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# Geochemical Evaluation of Soils and Road Deposited Sediments of Benin City Using GIS and Multi-variance Approaches'

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#### Authors' contributions

This work was carried out in collaboration between all authors. Authors ASO and AFA designed the study. Authors ASO, AFA and ITA performed the geochemical and statistical analysis and managed literature search. Author ITA wrote the protocol, and the first draft of the manuscript. All authors read and approved the final manuscript.

**Original Research Article** 

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#### ABSTRACT

This study was carried out to determine the concentration and sources of trace elements in top soils, road deposited sediments and filling station dusts in Benin metropolis in order to evaluate the effect of increased urbanization on the environment.

Ninety-nine (99) samples were collected from the study area. These samples were air dried, disaggregated and digested using aqua regia. They were subsequently analyzed for metallic ion concentrations using inductively coupled plasma emission spectrometry (ICP-ES). The physico-chemical parameters were determined using appropriate probe to measure the pH, EC and TDS of the soil and dusts samples. GIS and multi variant analyses were used in the interpretation of the data analyzed.

The results of the analyzed topsoil in ppm showed that Cu ranged from 4 - 1125, Pb from 9 - 2889, Zn, from 29 - 5022, Ni, from 2 - 52, Co, from 1 - 12, Mn, from 53 - 132, Cd, from below detection limit (BDL) - 27.2, V, from 17 - 108, Cr, from 15 - 90, Ba, from 6 - 530 and As, from BDL - 6. The pH of the topsoil samples ranged from 5.5 to 7.8, Electrical Conductivity from 37. 0 - 860.0  $\mu$ S/cm, while TDS ranged from 24.0 - 328.25mg/L. The results of the concentrations of these metals in the Road deposited

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sediment, equally showed varied concentrations at different location. The geochemical results of both media are more than the background concentration for most of the elements.

Keywords: Benin City; Geo-accumulation index; Geochemical evaluation; Road deposited sediment.

#### 1. INTRODUCTION

Most cities of the world, especially those in developing countries have continued to experience increase in population, with attendant increase in associated activities without commensurate planning. Rapid urbanization and continuous demand for infrastructural development has direct effect on the environment [1]. These activities include dumping of vehicle related and solid and liquid wastes indiscriminately on the surface of the urban environment. These wastes have negatively led to abnormally high concentrations of metallic ions in soils, air, water, sediment and dust of the urban environment, [2-6].

Studies of heavy metals in ecosystems revealed that many areas near or within urban cities, contain high concentration of these metals. Urban soils and dust serves as sink for metallic ions and other harmful pollutants. These pollutants as they continue to increase, posses great danger to living things because of the non-biodegradable nature and long biological half-lives for elimination from the body [7]. When these pollutants are consumed either directly or indirectly, accumulating in the body causing physiological damage to the body internal system, heavy metal poisoning and acting as cofactors in many other diseases [9-13].

The distribution of metallic ions in urban soils and their relationship to soil pollution, bedrock composition, mining activities, Industrial and land use have been assessed by several authors [14-21]. The works of these authors concluded that there is the need to institute a systematic and continuous monitoring of metallic ions and other forms of pollutants and problems associated with the quality of environmental media. Their study also indicated that urban soils have elevated concentrations of Cd, Cu, Pb and Zn, high metal concentrations are located in old urban commercial districts and industrial areas.

Many developed countries in the world have continued to pay attention to the environmental problems associated with urban growth and the relative increase in activities through urban geochemical mapping; examples are the Europe, Asia, and America countries [22-25]. In Nigeria, research works have been carried out in cities like Ibadan, Warri, Abeokuta and Lagos [19,26]. Most of these past works in Nigeria major cities have been limited to metallic ions concentration in soil or sediments excluding road deposited sediments which is done in this present study and none of the work has been carried out in the study area.

Benin City, one of the major cities in Nigeria, has continued to witness population explosion with over 1,531555 million in population [27] in last decade with little or no infrastructural developmental planning. This has led to increase in solid and liquid waste generation, indiscriminate refuse disposal, machinery and vehicular exhausts that come from fuel combustion and emission, particulates from wear and tear of tires, automobile bodies and break lining [21]. All these can be harmful to the human system as the concentration increases to intolerable limit.

Studies have also revealed the use of Geographic Information System (GIS) which is a computer system package that can capture, store, check, integrate, manipulate analyses as well as help to display information geographically with references, are now being used to delineate metallic ions concentration and distribution in the environment, [28,29]. [19-21], have also used factorial and indicator krigging methods with GIS package to overlay and delineate the variations and pollution sources of soils metallic ions in the urban cities. From the result, the short and long-range variations and soil pollution by Cd, Pb, Zn, Cu, Mo, Ni, As Mn Cr and B was as a result of the land use pattern of the investigated area. Several hot spots of metal concentration were identified from the composite metal geochemical map, mainly in industrial areas as well as areas with high population density and vehicular activities.

This study therefore is aimed at investigating the concentration of metallic ions in topsoil and road deposited sediments (RDS) within the developed area of the city and infers the sources and implication of these metallic ions on the populace. With respect to ecotoxicity, it is apparent that Cu, Pb, Zn, Ni, Co, Mn, Cd, V, Cr, and As is of particular concern in Benin city, hence the reason for the selection of these metals.

