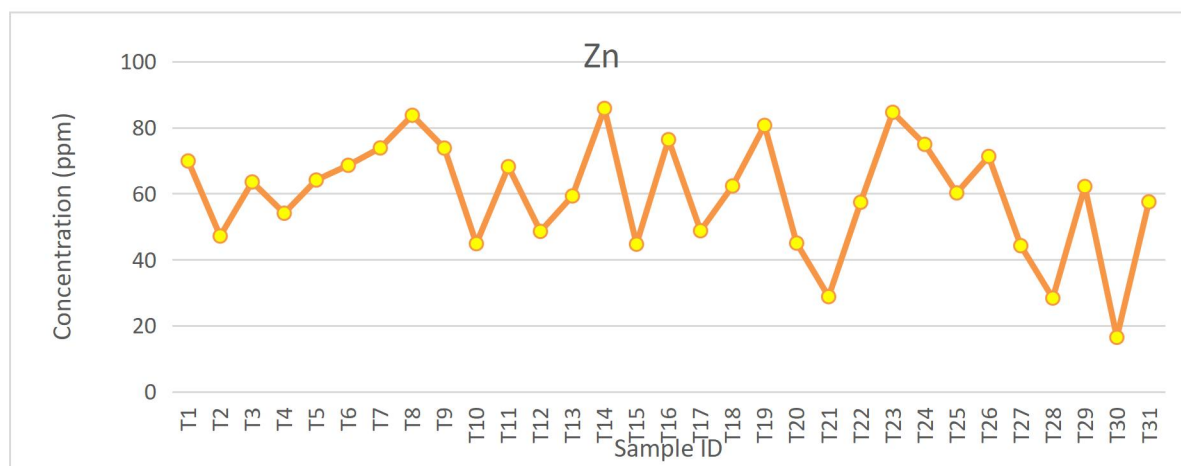


Fig. 8: Sample ID Vs Zinc metal concentration (Zn).

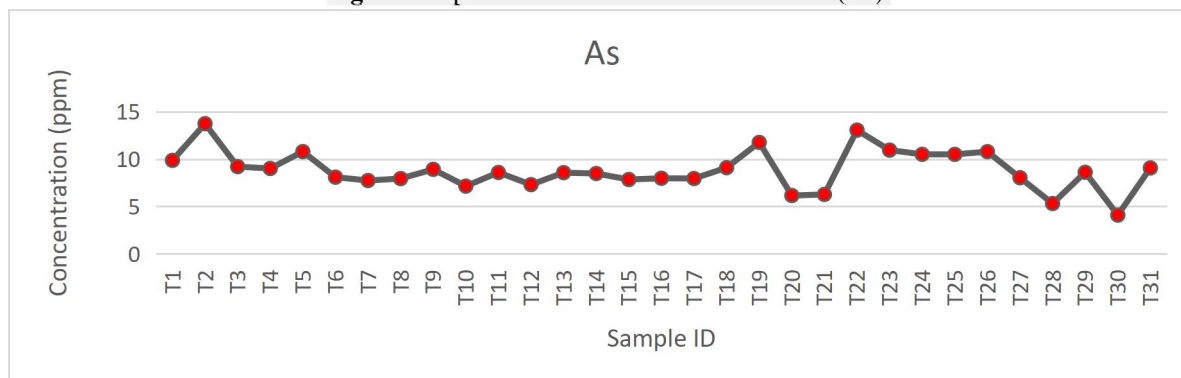


Fig. 9: Sample ID Vs Arsenic metal concentration (As).

