Journal of Geology & Geosciences
ISSN: 2381-8719

Olatunji et al., J Geol Geosci 2014, 3:4
DOI: 10.4172/2329-6755.1000160

Research Article Open Access

Geochemical Evaluation of Metal Content of Soils and Dusts of Benin City Metropolis, Southern Nigeria

Olatunji AS*, Asowata TI and Abimbola AF

Department of Geology, University of Ibadan, Ibadan, Nigeria

Abstract

Forty-two (42) composite soils samples and fifty- seven (57) dusts samples were collected from within Benin City metropolis, southern Nigeria. All the samples were air dried, disaggregated and subsequently analyzed to determine the concentration of heavy metals using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The pH, Electrical conductivity (EC) and Total Dissolved Solids (TDS) of the samples were also determined. The pH ranges from slightly acidic to alkaline (5.5-7.1) and (6.0-7.2); EC (37.0-860.0 μS/cm) and (100.0-1437.0 μS/cm) as well as TDS (24.1-559.0 mg/L) and (65-934 mg/L) for soils and dusts respectively. Metals concentration in the soils and dusts are: Cu (4-1125 ppm) and (31.0-210.0 ppm); Pb (9.0-2889.0 ppm) and (40.0-440.0 ppm); Zn (29.0- 10000.0 ppm) and (116.0-729.0 ppm); Ni (2.0-52.0 ppm) and (10.0-28.0 ppm); Sr (4.0-969.0 ppm) and (10.0-196.0 ppm); Cd (Below Detection Limit, Bdl-27.2 ppm) and (Bdl-1.20 ppm); Cr (15.0 ppm-90.0 ppm) and (32.0-64.0ppm) and As (Bdl-6.0 ppm) and (Bdl-4.0 ppm) respectively.

The geochemical and geo-accumulation index maps produced showed large variability in the spatial distributions of elements in topsoil and dusts respectively as well as their pollution status. Further evaluation of the results using contamination indices revealed that Pb, Cu, Zn, Cr, Cd, Ni and As are enriched in soils and dusts obtained from areas with dense human and vehicular population as well as areas with considerable commercial activities.

Keywords: Benin-city; Geochemical; Heavy metals; Geo-accumulation; Contamination indices

Introduction

The mobilization of metals into the atmosphere as a result of anthropogenic activities is an important process in the geochemical cycling of metals. This is more evident in urban areas where various stationary and mobile sources release large quantities of metals into environmental media resulting in elevated concentrations that exceed pre-industrial and pre-urbanization levels.

Potentially toxic metals can be introduced into soils, dusts and sediments by geologic processes (weathering of primary minerals) [1-3] and anthropogenic sources (smelting, gas production, industrial activities, vehicular emissions, agricultural activities, waste disposal, urban effluents and combustion of coal) [4-9].

Thus, knowledge of metal concentrations in urban soils is of critical importance in assessing human impacts on urban environmental media [3,10-13].

In-effective urban-planning, increased and uncontrolled levels of urbanization in addition to continuous industrialization have led to development of unplanned housing districts, traffic congestion and consequent environmental degradation in many Nigerian cities. These processes of urbanization had led to the generation of increased wastes in these cities leading to indiscriminate disposals of solid wastes, household and industrial effluents. All these impair the quality of environmental media and ultimately pose enormous threat to human health. This work was therefore aimed at the determination of quality of some of the environmental media in Benin City by ascertaining the heavy metal contents of the soils and road dusts from the city.

The Study Area and Geological Setting

The study area is Benin City, southern Nigeria. It is defined by latitudes 60 17' to 60 25' N and longitudes 50 33' to 50 43' E (Figure 1). The City is characterized by flat plains in most part of the area and isolated hills in a few places.

Benin City is underlain by the sedimentary sequences belonging to the Niger Delta sedimentary province. Benin Formation [14] underlies the City and it is made up of sands, clayey sands and discontinuous clay sequences [15] (Figure 2). The Benin Formation is made up of reddish earth consisting loose poorly sorted sands underlying recent Quaternary sedimentary deposits of Southern

Nigeria found in Benin City and environs. This characteristic can be recognized in many road cuts in the city, with reddish clayey sand horizons that are covered by light brown to red top-soil [16].

Materials and Methods

To achieve representative sampling, the base map [17] was divided into squared grids. Top soil samples (depth from 0-20 cm) were collected from the four corners and the center of each grid. These samples were sieved on site to remove stones, dirt and organic debris using nylon sieves of greater than 2 mm diameter. The five samples from each grid were then aggregated to form a composite sample for such grid. Road dusts and dusts samples from Petrol filling stations were also collected from major highways within the cities. 42 composite topsoil samples, 52 road dust samples and five (5) samples from Petrol filling station were collected in all.

The soil samples were sieved to determine their grain size distribution in order to classify the soil types. 50 g of soil samples were weighed into a beaker containing 100 ml of distilled water and allowed to soak for 48 hours under room temperature. The pH, electrical conductivity and Total Dissolved Solids of the soaked samples were subsequently measured using a digital hand held meter (each Eco

***Corresponding author:** Olatunji AS, Department of Geology, University of Ibadan, Ibadan, Nigeria, Tel: 234(22)8103168; E-mail: akinadeshadrach@yahoo.com

Received April 21, 2014; **Accepted** May 29, 2014; **Published** June 04, 2014

Citation: Olatunji AS, Asowata TI, Abimbola AF (2014) Geochemical Evaluation of Metal Content of Soils and Dusts of Benin City Metropolis, Southern Nigeria. J Geol Geosci 3: 160. doi: 10.4172/2329-6755.1000160

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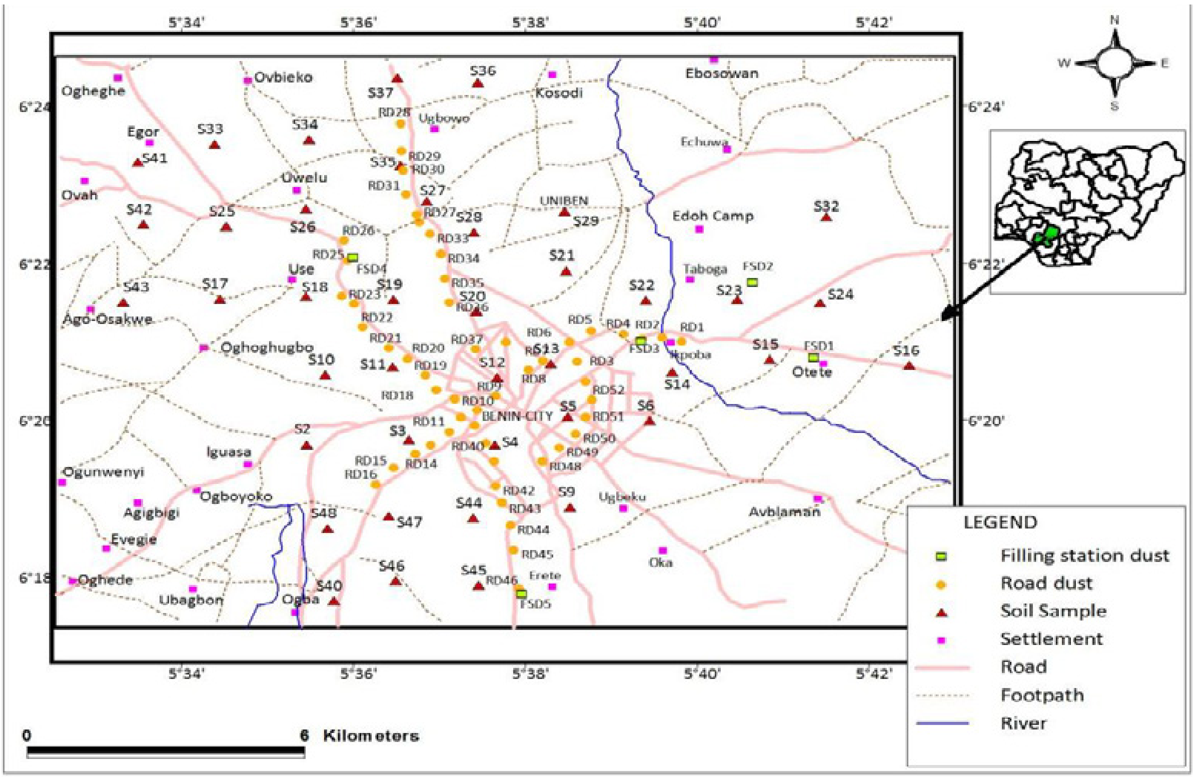

Figure 1: Sample Location map of the Benin City Area.

