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An assessment of heavy metal contamination in old town and Gnanapuram of Visakhaptanam

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ABSTRACT

The present study areas (Old town and Gnanapuram) have been severely threatened by the growing levels of heavy metal pollution due to the discharges from Visakhapatnam Port Trust (VPT) and other industries in the vicinity. The anomalous concentrations of Cu, Cr, Co, Ni, Pb, and Zn in the vicinity of the study areas are of anthropogenic origin. The metal depletion in the soil samples are of EF<1 was observed for most elements indispensable to the proper growth of plants. The low EF for Zinc in soils observed is deficiency to minimal enrichment may indicate soil depletion in this metal. It has been found that an increase in solubility under low pH conditions affects Zinc mobility. The overall degree of contamination observed in the Old Town area (28.14) is greater than the Gnanapuram area (26.47); observed to be of a very slight variation and these two areas were under considerable degree of contamination range.

Key words: Heavy metal contamination, Geoaccumulation, Enrichment factor, Contamination factor, Degree of contamination, Old Town, Gnanapuram.

INTRODUCTION

Visakhapatnam city has a glorious past and is called as jewel of East Coast. The only historical part of the city is the Old Town area. Historians point out that this was the place where civilization began about 800 years ago. The locality and its surrounding are still littered with structures that are old enough to be termed as heritage buildings or sites. The present study is highly affected by the discharges of VPT and the industries nearby.

The inhabitants are being threatened by the growing levels of pollution and insecurity over relocation. A part from the health problems, the residents also fear the issue of displacement knocking their doors, courtesy the proposed expansion and takeover plans of the VPT. These are the large contaminated sites often share critical properties such as high acute and or chronic toxicity, high environmental persistence, often high mobility leading to contamination of groundwater and high lipophilicity leading to bioaccumulation in food web(32). There is a growing level of discomfort between the port authorities and the residents.

The mobilization of heavy metals into the biosphere by human activity has become an important process in the geochemical cycling of these metals. This is acutely evident in urban areas where various stationary and mobile sources release large quantities of heavy metals into the atmosphere and soil, exceeding the natural emission rates (6,31).

Heavy metals in urban soils may come from various human activities, such as industrial and energy production, construction, vehicle exhaust, waste disposal, as well as coal and fuel combustion (11,18,21,25,27,33,35,41). These activities send heavy metals into the air and the metals subsequently are deposited into urban soil as the metal containing dust falls. Sakagami*et al*. (1982) reported that there was a close relationship between heavy metal concentrations in soils and those in the dust falls (36). Heavy metals in the soils can also generate airborne particles and dusts, which may affect the air environmental quality (5,10,12,16).

MATERIALS AND METHODS

Old Town area is located in the East coast of Visakhapatnam city, Andhra Pradesh, India. The area of experimental region is in between the $17^{0}42^{I}44.42^{II}$N $83^{0}17^{I}41.16^{II}$E as shown in the Map.(fig.1).