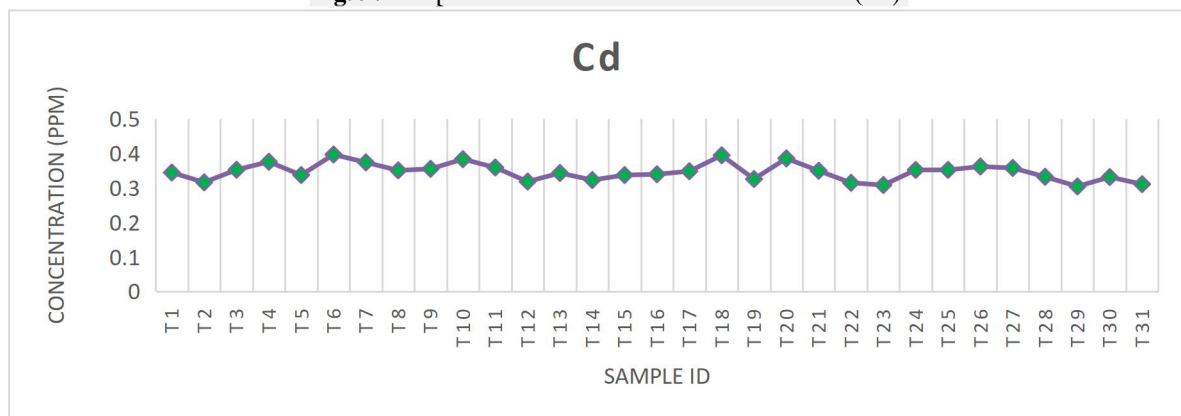
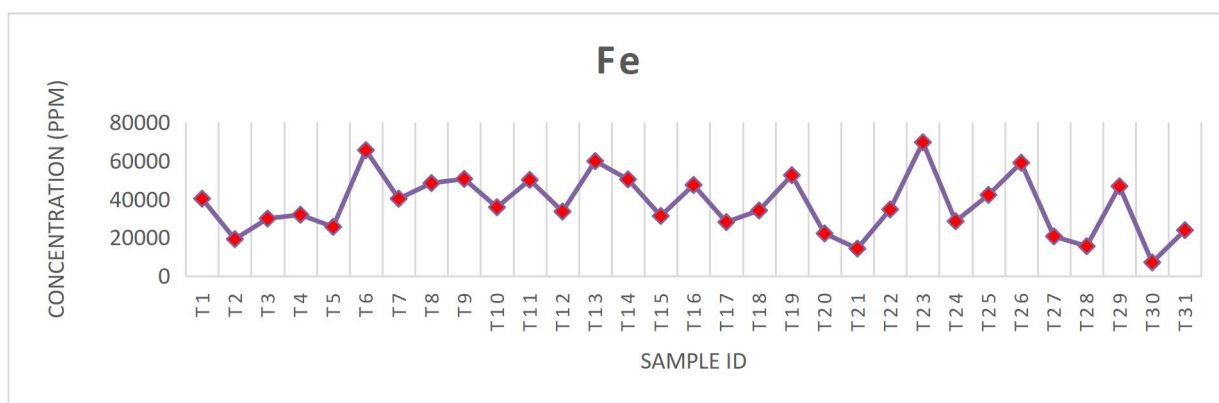
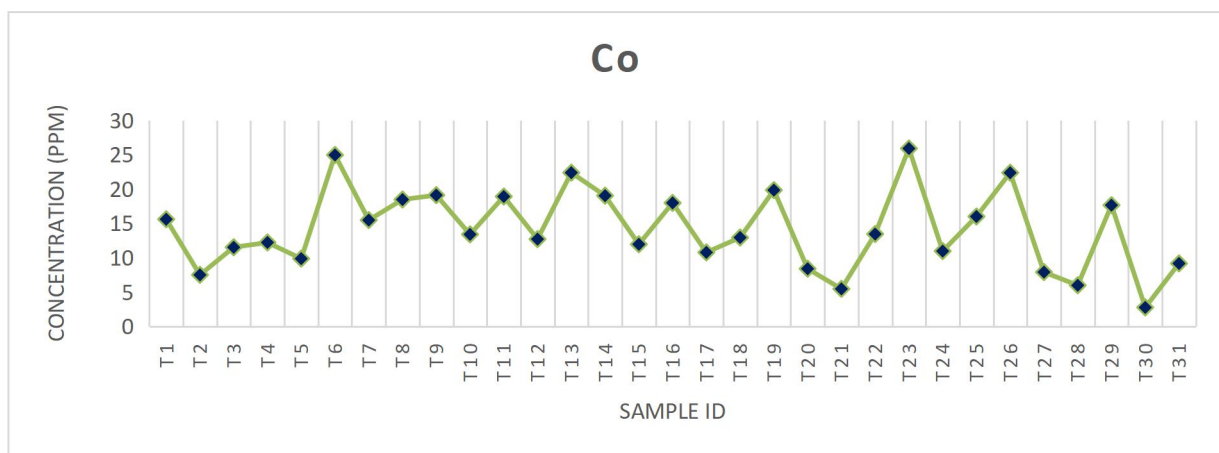
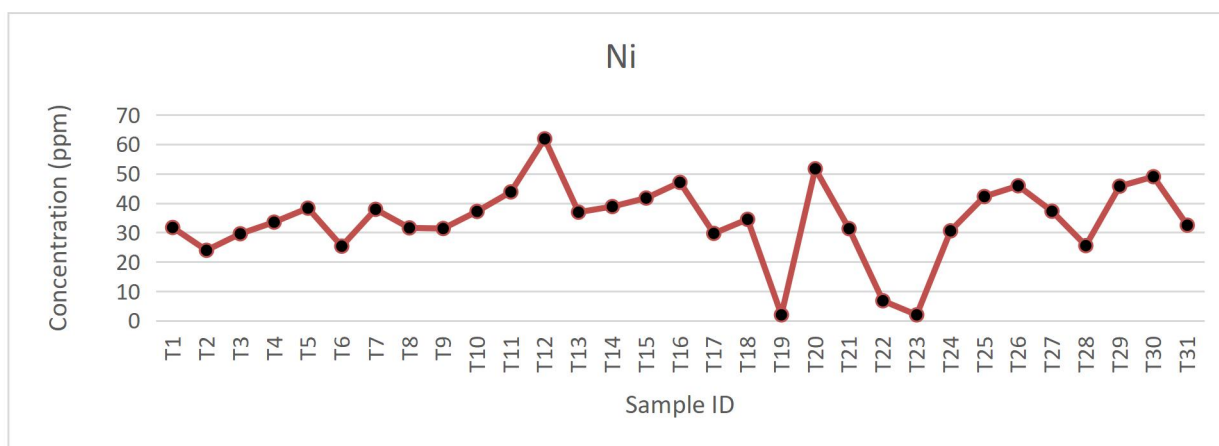