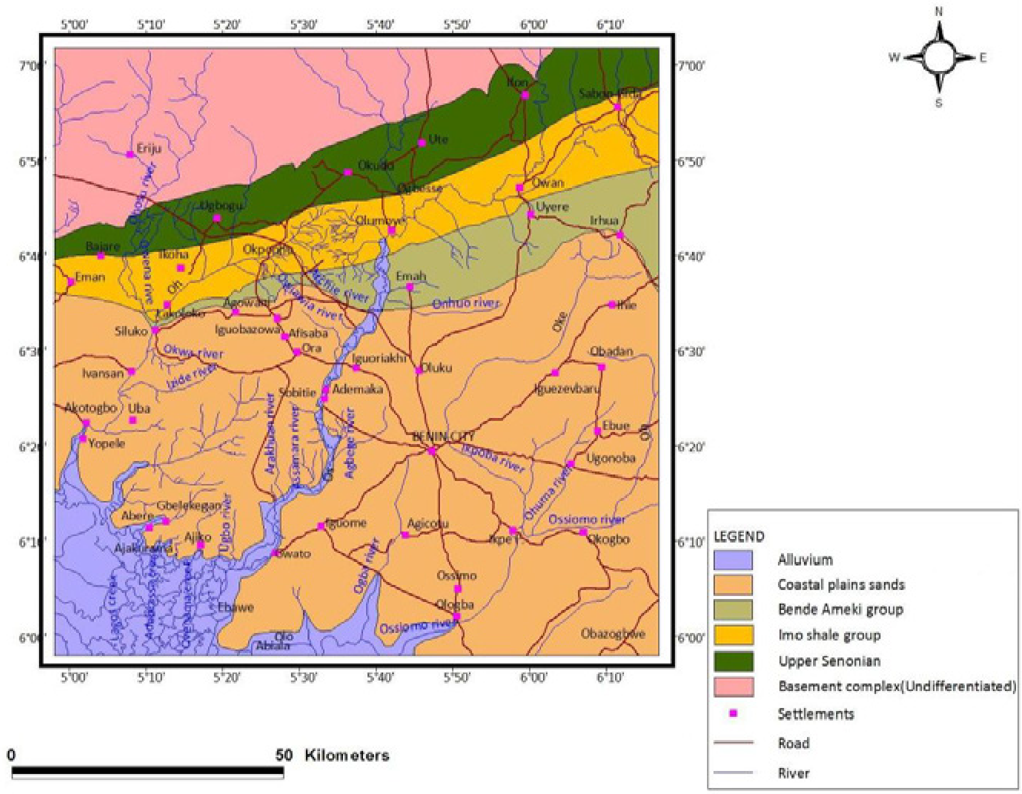

Figure 2: Geologic map of Benin City and Environs [16].

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	Soils		Dusts	
Parameter	**Range**	**Mean**	**Dusts**	**Mean**
pH	5.5-7.1	6.57 ± 0.3	6.0-7.2	6.8 ± 0.3
EC (µS/cm)	37.0-860.0	209.3 ± 1 70.2	100.0-1437.0	311.4 ± 231.6
TDS (mg/l)	24.1-559.0	136.0 ± 110.6	65.0-934.0	202.4 ± 150.5
Cu (ppm)	4.0-1125.0	119.7 ± 217.4	31.0-210.0	81.2 ± 31.6
Pb (ppm)	9.0-2889.0	232.3 ± 488.2	40.0-440.0	111.0 ± 78.8
Zn (ppm)	29.0-10000.0	758.5 ± 1668.8	116.0-729.0	290.9 ± 118.6
Ni (ppm)	2.0-52.0	13.7 ± 11.0	10.0-28.0	15.3 ± 3.9
Sr (ppm)	4.0-969.0	59.6 ± 149.3	10.0-196.0	27.6 ± 26.0
Cd (ppm)	Bdl-27.2	1.5 ± 4.3	Bdl-1.20	0.3 ± 0.4
Cr (ppm)	15.0-90.0	45.3 ± 14.8	32.0-64.0	45.6 ± 6.7
As (ppm)	Bdl-6.0	1.6 ± 1.9	Bdl-4.0	0.2 ± 0.7

Table 1: Statistical summary of the results of selected metals from the soils and dusts of Benin-City. Bdl-Below Detection Limit.

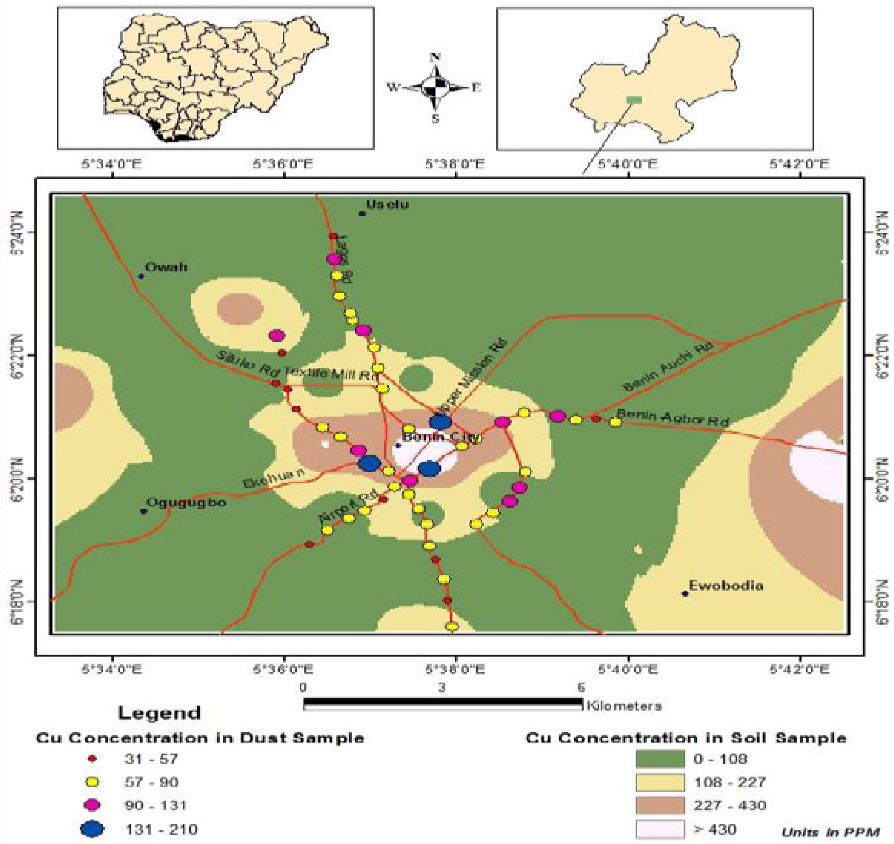

Figure 3: The spatial distribution of Cu in soil of Benin City metropolis.

90 model) capable of measuring the three parameters after proper calibrations using appropriate buffer solutions.

The <75 µm fractions of the samples were subsequently digested using aqua-region, the digests were then analyzed for elemental compositions using the inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Duplicate samples, standard samples as well as blanks were analyzed intermittently to ensure instrumental precision and consistency in results. 53 elements were identified from the analysis of the media; however, only 11 metals that were found to be ubiquitous in all the samples were further evaluated for this study (Table 1).

Results and Discussion

A summary of the results for the physico-chemical as well as the metal content analysis is presented in Table 1. For the soil samples, the pH revealed slightly alkaline to slightly acidic conditions with the values ranging from 6.0-7.2; EC ranges from 100-1437 µS/cm while the TDS ranges from 65-934 mg/l respectively and for the dusts samples, the pH ranges from 6.0-7.2, EC ranges from 100-1437 µS/cm and TDS ranges from 24.0-328.25 mg/L) (Table 1).

Metal distribution in environmental media

The metal concentrations were plotted on the base maps to generate spatial distribution maps in order to establish possible linkages between prevailing urban activities and the metal concentration in the samples (Figures 3-10).