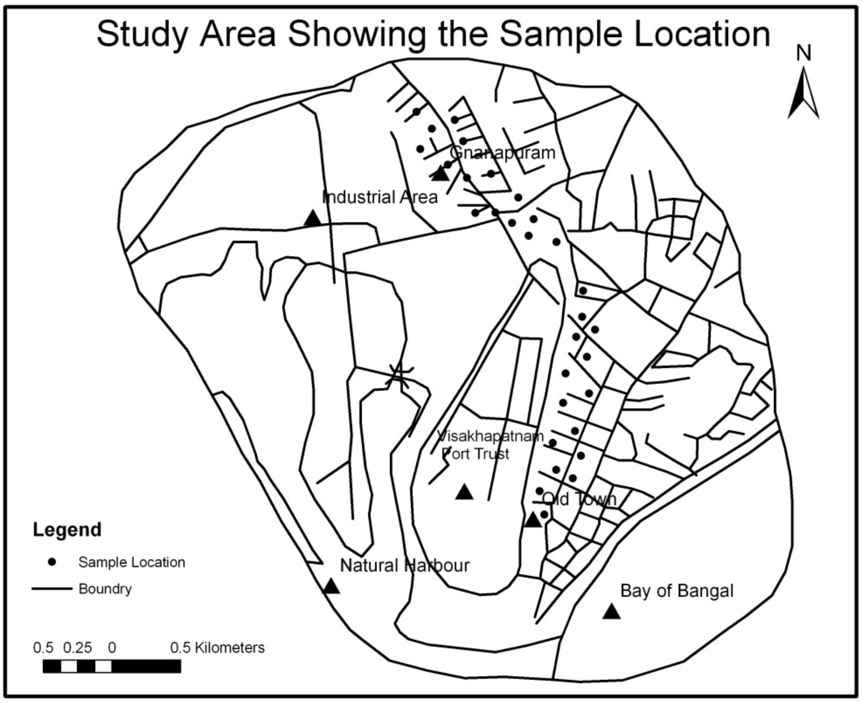

Fig.1.Map showing the study area (Quick bird view of Google terrain maps)

Sampling and Analysis

Depending on the area, the total number of soil samples collected was 32 from both the areas of 16 each. Soil samples were collected from the outer surface, i.e., 5-15 cm depth to study the contamination. The samples were collected in self-locking polythene bags and were sealed in double bags. Use of metal tools was avoided and a plastic spatula was used for sample collection. Figure 1 shows the location of soil sample collection in the study area. Soil samples were dried for two days at 60^{o}C. The dry soil sample was finely powdered to –250 mesh size (US Standard) using a swing grinding mill. Sample pellets were prepared for analysis by X-ray fluorescence spectrometry (XRF), using a backing of boric acid and pressing it at 25 tons of pressure. A hydraulic press was used to prepare pellets for XRF analysis to determine trace elements. To monitor the quality of chemical analysis and examine the accuracy of the data, soil reference materials, ***SO-2*** issued by Canadian reference materials were analyzed with the soil samples during the course of analysis. The analytical concentrations of the metals are listed in ***Table 1.***It seems that our analytical values are within the range of the certified values of the reference materials.

To assess the heavy metal dynamics the present study was carried out on soil contamination by using Index of Geoaccumulation, Enrichment Factor, Contamination Factor and Degree of Contamination (23).

Table.1: Results of analytical values of the soil standard reference materials SO-2 (podzalic B horizon soil) in comparison with the certified values.

CRM	As	Ba	Co	Cr	Cu	Mo	Ni	Pb	Rb	Sr	V	Y	Zn	Zr
SO-2	0.9	935.5	14	17.7	11.1	1.2	10.6	25.6	57.8	330	177.2	20.9	115.2	407.8
	1.17	1000	7.6	12.3	8	2	8	20	77	331	57	40	115	760

First row indicates measured values
Second row indicates certified values

RESULTS AND DISCUSSION

The individual contents of metals obtained are in (Table. 2) and (Table. 3) shows descriptive statistical data contents of the metals in the soil and also contains contents of the metals in Earth's crust, which served as reference values (39).High levels of some elements are observed in some pockets only.

Table.2. Metal content in Soil of Old Town area and reference value (Taylor and McLennan 1995) mg/kg.

	As	Ba	Co	Cr	Cu	Mo	Ni	Pb	Rb	Sr	V	Y	Zn	Zr
Min	0.32	246.7	8.5	40.2	8	0.5	18.6	19.3	49.2	326.4	114.7	26.5	76.5	334.6
Max	1.02	906.2	39.6	154.3	37.6	9.1	79.1	75	150	335.9	350.9	56.3	164.8	928.2
Mean	0.68	622.26	24.99	105.13	23.28	4.54	48.20	43.78	104.76	332.53	260.02	36.03	115.96	582.78
Skewness	-0.17	-0.31	-0.03	-0.61	-0.06	0.27	0.19	0.56	-0.17	-1.00	-0.60	0.91	0.39	0.54
Kurtosis	-0.56	-1.10	-1.10	-0.73	-0.51	-1.27	-1.28	-1.41	-1.34	-0.09	-0.85	-0.62	-0.44	-0.78
STDEV	0.20	215.83	10.28	33.56	7.98	2.68	20.28	20.57	34.08	3.01	81.65	9.90	26.17	181.78
Median	0.68	655.15	25.4	118.75	23.1	3.4	45.35	35.65	105.5	333.75	255.45	31.4	117.25	552.85
reference	1.5	550	10	35	25	1.5	20	20	112	350	60	22	71	190

Table.3. Metal content in Soil of Gnanapuram area and reference value (Taylor and McLennan 1995) mg/kg.