Fig. 10: Sample ID Vs Cadmium metal concentration (Cd).

**Fig. 11:** Sample ID Vs Iron metal concentration (Fe).**Fig. 12:** Sample ID Vs Cobalt metal concentrations (Co).**Fig. 13:** Sample ID Vs Nickel metal concentration (Ni).

3.3. Spatial Distributions of Heavy Metals

The Spatial Distribution of the Heavy Metal As shown in Fig (14 a) to (14 l) in the study area shows an increase in the spatial trends for As Fig(14 j). On the other hand, modest amounts of Cu, Co, & Zn were present in the northwest of the research region. The east portions of the research area Fig (14 g), (14 e), (14 h) had significantly concentrations of Fe, V, Sr which may be related to local people's activity and anthropogenic activities. According to the interpolation map in Fig (14 d), (14 a), (14 k) The heavy metals Cu and Ba, are in the south, east, and center of the study area Fig (14 g), (14 i).

The highest values for Cr whereas the spatial distribution of Co, Cd was irregular since the highest values were dispersed throughout the north and west of the study region Fig (14b), (14 e), (14 l). The primary contributors to soil nickel (Ni) pollution are enterprises engaged in metal plating, fossil fuel combustion, nickel mining, and electroplating (Fig. 14 f). This includes anthropogenic sources such as sewage sludge and other waste materials used as soil conditioners, phosphate-based farm fertilizers, atmospheric deposition, and inorganic fertilizers [43-48]. The regional trends show that concentrations of copper (Cu) and zinc (Zn) grew from the north to the southwest Fig (14g), (14h).

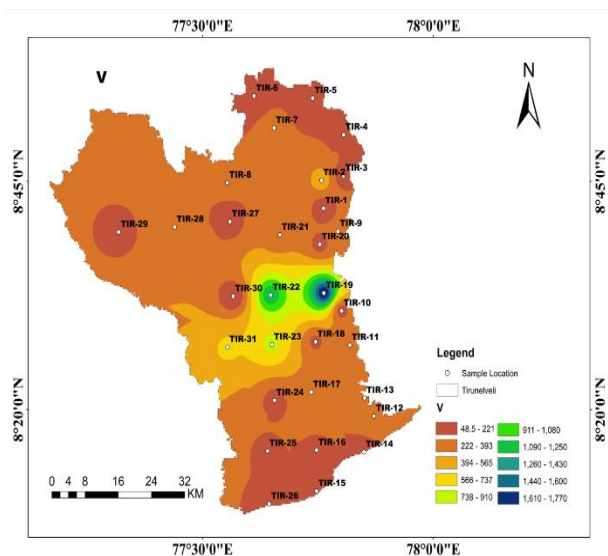


Figure 14 (a)