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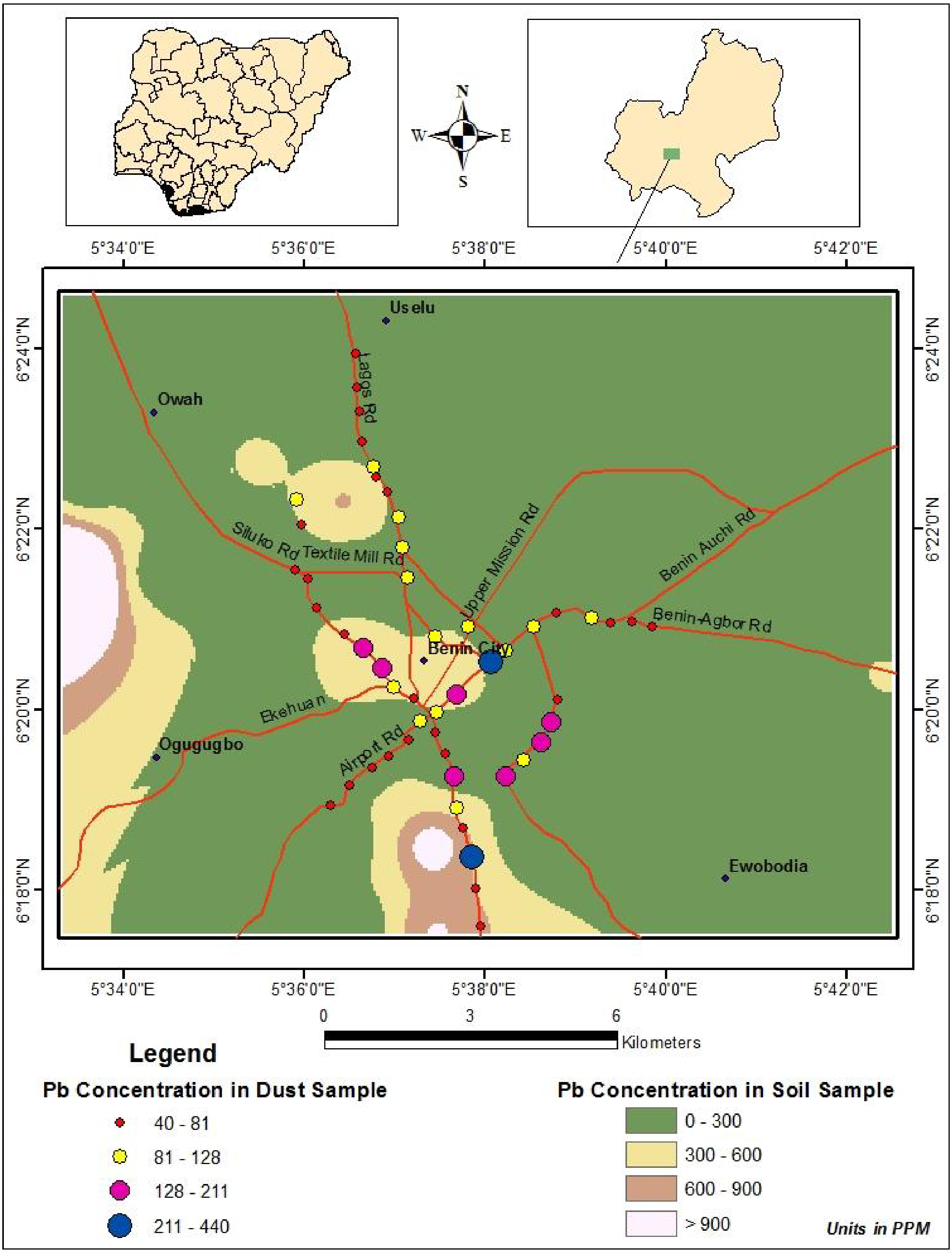

Figure 4: The spatial distribution of Pb in soil of Benin City metropolis.

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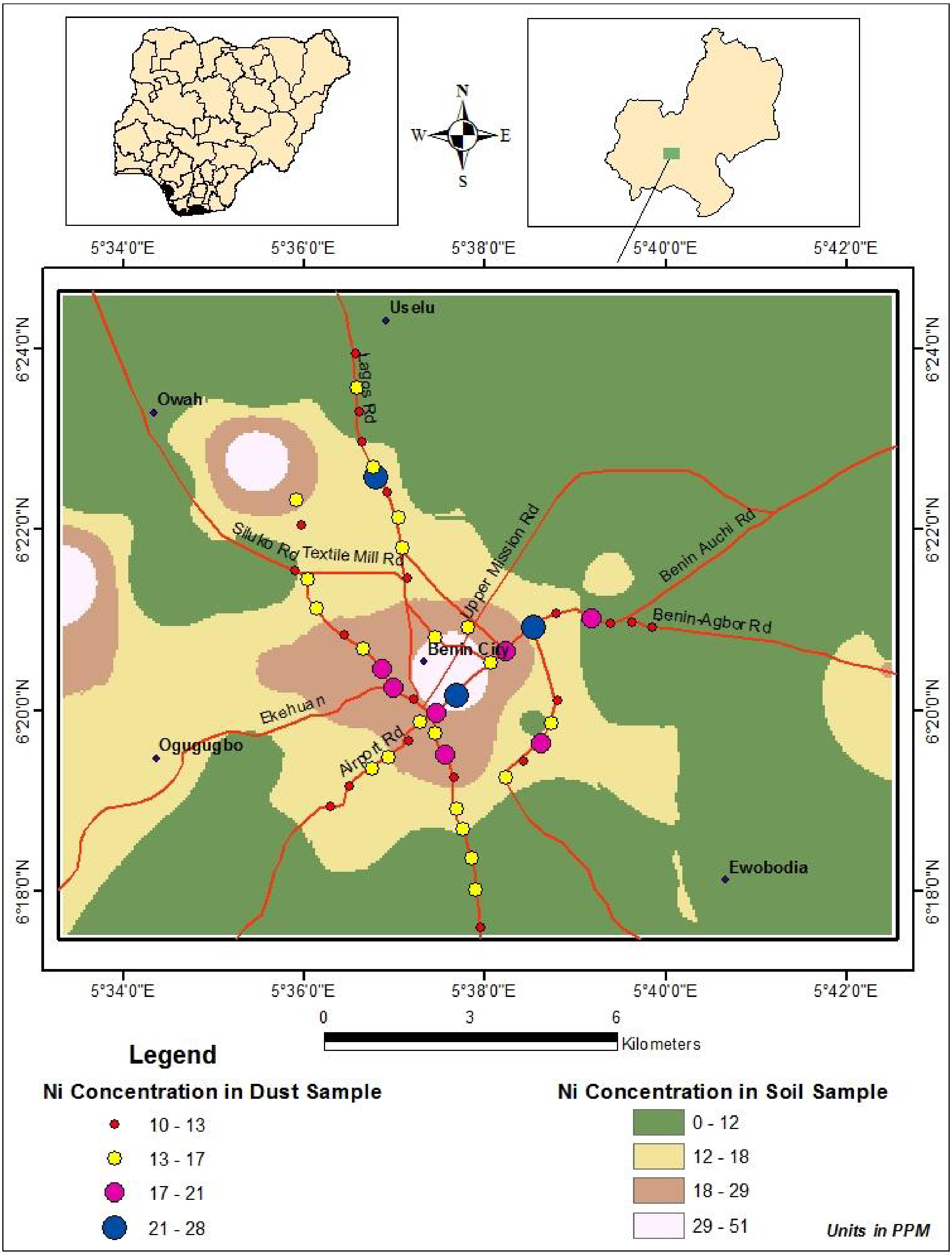

Figure 5: The spatial distribution of Zn in soil of Benin City metropolis.