	As	Ba	Co	Cr	Cu	Mo	Ni	Pb	Rb	Sr	V	Y	Zn	Zr
Min	0.16	390.4	0.6	32.8	0.5	0.5	16	14.5	45.8	330.9	80.6	16.7	85.4	321.8
Max	1.13	906.2	47.1	77.9	38.4	4.1	75.2	45.1	149.1	334.6	580.4	55.1	157.7	876.2
Mean	0.84	693.44	27.58	55.94	23.35	2.84	44.29	30.21	96.83	332.80	351.14	36.17	122.13	523.60
Skewness	-1.22	-0.75	-0.65	-0.13	-0.75	-0.87	0.14	0.00	-0.15	-0.23	-0.10	0.23	-0.13	0.78
Kurtosis	1.62	-0.36	-1.18	-1.29	-0.50	0.54	-1.86	-1.81	-1.40	-1.07	-1.07	-0.97	-1.72	-0.26
STDEV	0.26	157.25	17.42	15.73	12.87	1.06	23.64	11.17	34.03	1.11	159.54	12.65	27.87	168.74
Median	0.94	730.8	35.25	60.05	23.7	2.9	40.3	28.95	104.5	332.95	352.75	32.65	125.4	483.45
reference	1.5	550	10	35	25	1.5	20	20	112	350	60	22	71	190

In the Old town area, the mean Igeo value of As, Ba,Cu, Rb and Sr fell into class '0' which is practically uncontaminated.Uncontaminated to moderately contaminate with Co, Cr, Mo, Ni, Pb, Y, Zn and Zr these elements fell into class '1'. Moderately contaminated with V and this element fell into class '2' according to Muller (1981) six class index of Geoaccumulation(Fig.2). Where as in Gnanapuram area is practically uncontaminated with the As, Ba, Cu, Pb, Rb and Sr these elements fell into class '0' according to Muller six class index. Uncontaminated to moderately contaminate with Co, Cr, Mo, Ni, Y, Zn and Zr these elements fell into class '1' and Moderately contaminated with V, fell into class '2' according to Muller (1981) six class index of Geoaccumulation. (Fig.3)