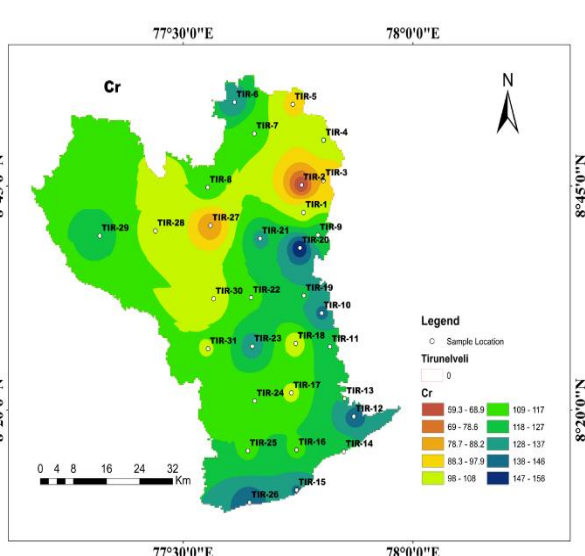


Figure 14 (b)

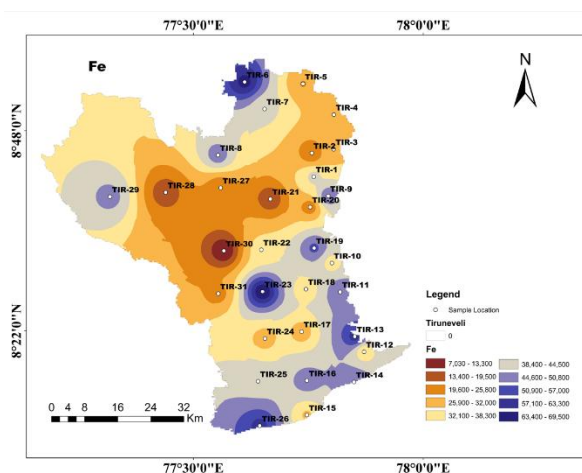


Figure 14 (c)

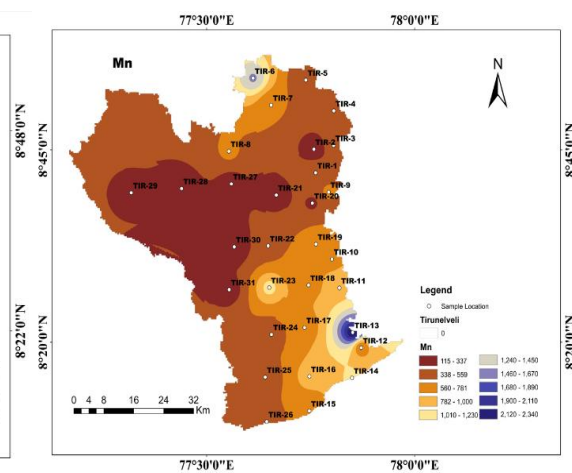


Figure 14 (d)

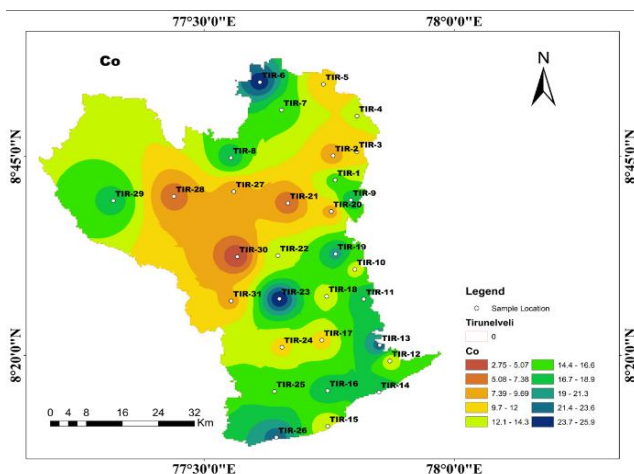


Figure 14 (e)

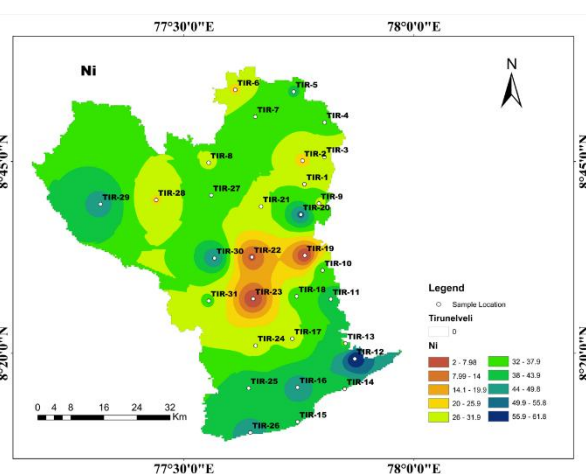


Figure 14 (f)