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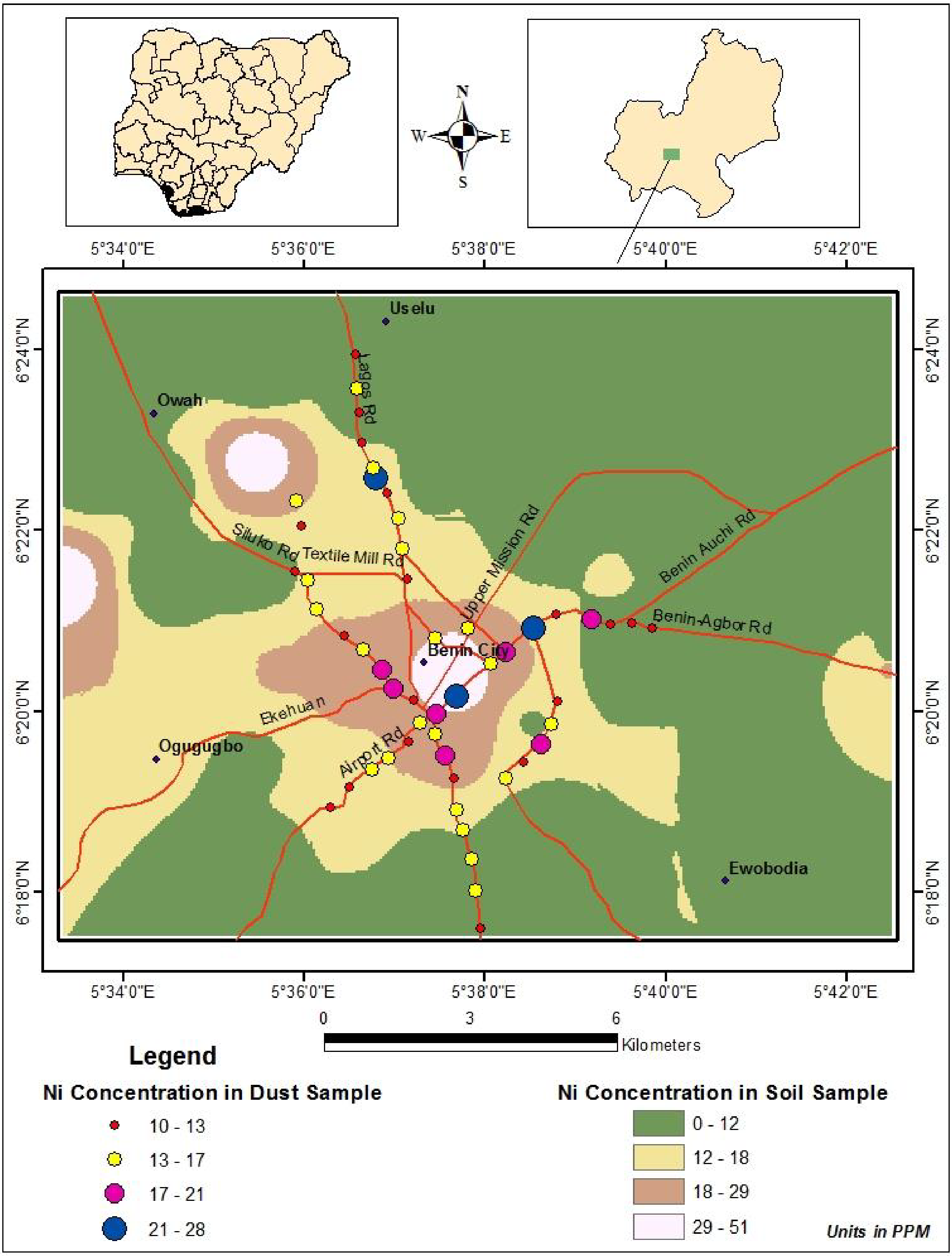

Figure 6: The spatial distribution of Ni in soil of Benin City metropolis.

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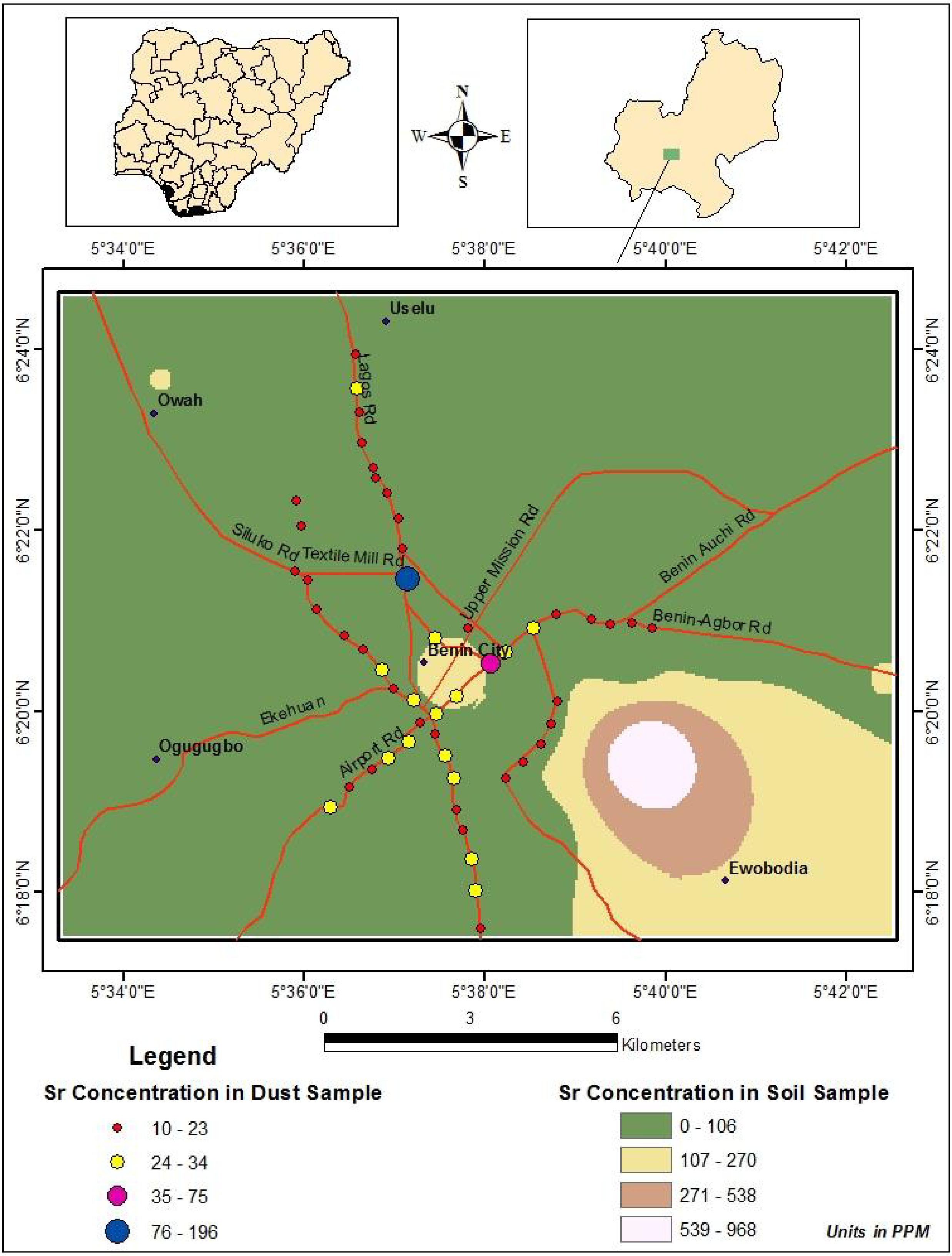

Figure 7: The spatial distribution of Sr in soil of Benin City metropolis.

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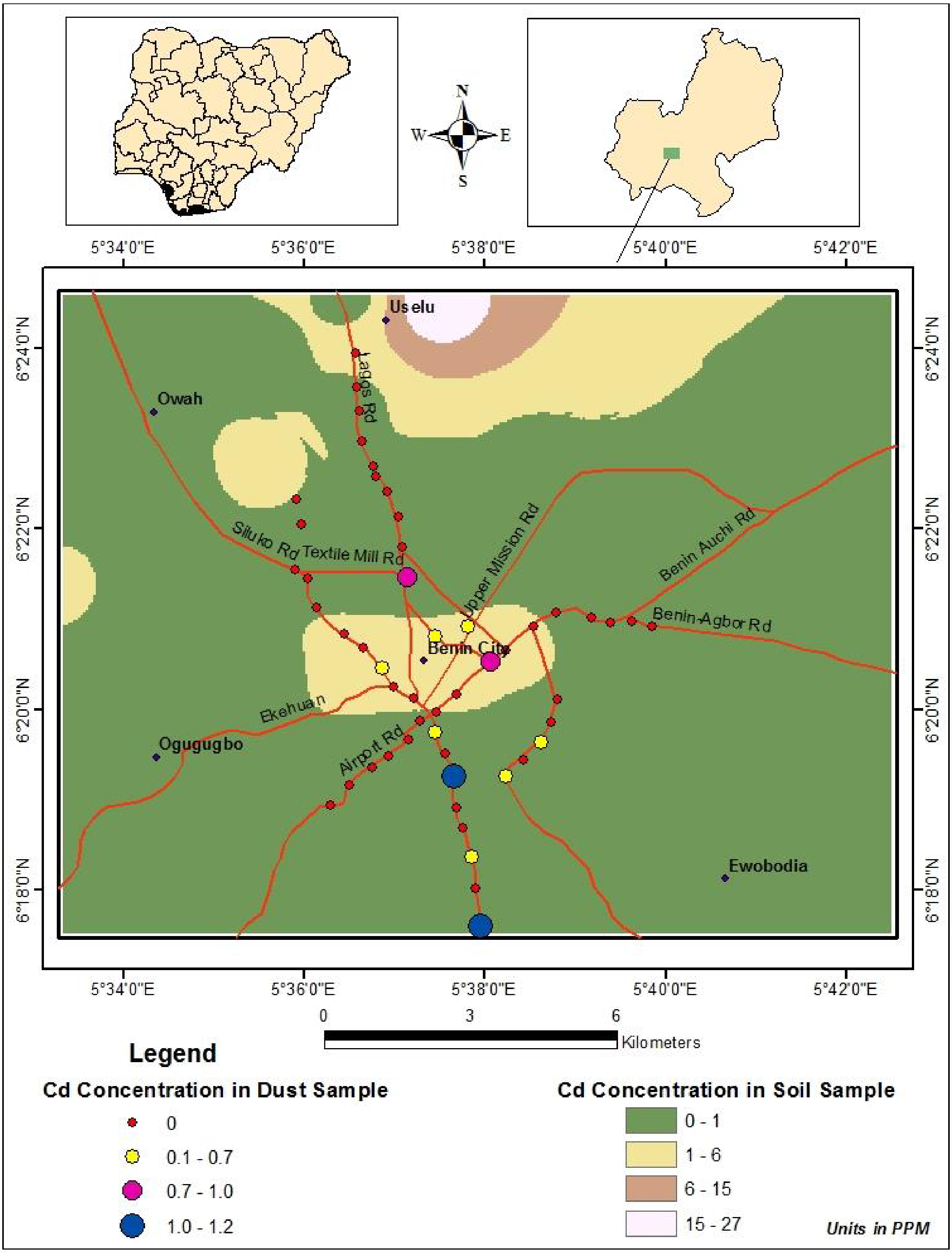

Figure 8: The spatial distribution of Cd in soil of Benin City metropolis.