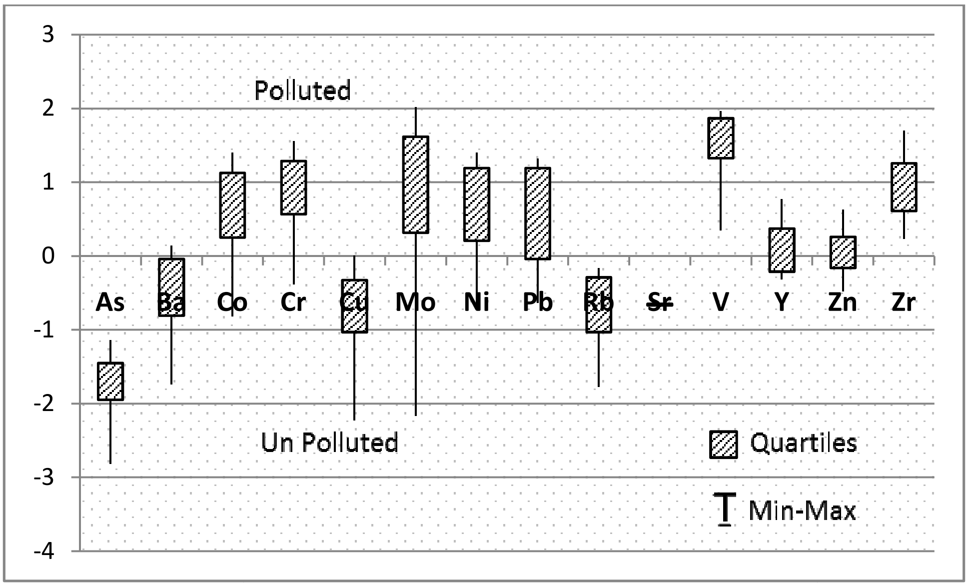

Fig.2. Igeo chart of Old Town area

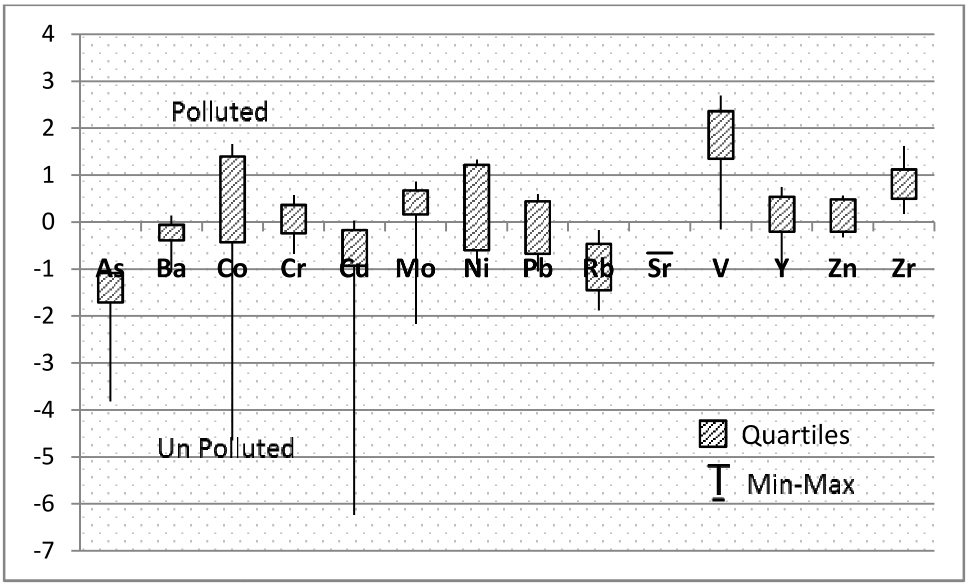

Fig.3. Igeo chart of Gnanapuram area

The Old town area is Deficiency to minimal enrichment with the As, Ba, Cu, Rb , Sr, Y and Zn. Moderate enrichment with the Co, Cr, Mo, Ni, Pb, V and Zr according to Hakanson (1980) five contamination categories of Enrichment factor (Fig.4). Gnanapuram area isDeficiency to minimal enrichment with the As, Ba, Cr, Cu, Mo, Pb, Rb, Sr, Yand Zn. Moderate enrichment with the Co, Ni and Zr. Significant enrichment with the Vaccording to Hakanson (1980) five contamination categories of Enrichment factor(Fig.4).

Arsenic
The mean arsenic content in the soils examined was 0.68 mg/kg (Old town area) and 0.84 mg/kg (Gnanapuram), which is below the mean content in average soils of 2 mg/kg (1,9). The mean Igeoobserved was indicating class '0' of practically uncontaminated soil (Fig. 2 & 3) (29). The mean E.F obtained indicating the deficiency to minimal enrichment as per the five categories recognized on the basis of EF (38) with arsenic (Fig.4). The slight increase in As content in the study areas is brought about by some industrial activity. An increase in As content in the environment is caused mainly by the metallurgical industry and coal combustion (13,30), hence its content in the areas affected by industrial activity may be elevated.