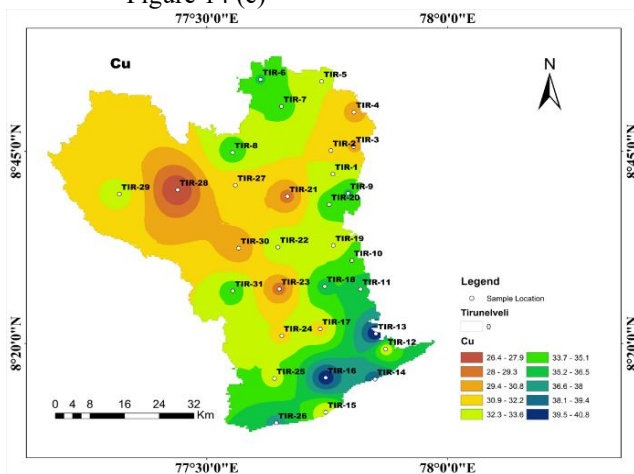


Figure 14 (g)

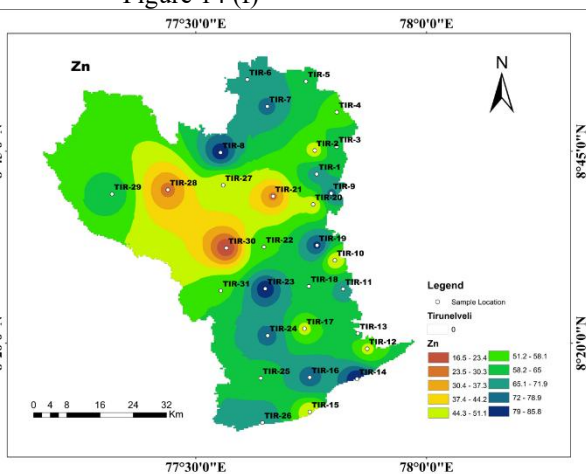


Figure 14 (h)

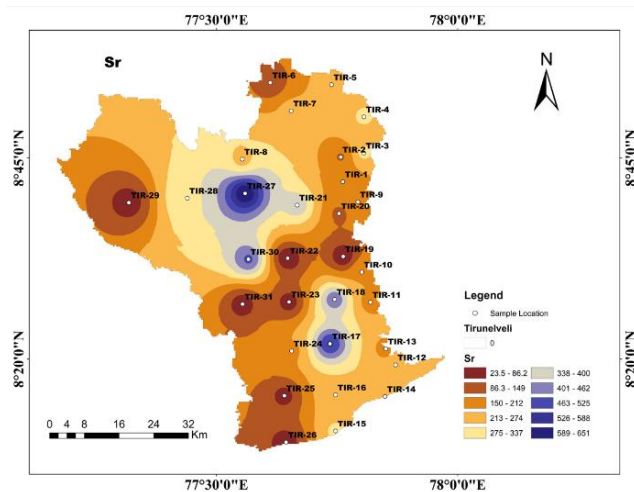


Figure 14 (i)

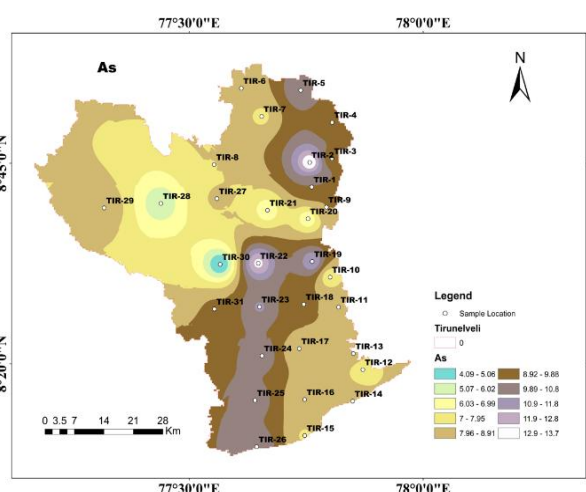


Figure 14 (j)

4. Ecological risk factor (Er^i)

Ecological risk factor (Er^i) quantitatively expresses the potential ecological risk of a given single contaminant Hakanson 1980 [49] and is given as:

$$Er^i = T^i_r C^i_f \text{ -----(1)}$$

where T^i_r = toxic response factor of a given substance (Chromium = 2, Manganese = Nickel = Copper = 5, Zinc = 1, Arsenic = 10, Cadmium = 30); C^i_f is the contamination factor which has been evaluated from Eq. (3).