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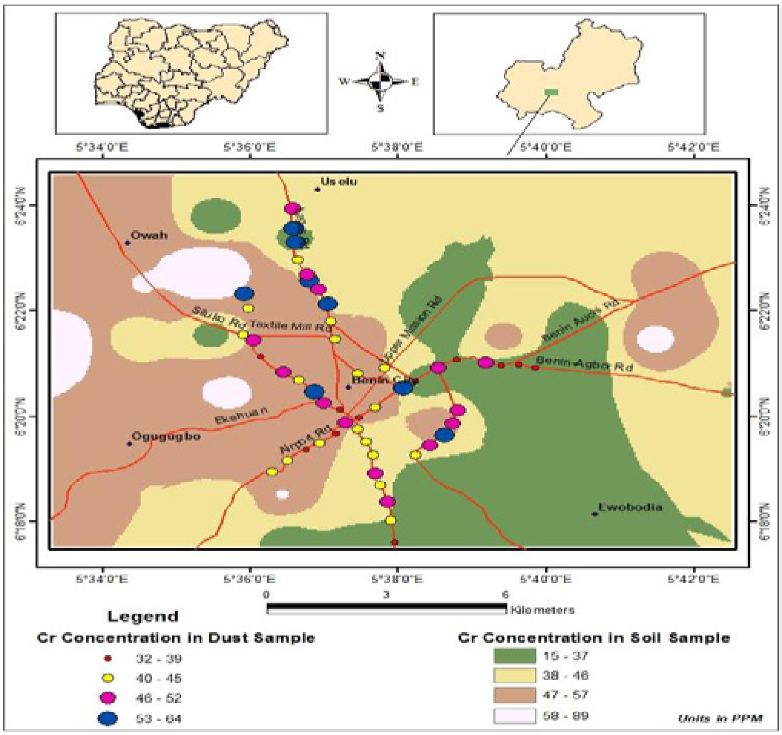

Figure 9: The spatial distribution of Cr in soil of Benin City metropolis.

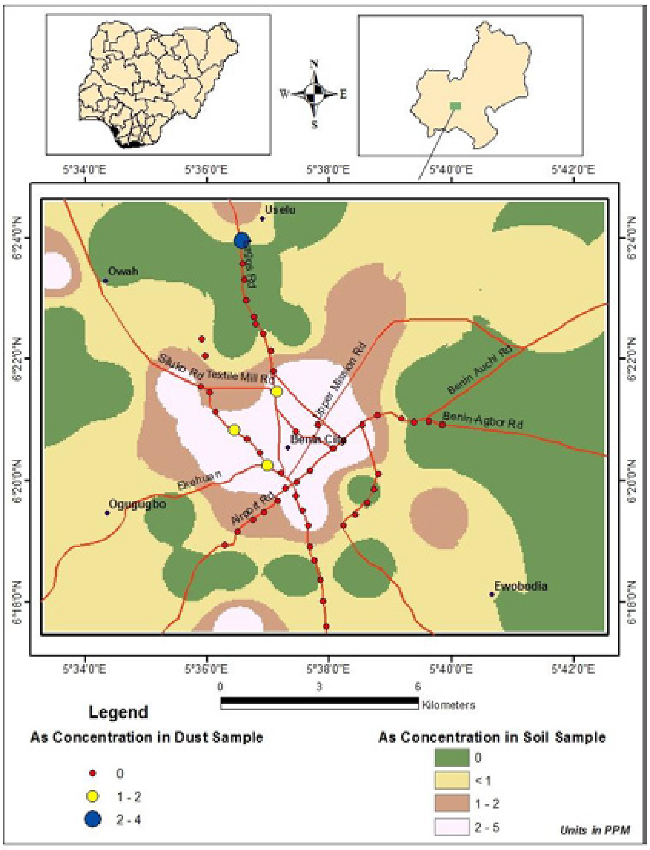

Figure 10: The spatial distribution of As in soil of Benin City metropolis.

Metals(ppm)	Benin City	Ibadan*	UK**	USA**	JAPAN**	Netherland **	Aberdeen***	Uppsala****
As	1.6	3.9	50	41	15	55	NA	NA
Cd	1.5	8.4	3	39	NA	12	NA	0.21
Zn	758.5	228.6	250	2800	150	720	58.5	90.4
Pb	232.3	95.1	300	300	400	530	94.4	24.6
Cr	45.3	64.4	400	1200	NA	380	23.9	37.7
Ni	13.71	20.2	60	420	100	210	NA	21.1

Table 2: Comparison of Average Metal Contents in Soil of Study Areas with soils in other places.
*Odewande and Abimbola, [9], **Chen et al., [4], ***Paterson et al, [30], ****Ljung et al, [1], NA=Not Available.

City	Cu(ppm)	Cd(ppm)	Pb(ppm)	Zn(ppm)	Cr(ppm)	Ni(ppm)
Benin City	81.2	0.3	111	290.9	45.6	15.3
Amman*	177	1.7	236	358	-	88
Aviles**	183	22.3	514	4829	41.6	-
Bahrain**	-	72	697.2	151.8	144.4	-
Birmingham**	466.9	1.6	48	534	-	-
Coventry**	226.4	9	47.1	385	-	-
Hong Kong**	173	3.8	181	1450	-	-
Kayseri**	66.7	10.1	165.5	-	72.8	57
London**	155	3.5	1030	680	-	-
Manchester**	113	-	265	653	-	-
Luanda**	42	1.1	315	317	26	10
Tokat**	38	5.4	266	98	41	128
Xian**	94.9	-	230.5	421.4	167.3	-
Yozga**	37.7	3	69.2	-	32.7	77
Aqaba City**	53	2.5	206	153	36.2	90.5

Table 3: Mean concentration of metals (ppm) in street dust from Benin City and several cities in the world. *Al-Khashman [27]**Al-Khashman [28].

Metals	Soils	Dusts
Cu	0-20	1.0-4.0
Pb	1.0-181	1.0-4.0
Zn	0-52	1.0-3.0
Ni	0-62	5.0-14.0
Cr	1.0-4.0	1.0-2.0
Sr	0-75	1.0-5.0
Cd	0-34	0-1.0
As	0-3.0	0-2.0

Table 4: Summary Enrichment/Depletion Ratio of Trace Metals in the soils and Dusts.

Classes	Ranges	Indications/Soil quality
0	Igeo<0	Practically Uncontaminated
1	0<Igeo<1	Uncontaminated to moderately contaminated
2	1<Igeo<2	Moderately contaminated
3	2<Igeo<3	Moderately to heavy contaminated
4	3<Igeo<4	Heavily contaminated
5	4<Igeo<5	Heavily to extremely contaminated
6	Igeo> 5	Extremely contaminated

Table 5: Geo-accumulation Index Classes proposed by Muller [18].

Metal	Soils	Road Dusts
Cu	1.4-3.9	3.1-3.9
Pb	2.0-4.5	3.1-4.3
Zn	3.6-6.1	4.1-4.9
Ni	1.1-2.5	1.1-1.6
Cd	0.6-1.2	0-0.6
As	0-0.9	0-0.7

Table 6: Summary of the geo-accumulation indices of selected metals in soils and dusts from the Benin City, Nigeria.

The various distribution patterns indicated that considerable elevation in metal concentrations were obtained from areas with dense human population, markets areas, waste dumps sites, industrial zones as well as areas with dense vehicular activities.