Barium
The mean Igeo obtained for both the areas revealed that nearly all the samples examined fell into class '0' practically uncontaminated with barium as per Muller's six classes of the geoaccumulation index also showed nearby to mean content in unpolluted range (Fig.2 & 3). The EF was confirming the deficiency to minimal enrichment with barium.(Fig.4)

Cobalt
Cobalt emission may be from wind borne soil particle, sea salt spray and biogenic process, port dealing oil import and export are the sources of other anthropogenic load. The mean cobalt in the soils of both the areas observed 24.99mg/kg for old town and 27.57 mg/kg for gnanapuram, not similar to normal distribution in soils of 17 mg/kg (4). The Igeoranged fell into class 1, denoted uncontaminated to moderately contaminated (Fig.2 & 3). The EF was confirming a moderateenrichment of soils in both the areas. (Fig.4)

Chromium
Chromium compounds are present in the vicinity of Port as general electric plastics and in paints. The mean Chromium content in the soils is 50 mg/kg. The values obtained 105.125 mg/kg and55.9375 mg/kg in soils of both the areas Old Town and Gnanapuram respectively. Much higher values were also reported in industrial areas as up to 2,000 mg/kg reported by Ansari *et al*. (1999). The Igeo obtained fell into class 1, denoted uncontaminated to moderately contaminated (Fig.2 & 3). The EF obtained for Cr, which falls under the class of moderate enrichment (38) in Old Town area (Fig.4) and deficiency to minimal enrichment in Gnanapuram area(Fig.4). Chromium and its compounds are primarily used in the manufacture of steel and other alloys, chrome plating and pigment production (14,23). However, inadequate disposal of waste containing chromiumat industrial sites in the past decade has contaminated both land and groundwater.

Copper
The average copper content in the soil examined was 23.28 mg/kg and 23.35 mg/kg in both the areas old town and gnanapuram respectively. Its value in generally non-contaminated soils is 50 mg/kg. The mean Igeo observed was indicating class ‘0’ of practically uncontaminated soil (Fig. 2 & 3) as per Muller’s 1969, six class index of geoaccumulation. The mean E.F obtained indicating the deficiency to minimal enrichment as per the five categories recognized on the basis of EF (38) with Cu (Fig.4).

Molybdenum
The Igeo indicated that the soils in the study areas fall under class 1 (28) uncontaminated to moderately contaminated (Fig.2 & 3). Similarly in the case of EF it showed moderate enrichment in most of the samples in Old Town area and deficiency to minimal enrichment in Gnanapuramarea (Fig.4). The element occurs in fossil fuels and is immobilized by combustion processes, which can result in soil contamination via atmospheric deposition.

Nickel
The Nickel content in soils obtained average of 48.2 mg/kg in Old Town area and 44.28 mg/kg for Gnanapuramarea. In soils Ni is usually present in the organically bound form, which under acidic and neutral conditions increases its mobility and bioavailability. (2,19). The Igeo values obtained most of the samples falling into class 1 of uncontaminated to moderately contaminated (28) (Fig.2 & 3); similar to the EF’s, which pointed to be showing moderateenrichment of Ni in soils of study areas (Fig.4).

Lead
Pb usually varies considerably with soil type; it is mainly associated with clay minerals, Mn oxides, Fe and Al hydroxides and organic matter. In some soil types, Pb may be highly concentrated in Ca carbonate particles or in phosphate concentrations and a baseline Pb value for surface soil (15). The Pb value for surface soil on the global scale has been estimated to be 25 mg/kg levels above this suggest an anthropogenic influence (20). The mean values obtained 43.77 mg/kg and 30.21 mg/kg in soils of both the areas Old Town and Gnanapuram respectively showing the elevated content of Pb. The Igeo obtained fell into class 1, denoted uncontaminated to moderately contaminated (Fig.2 & 3). Similarly in the case of EF it showed moderate enrichment in most of the samples in Old Town area and deficiency to minimal enrichment in Gnanapuram area (Fig.4).

Rubidium
The Igeo indicated that the soils in both the study areas fall under class ‘0’ which denotes practically uncontaminated (Fig.2 & 3). The EF’s indicated deficiency to minimal enrichment in the soils of Old Town area and significant enrichment observed in Gnanapuram area (Fig.4).

Strontium
Strontium used as reference element due to its low occurrence. Strontium is also one of the main components of the Earth’s crust and its concentration in soil is also connected with some matrix.

Vanadium
The Igeo indicated that the soils in both the study areas fall under class 2 which denotes moderately contaminated (Fig.2 & 3). The EF’s indicated moderate enrichment in the soils of Old Town area and significant enrichment observed in Gnanapuram area (Fig.4).