Table 5: Eri and RI Values of Heavy metal concentrations of soil samples.

SAMPLE ID	Potential Ecological risk factor (Eri)							RI
	Cr	Mn	Ni	Cu	Zn	As	Cd	
TIR-1	2.3	3.1	2.3	3.7	0.7	7.6	34.5	54.2
TIR-2	1.3	0.9	1.8	3.5	0.5	10.6	31.6	50.2
TIR-3	2.0	2.4	2.2	3.4	0.7	7.1	35.3	53.0
TIR-4	2.4	2.7	2.5	3.4	0.6	6.9	37.6	56.1
TIR-5	2.1	2.0	2.8	3.6	0.7	8.3	33.7	53.3
TIR-6	3.0	8.7	1.9	3.9	0.7	6.2	39.7	64.2
TIR-7	2.4	3.4	2.8	3.8	0.8	6.0	37.4	56.6
TIR-8	2.5	3.6	2.3	3.8	0.9	6.1	35.1	54.4
TIR-9	2.7	3.6	2.3	3.9	0.8	6.9	35.5	55.7
TIR-10	3.1	4.3	2.7	3.8	0.5	5.5	38.4	58.2
TIR-11	2.7	5.6	3.2	4.1	0.7	6.6	35.9	58.9
TIR-12	3.2	3.4	4.5	3.6	0.5	5.6	31.9	52.7
TIR-13	2.8	13.8	2.7	4.5	0.6	6.6	34.3	65.4
TIR-14	2.6	6.1	2.9	4.3	0.9	6.5	32.3	55.6
TIR-15	3.1	3.5	3.1	3.6	0.5	6.0	33.7	53.4
TIR-16	2.6	5.1	3.5	4.5	0.8	6.1	34.0	56.5
TIR-17	2.3	3.4	2.2	3.5	0.5	6.1	34.9	52.9
TIR-18	2.2	3.8	2.5	3.9	0.7	7.0	39.5	59.7
TIR-19	2.8	4.2	0.1	3.6	0.8	9.1	32.6	53.2
TIR-20	3.5	1.7	3.8	3.8	0.5	4.7	38.6	56.6
TIR-21	2.9	1.3	2.3	3.2	0.3	4.8	35.0	49.8
TIR-22	2.6	2.6	0.5	3.7	0.6	10.0	31.5	51.5
TIR-23	3.0	6.4	0.1	3.2	0.9	8.4	30.9	52.9
TIR-24	2.4	2.2	2.2	3.5	0.8	8.1	35.2	54.4
TIR-25	2.6	2.0	3.1	3.7	0.6	8.1	35.2	55.4
TIR-26	3.2	2.4	3.4	4.1	0.7	8.3	36.2	58.4
TIR-27	1.8	1.4	2.7	3.5	0.5	6.2	35.8	51.8
TIR-28	2.3	1.4	1.9	2.9	0.3	4.1	33.2	46.1
TIR-29	2.7	1.8	3.4	3.6	0.7	6.6	30.5	49.2

TIR-30	2.2	0.7	3.6	3.3	0.2	3.1	33.2	46.3
TIR-31	2.4	1.3	2.4	3.8	0.6	7.0	31.1	48.6
MINIMUM	1.3	0.7	0.1	2.9	0.2	3.1	30.5	46.1
MAXIMUM	3.5	13.8	4.5	4.5	0.9	10.6	39.7	65.4
AVERAGE	2.6	3.5	2.5	3.7	0.6	6.8	34.7	54.4

The following terminologies are used to describe the risk factor: $Er^i < 40$, low potential ecological risk; $40 \leq Er^i < 80$, moderate potential ecological risk; $80 \leq Er^i < 160$, considerable potential ecological risk; $160 \leq Er^i < 320$, high potential ecological risk; and $Er^i \geq 320$, very high ecological risk [49]. It was found that the value of Er^i from Table - 5 for chromium, manganese, nickel, copper, zinc, arsenic, cadmium was below 40 in all the sampling sites, thus indicating low potential ecological risk. Fig 15 gives the variations of locations with ecological risk factor.

4.1 Potential ecological risk index (RI)

To assess the cumulative ecological danger of the detected metals in the research area, the danger Index (RI) was computed as the aggregate of all seven risk variables (Table 5). RI could delineate the sensitivity of the local ecosystem to hazardous metals and signify the ecological risk arising from overall contamination. The potential ecological risk index (RI) was defined identical to the degree of pollution, as the aggregate of the risk elements.