Quality of environmental media

The mean concentration of the metals known to be of environmental significance in the soils and dusts of the study areas were compared to metal in soils and dusts from several other cities to ascertain the level of deterioration or otherwise in quality of the environmental media of Benin City (Tables 2 and 3).

The concentration of the selected metals in the soils revealed a steady decline in quality of the soils of the Benin City with average metal concentration greater than those of Ibadan, Aberdeen and Uppsala while the average level of Zn and Cu exceeded those UK and Japan soils (Table 2).

However, the concentration of selected metals in the dusts of the study areas revealed levels below the metal concentrations in the dusts of highly industrialized cities of the world while it compared favorably with cities with comparable level of development and urbanization (Table 3).

The results were further evaluated using some pollution quantification indices such as geo-accumulation index and metal ratio [3,8,9,13,18-24] was also undertaken (Tables 4, 5 and 6) to ascertain the degree of deterioration or otherwise of these media in terms of the selected metals.

Metal ratios

The calculated metal ratios for the metals revealed that the soils and dusts of the study areas have been impacted as observed from their levels of enrichment (Table 4).

Geo-accumulation index

The degree of metal contamination in the soils of the study area was also determined by calculating the calculated geo-accumulation index (Igeo).

Muller [18] proposed series of geo-accumulation classes to quantify the level of metal enrichment in environmental media (Table 5).

The calculated geo-accumulation indexes were then plotted on the base map to generate geo-accumulation index maps showing varied contamination classes (Figures 11-16). The summary of geo-accumulation index for selected metals from the study areas (Table 6) indicated the degrees of contamination varying from practically uncontaminated to extremely contaminated conditions. The distribution of the 'contamination hotspots' within the areas showed that the soils and dusts samples obtained from zones with considerable urban population, vehicular activities, commercial centers and industrial zones have greatly deteriorated in quality (Figures 11-16).

Geochemical Associations of metals

The geochemical results were statistically analyzed using Pearson Correlation and R-mode factor (Principal Component Analysis, PCA) to ascertain the salient relationships that exist among the analyzed metals.

Ni correlated positively with Cu, Pb and Cr with correlation co-efficient of 0.675, 0.537 and 0.653 respectively (Table 7) for the soil samples. For the dusts samples, Zn correlated positively with Ni, Pb, Cd and Sr with correlation matrixes of 0.588, 0.495, 0.735 and 0.541 respectively (Table 8). The relatively low correlation matrixes exhibited among the various metals indicated that the metals had been contributed into the soils and dusts of Benin City from diverse sources except for Ni, Cu and Pb in the soil samples and Zn, Ni, Pb Cd and Sr in the dust samples.

The Principal Component Analysis (PCA) carried out on the geochemical data similarly revealed three groups responsible for 62.7% and 70.3% of the observed variance in the data analyzed for the soils and dusts respectively [25-31] (Tables 9 and 10).

Group one (Component 1) in the soils included Cu, Pb, Ni and Cr while in the dusts it included Cu, Pb, Zn, Ni and Cd accounting for 32.2% and 37.0% of the total variance observed.

Group 2 comprised Zn and As (17.9% of the total variance) in the soils and Sr (19.5% of the variance) in the dusts analyses.

Only Sr was of strong contribution in the third group of the soils analyses while only as was prominent in the third group of the dusts analyses accounting for with 12.6% and 13.9% of the observed variance.

The metals in Group one and two of the soil analysis as well as groups one and three of the dusts analyses are believed to have been predominantly contributed by the various indiscriminate dumping of the wastes from automobile workshops, discharged battery wastes as

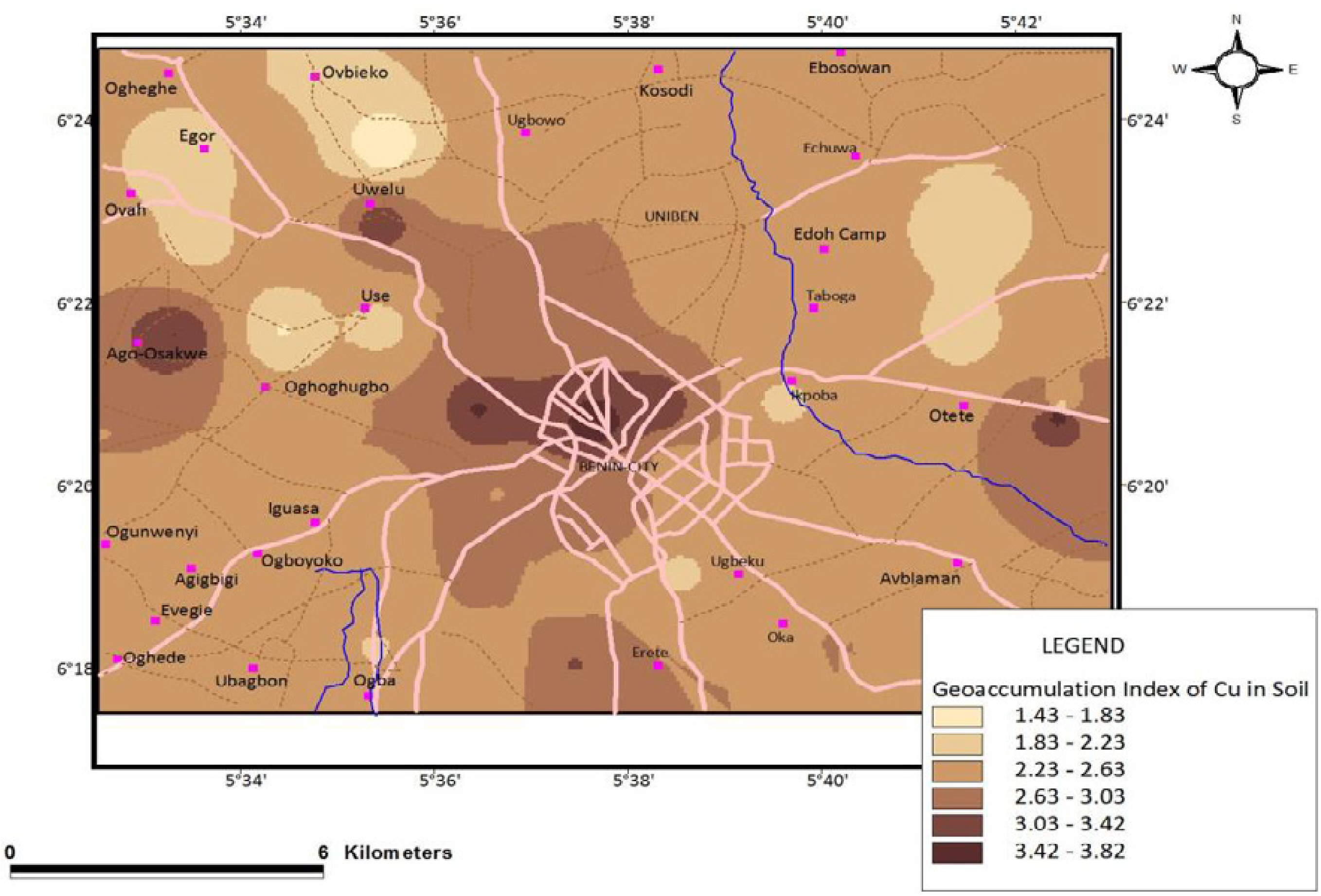

Figure 11: Geo-accumulation Index map of Cu in soils of Benin City.