Yttrium
The Igeo values obtained most of the samples falling into class 1 of uncontaminated to moderately contaminated (28) (Fig.2 & 3); similar to the EF’s, which pointed to be showing deficiency to minimal enrichment of Y in soils of study areas (Fig.4).

Zinc
The average Zinc content in the tested soils was 115.96 mg/kg in Old Town area ranging from76.5 to 164.8 mg/kg and 122.12 mg/kg in Gnanapuram area ranging from 85.4 to 157.7 mg/kg. Comparable contents were found in soils of Pali375 mg/kg, (22,34), rural soils of Vietnam 65.5 mg/kg (40). This is very mobile in soils. The mean Igeo classified the soils in the study areas as uncontaminated to moderately contaminated,with zinc (28) (Fig.2 & 3). The low EF for zinc in soils deficiency to minimal enrichment (Fig.4) may indicate soil depletion in this metal. It has been found that an increase in solubility under low pH conditions affects zinc mobility, and both its transfer to water bearing formations and possible increased uptake by plants under those conditions is reflected in EF values (7). The dependence of EF on the solubility of a given element and hence indirectly on the conditions prevailing in a given environment was also stressed by (34).

Zirconium
The Igeo values obtained most of the samples falling into class 1 of uncontaminated to moderately contaminated (28) (Fig.2 & 3); similar to the EF's, which pointed to be showing moderate enrichment of Zr in soils of study areas (Fig.4).

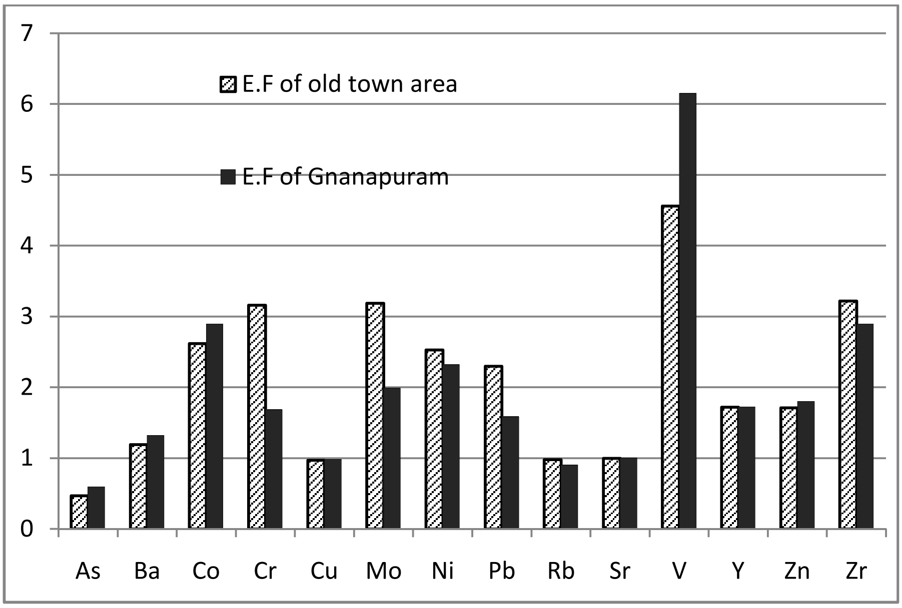

Fig.4. Enrichment Factor chart

In the Old town area the mean Contamination Factor values indicates that, Low contamination factor with As, Cu, Rband Sr. Moderate contamination factor with Ba, Co, Ni, Pb, Y and Zn. Considerable contamination factor with Cr, Mo, V and Zr according to Hakanson (1980) four categories index of contamination factor. (Fig.5)

In the Gnanapuram area the mean Contamination Factor values indicating that,low contamination factor with As, Cu, Rb and Sr. Moderate contamination factor with Ba, Co, Cr, Mo, Ni, Pb, Y, Znand Zr. Considerable contamination factor with V according to Hakanson (1980) four categories index of contamination factor. (Fig.5)