Where Er^i is the ecological risk factor and m is the count of the heavy metal species. The following terminology was used for the potential ecological risk index: $RI < 150$, low ecological risk; $150 \leq RI < 300$, moderate ecological risk; $300 \leq RI < 600$, considerable ecological

risk; and $RI \geq 600$, very high ecological risk [49].

$$RI = \sum_{i=1}^m Er^i \text{ -----} \quad (2)$$

The RI value for all the locations are found to be less than value of 150, signifies the low ecological risk. The locations with potential ecological risk index is given in figure 16.

4.2 Pollution index

In this study, the pollution load index (PLI) is applied to assess the degree of heavy metals polluted in soils at the sampling stations by calculating the n^{th} root of the product of the n CF. Tomlinson 1980 [50-52] records that the study soil is considered to be significantly polluted if the PLI value is greater than 1, but not when it is less than 1.

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \text{ ---} \quad (3)$$

This empirical index offers an easy, comparable method for determining the extent of heavy metal contamination. The PLIs calculated according to the contamination factor of heavy metals in soil and it is given in Table 3. The PLIs in all soil samples varied from 0.5 to 1.0 with a mean of 0.8 indicating that the soils are very not contamination by the heavy metals. The variation of PLI with the sample location is given in figure.17.

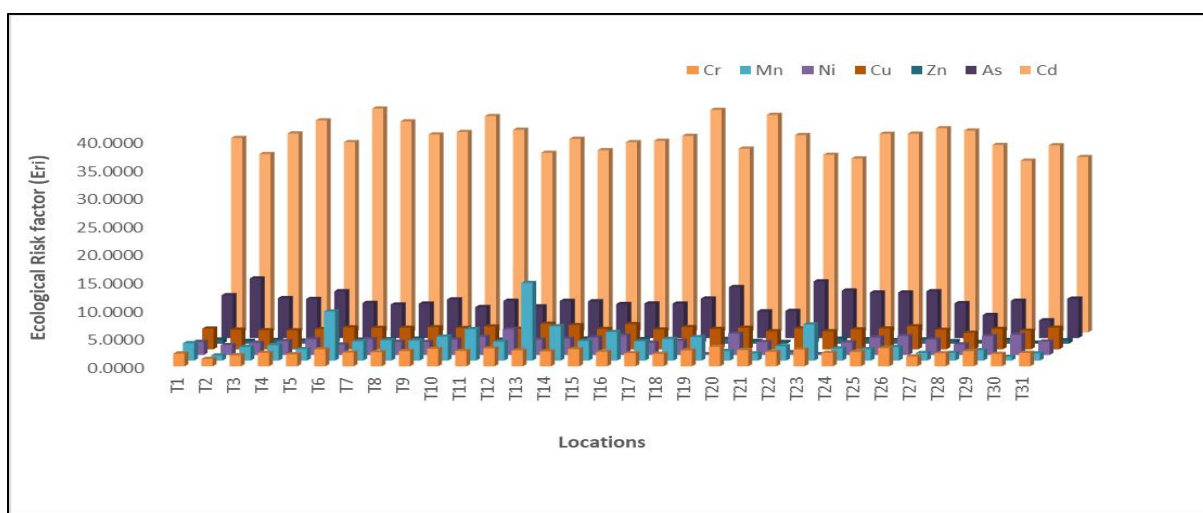


Fig.15. Locations Vs Eri.