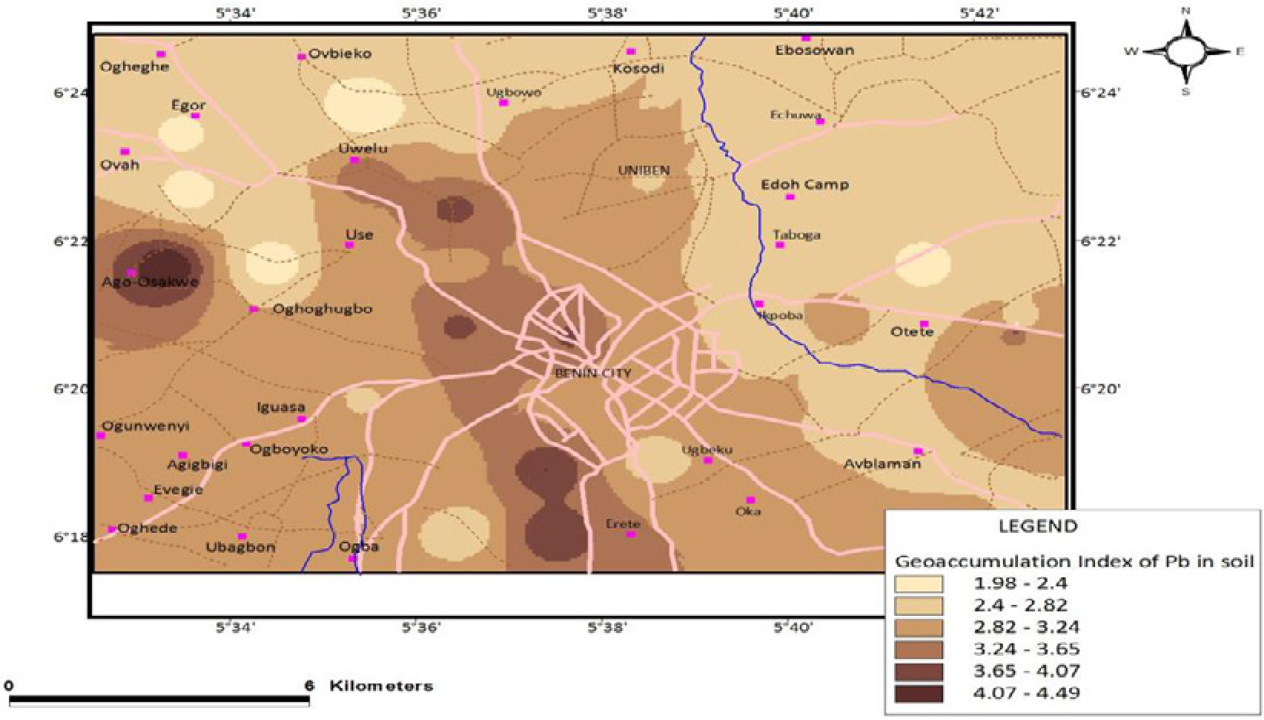

Figure 12: Geo-accumulation Index map of Pb in soils of Benin City.

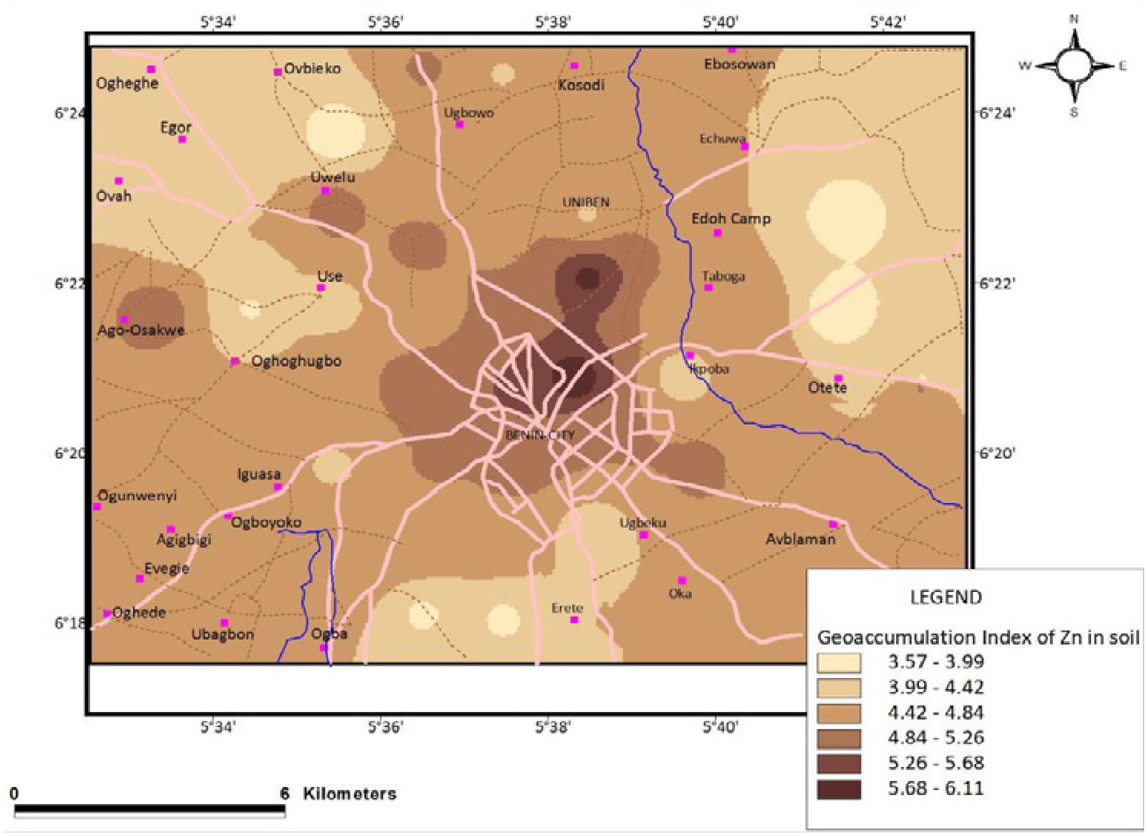

Figure 13: Geo-accumulation Index map of Zn in soils of Benin City .

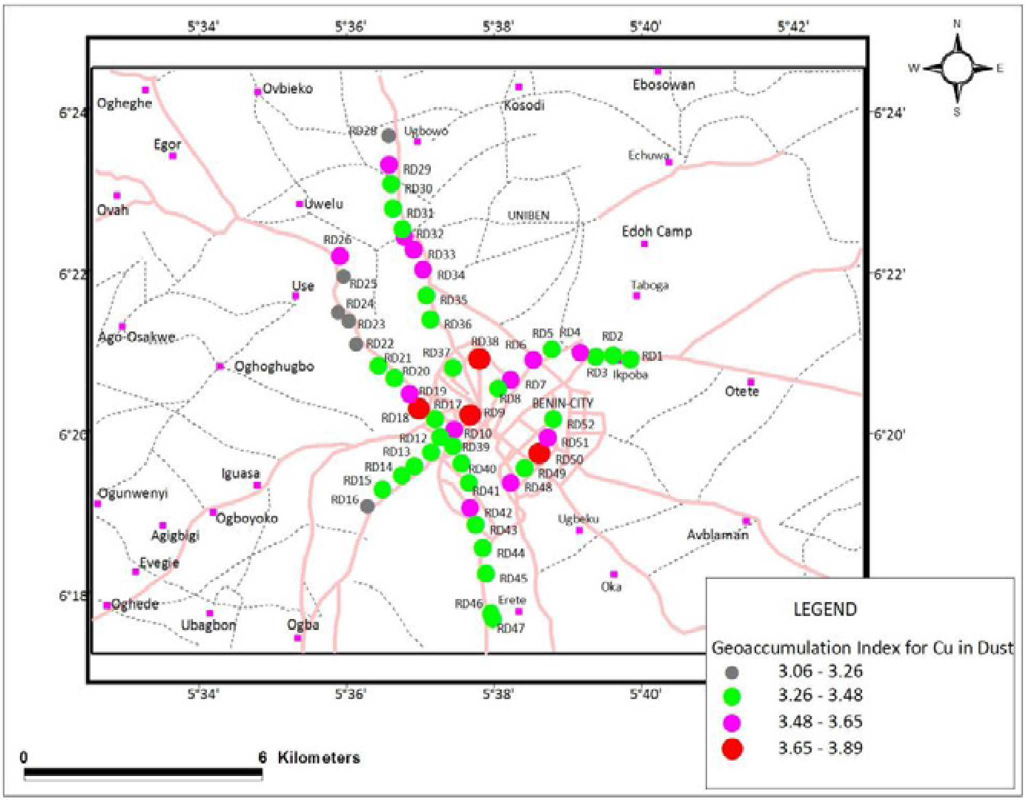

Figure 14: Geo-accumulation Index map of Cu in Dusts of Benin City .