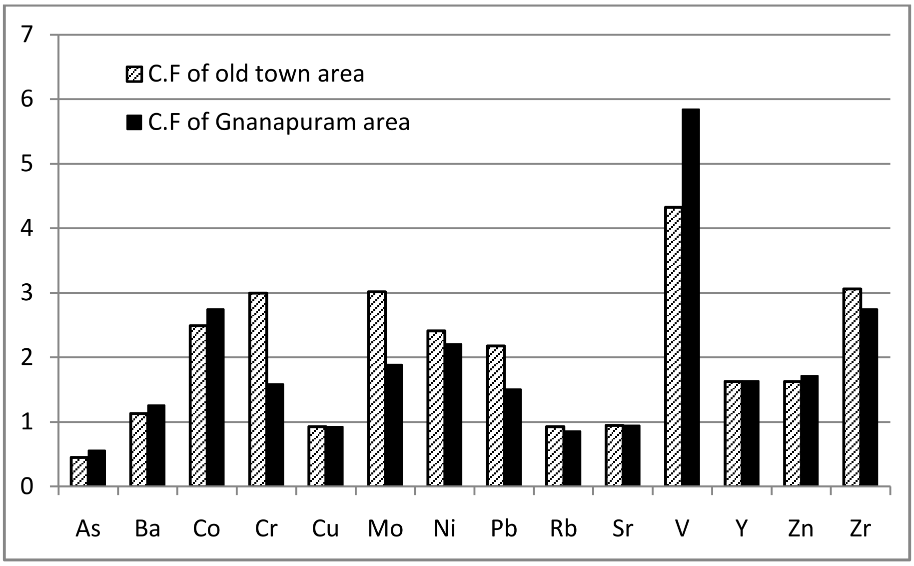

Fig.5. Contamination Factor Chart

Degree of contamination:
The overall degree of contamination observed in the Old town area (28.14) is greater than the Gnanapuram area (26.47) but there is slight variation observed (Table.4). These two areas were under considerable degree of contamination range (17). (Fig.6)

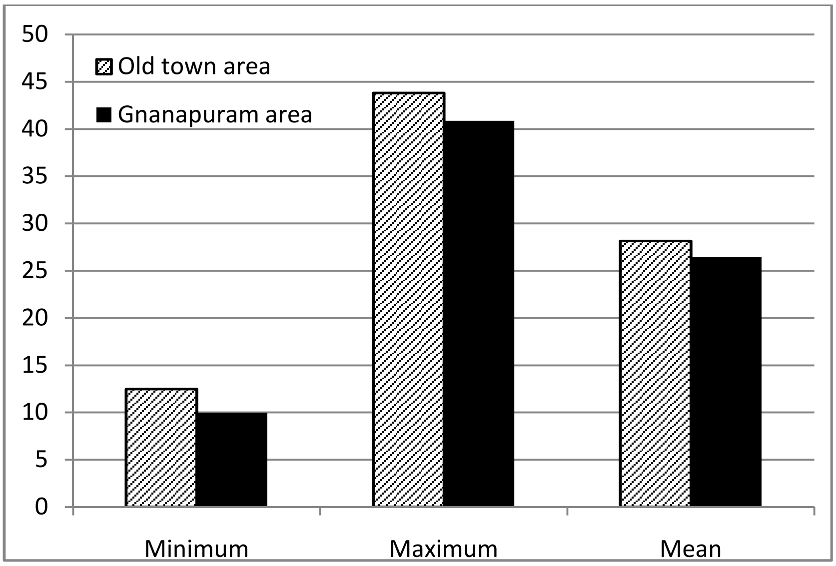

Fig.6. Degree of Contamination Chart

The degree of contamination observed in Old Town area is as follows the order V>Zr>Mo>Cr>Co>Ni>Pb>Y>Zn>Ba>Sr>Cu>Rb>As, high degree of contamination with V and low degree of contamination with As. Where as in the Gnanapuram area the order of elements observed the percentage of degree of contamination with V>Co>Zr>Ni>Mo>Zn>Y>Cr >Pb>Ba>Sr>Cu>Rb>As, high and low degree of contamination elements are V and As same as in Old town area observed. (Table.4)(Fig.7).