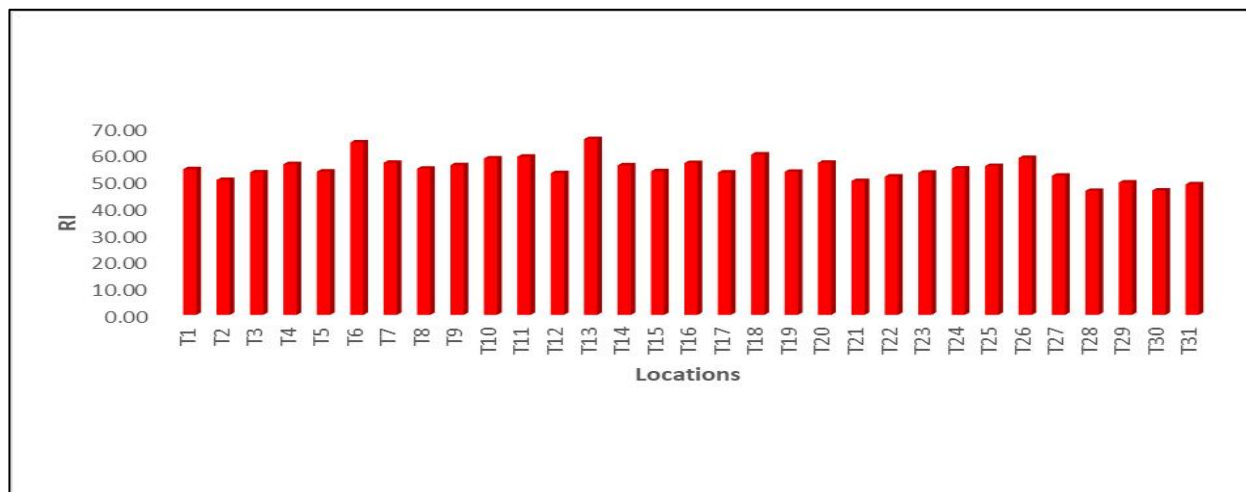


Fig.16. Locations Vs RI.

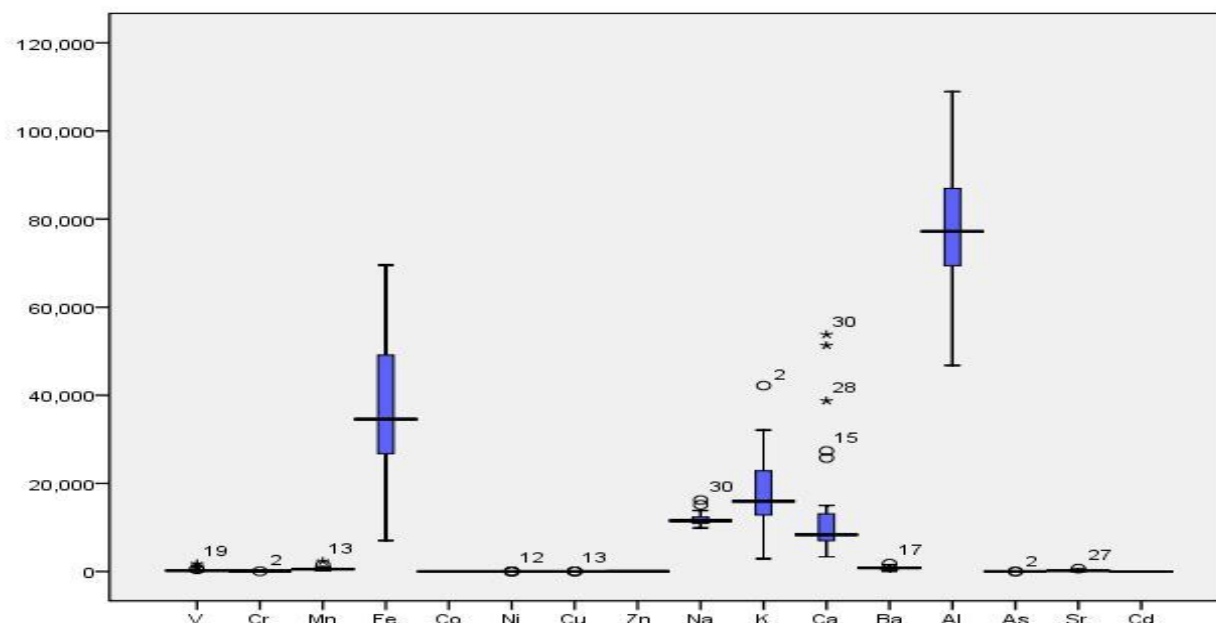


Fig. 17. Box-plots of pollution load index (PLI) for heavy metals.

5. Conclusion

The content of heavy metals in the soils of Tirunelveli District, Tamil Nadu, have been measured using the EDXRF technology. The average concentrations of the studied heavy metals significantly exceeded the background values. This may be attributable to anthropogenic inputs in the studied area. The spatial maps illustrated the distribution pattern of heavy metals in the research area. The ecological risk index (RI) for heavy metals suggested low risk while the pollution load index (PLI) showed that the research area is not significantly impacted.

The findings of the research indicate the influence of anthropogenic factors on heavy metal contamination in the soils of the investigated area, ascribed to the disposal of hazardous waste and the uncontrolled discharge of effluents. Increased concentrations of hazardous metals in certain areas may lead to a significant increase in their concentration in groundwater due to leaching. This study points out the necessity for immediate control measures to address the current severe heavy metal pollution in the area. The soils need various remediation technologies, such as bioremediation and phytoremediation through the cultivation of certain plants that can reduce contamination rates and prevent future pollution issues.

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