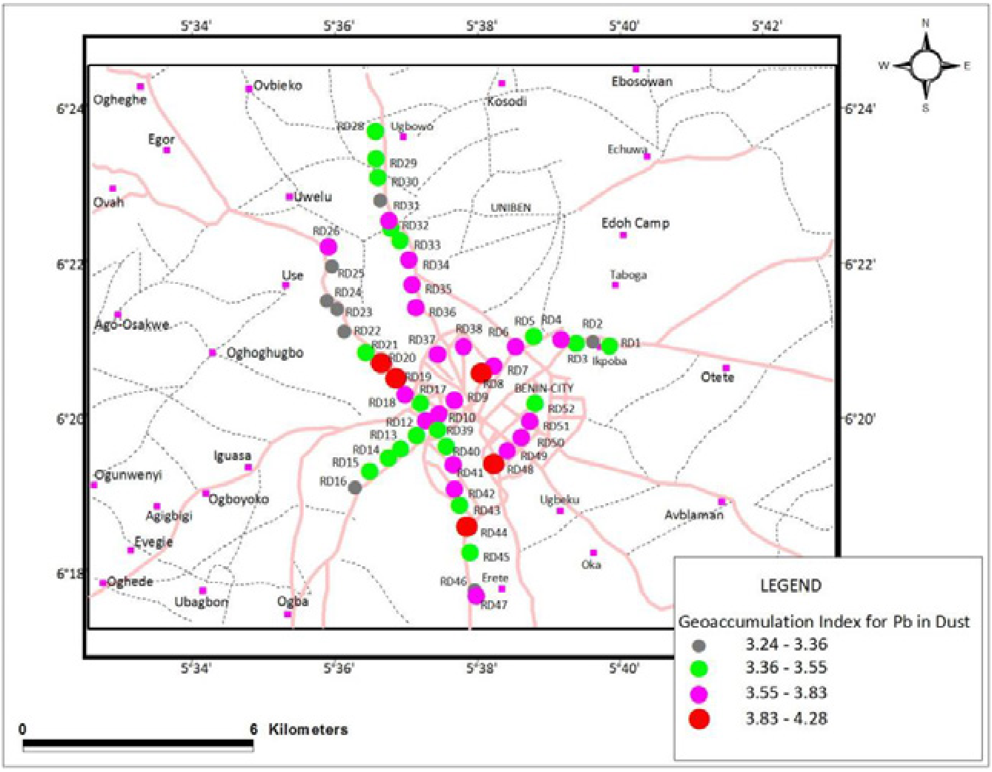

Figure 15: Geo-accumulation Index map of Pb in Dusts of Benin City.

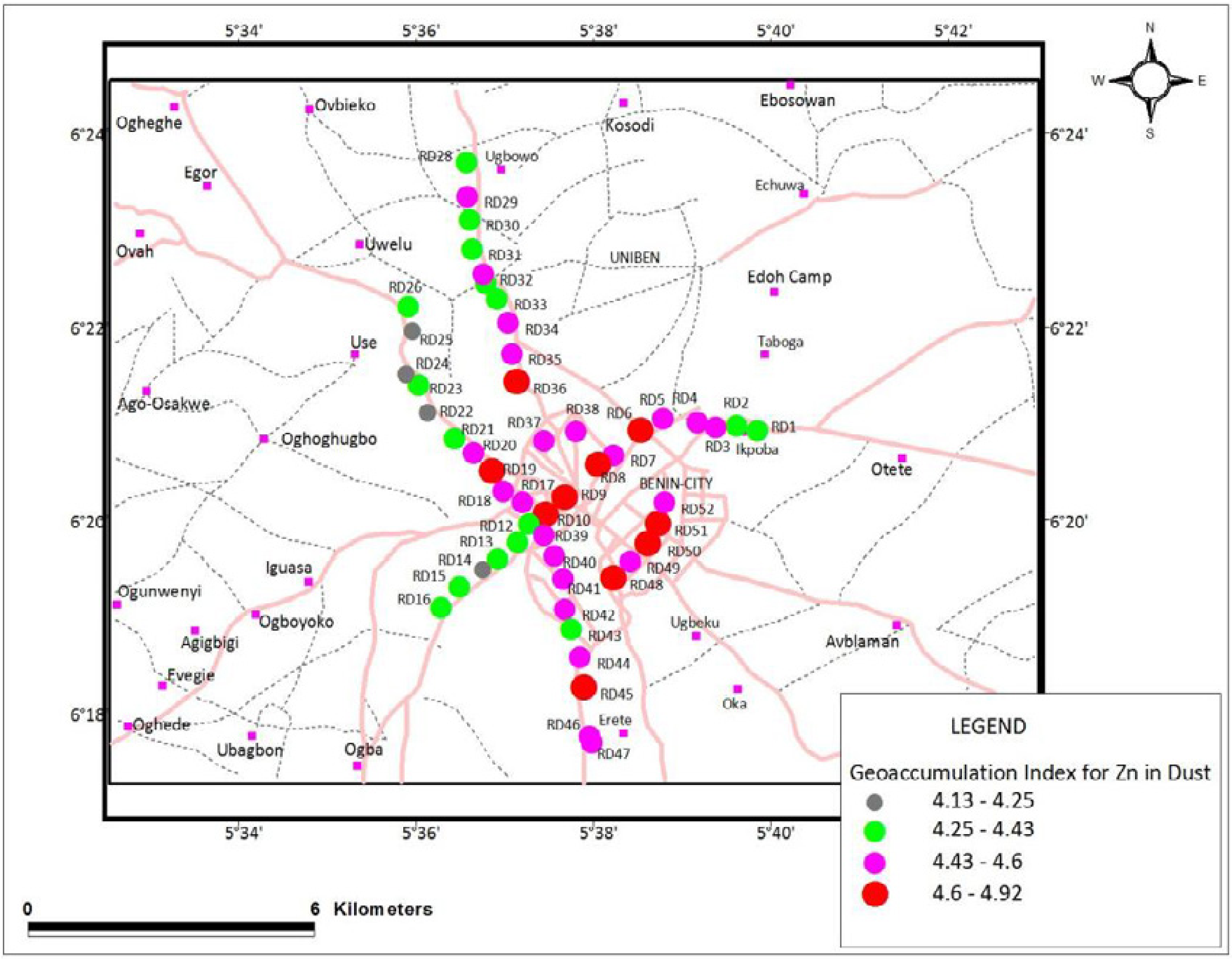

Figure 16: Geo-accumulation Index map of Zn in Dusts of Benin City.

	Cu	Pb	Zn	Ni	Sr	Cd	Cr	As
Cu	1							
Pb	0.404	1						
Zn	0.239	0.05	1					
Ni	0.675	0.537	0.234	1				
Sr	0.17	0.001	0.017	0.167	1			
Cd	0.138	0.062	0.105	0.223	0.029	1		
Cr	0.179	0.343	-0.112	0.653	-0.046	0.097	1	
As	0.147	-0.084	0.357	0.212	0.113	-0.02	0.039	1

Table 7: Correlation Matrix showing inter-elemental relationships for top-soils.

	Cu	Pb	Zn	Ni	Sr	Cd	Cr	As
Cu	1							
Pb	0.266	1						
Zn	0.404	0.495	1					
Ni	0.588	0.238	0.458	1				
Sr	-0.009	0.235	0.735	0.066	1			
Cd	0.098	0.512	0.541	0.164	0.435	1		
Cr	0.275	0.352	0.246	0.278	0.044	0.112	1	
As	-0.031	-0.09	0.059	-0.143	0.284	-0.043	0.098	1

Table 8: Correlation Matrix showing inter-elemental relationships for dusts.

	Component		
	1	2	3
Cu	0.761	0.139	0.139
Pb	0.659	-0.354	-0.021
Zn	0.313	0.711	-0.345
Ni	0.948	-0.06	0.007
Sr	0.192	0.288	0.898
Cd	0.286	0.022	-0.151
Cr	0.618	-0.456	-0.135
As	0.259	0.701	-0.14
Eigen Values	2.6	1.4	1
% of Variance	32.2	17.9	12.6
Cumulative % variance	32.2	50.2	62.7

Table 9: Principal Component Analysis for the Benin City soils.

	Component		
	1	2	3
Cu	0.552	-0.588	0.251
Pb	0.699	-0.026	-0.286
Zn	0.896	0.201	0.013
Ni	0.597	-0.561	0.11
Sr	0.6	0.665	0.106
Cd	0.666	0.326	-0.411
Cr	0.453	-0.299	0.362
As	0.038	0.465	0.799
Eigen Values % of Variance Cumulative % variance	2.9	1.6	1.1
	37	19.5	13.9
	37	56.5	70.3

Table 10: Principal Component Analysis for the Benin City dusts.

well as indiscriminate solid and metallic wastes into the environment; while Sr in group three in the soils analysis and group two in the dusts analysis as well as the lack of significant positive correlation with other metals (except with Zn in the dusts samples) clearly indicated that the Sr in the soils and the dusts had been contributed by principally by lithogenic processes.

Conclusions

This study had revealed that the metal contents of the soils and dusts of Benin City are influenced by the prevailing human activities within the area. It had also further reinforced the notion that urbanization and associated infrastructural development without proper planning, management and sufficient regards for environmental safeguards pose serious threats to the quality of the environment and the society at large.

It has been shown conclusively that the quality of the environmental media (soils and road dusts) in Benin-City has deteriorated principally as a result of indiscriminate discharge of various types of wastes and emissions from automobiles that have resulted from dense human population and unplanned commercial activities; accounting for elevated concentrations and distribution of Cu, Pb, Cd, Zn, Cr and As in the soils and dusts of the city.

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