Table.4. showing the Degree of contamination values obtained:

Element	Mean (Old town)	Mean (Gnanapuram)	in % (Old town)	in % (Gnanapuram)
As	0.45	0.56	1.60	2.12
Ba	1.13	1.26	4.02	4.76
Co	2.49	2.75	8.85	10.39
Cr	3	1.59	10.66	6.01
Cu	0.93	0.93	3.30	3.51
Mo	3.02	1.89	10.73	7.14
Ni	2.41	2.21	8.56	8.35
Pb	2.18	1.51	7.75	5.70
Rb	0.93	0.86	3.30	3.25
Sr	0.95	0.95	3.38	3.59
V	4.33	5.85	15.39	22.10
Y	1.63	1.64	5.79	6.20
Zn	1.63	1.72	5.79	6.50
Zr	3.06	2.75	10.87	10.39
Deg.Con	28.14	26.47		

CONCLUSION

The application of the index of geoaccumulation, enrichment factor and contamination factor enabled us to find elevated contents of some toxic metals in the study areas viz., As, Co, Cr, Cu, Ni, Pb, V and Zn.Metal depletion in soil of EF< 1 was observed for most elements indispensable to the proper growth of plants may be caused by both leaching of the elements from the soil into water-bearing formations and intensive intake during vegetation period. Both processes take place easily due to the relatively low pH of the soil. Most samples were composed of acidic soil, that acidic pH increases the mobility of toxic elements, which, although are indispensable to the growth of plants, are easily taken in by them may enter the food chain and thus pose a hazard to human and animal health.

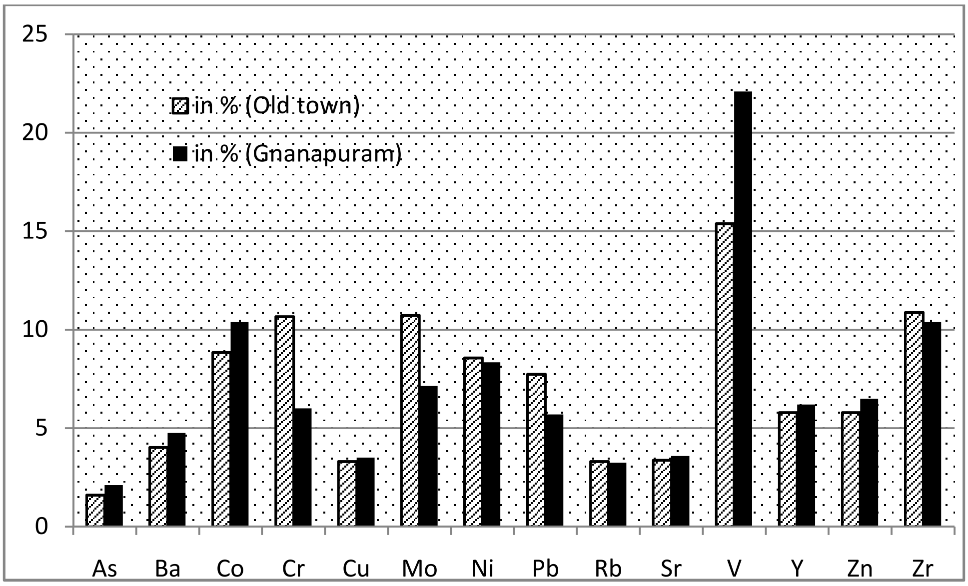

Fig.7. Degree of contamination in % chart

The anomalous concentrationsof Cu, Cr, Co, Ni, Pb, and Zn in the vicinity of the industry are of anthropogenic origin. Copper is characterized by strongly scattered anthropogenic influence. The overall degree of contamination observed in the Old town area (28.14) is greater than the Gnanapuram area (26.47) but there is a slight variation only observed and these two areas were under considerable degree of contamination range.The degree of contamination obtained in the soil samples show that there is a considerable heavy metal pollution, which could be correlated with the industries in the area. Risk assessments based upon soil quality guidelines limits prove that the soil is a serious health risk to humans. It is strongly advised to utilize various remediation technologies like Permeable Reactive Barriers, and Phytoremediation by growing some plants in the area to minimize the rate of contamination, and extent of future pollution problems.

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