# 2. MATERIALS AND METHODS

## 2.1 Geology of the Study Area

The study area lies between latitudes 6° 17' to 6° 25' N and longitudes 5° 33' to 5° 43' E within the Niger Delta Basin, Southern Nigeria. The total area coverage is about  $261 \text{km}^2$  and with a population growth of 301,862 in 1963 to 1,289540 in 2000 [30]. At the moment the population of the area is estimated to be of about 1,531555million [30].

The area is characterized by undulating relief and visibly drained by two rivers, lkpoba and Ogba flowing from the northeast and northwest to the southern part of the city respectively, Fig. 1.

Benin City is underlain by sands, clayey sands and discontinuous clay sequences of Benin Formation of the Niger delta Basin, [30] Fig. 2. The Benin sands are generally loose poorly sorted reddish clayey sands lacking proper bedding structures). In Benin City, the sand thickness is on average of about 800m, with high water bearing capacity, [29]. The sand is generally believed to be highly permeable, porous and prolific in water yields, [29,30].

The study area was divided into grids  $(1.9\text{km}^2)$  with the aid of topographic map (sheet 298) of Benin, on a scale of 1: 100,000. Composite topsoil samples (0 - 20cm) were collected at a sampling density of five samples per grid of  $1.9\text{km}^2$ . Such a sampling strategy was adopted in order to reduce the possibility of random influence of urban wastes that are not clearly visible. While the road deposited sediments (RDS) samples were collected on both main roads and minor roads at the city center at interval of 500m. The topsoil sampling was carried out using a stainless steel hand auger and stored in a plastic bucket before aggregation. The composite topsoil samples were sieved in the field and stored in the polyethylene bags and labeled, 42 composite topsoil samples and 57 road deposited sediments (RDS) samples. The already air- dried topsoil samples and RDS samples were sieved through a <0.75µm polyethylene sieve to remove roots, coarse materials, stones and other unwanted debris. 0.5g of each sample was digested using aqua regia for 2 hours at 950C.

analyzed using inductively coupled plasma emission spectrometer (ICP-ES) at the Geochemical Laboratory of the Activation Laboratories' Limited Ontario, Canada, while the physical chemical analyses were done with a standard pH meter (JEWWAY 3150 MODEL).



Fig. 1. Location map of benin city showing the sampling points



Fig. 2. Geologic map of benin city and environs [32] sampling

#### **3. RESULTS AND DISCUSSION**

#### 3.1 Geochemistry of the soils

Metals concentration in the top soils ranges from Cu (4 – 1125 ppm), Pb (9 - 2889 ppm), Zn (29 - 5022 ppm), Ni (2 - 52 ppm), Co (1 – 124 ppm), Mn (53 – 132 ppm 7), Cd(BDL – 27.2 ppm), V (17 – 108 ppm), Cr (15 – 90 ppm), and As (BDL – 6 ppm), (Table 1) The average result of the metallic ion concentration observed, showed a decreasing order of magnitude, Zn > Pb > Mn > Cu > Co > V > Cr > Ni > Cd > As. The high concentration of Zn, Pb, Cu, and Mn metals in several locations could be linked to several human activities which include indiscriminate dumping of solid and liquid waste, and vehicular activities. High Zn concentration occurs around areas very close to waste dump site, abattoir, and metal scraps

dump site as well as erosion prone areas. These areas include Upper Lawani/ Okhoro areas, Oko/ Airport road area, Etete/ Ogba areas, Oregbeni Barack and Uwelu market areas. While high concentration of Cu and Pb are found to be high in Ago Osakwe and New Benin areas, characterized by mechanic activities and major markets. Ni, Co and Mn metals are found to have high concentration around the city center; Table1 shows the summary result for soil. Comparing the observed concentration of elements with the back ground (BGD) values which was sample collected at isolated area from the urbanized area, it was found that the concentration of element in the soil where far higher in all the sampling points than the BGD values. Geochemical maps produced using the (Arcview GIS) modeling through geostatistical interpolation show spatial distribution of some of these metals across Benin City Figs. 4(a-g). The maps showed the distribution pattern of selected metals in the study area are being influenced by various urban activities in the adjoining areas. These include commercial activities, domestic waste, population influence, wear and tear of vulcanized rubber tires as well as settlement pattern.

Pearson's correlation (statistical) matrix was used to ascertain the level of relationship between the metals in the topsoil samples. The inter-elemental relationship for the data obtained for the topsoil geochemical analysis revealed a strong direct relationship between Ni and Cu, (0.68), Ni and Pb (0.54), Mn and Ni (0.61), Ni and Ba (0.72), Cr and Ni (0.66), Cr and Mn (0.58). The correlation of these elements is an indication of possible relationship between them.

The results were further analysed with R- Mode factor statistical method, (Table 3) to ascertain the relationship among the various metallic ions in the topsoils. The summary of the results is presented in Table 3. It revealed five groups. The first group are made up of Cu, Pb, Ni, Mn, Sb, Cr and Ba, which accounted for 20.5% variance of the variables with Eigen value of 4.4. their association show elements with characteristics of hydrated oxides and are from common source most likely from municipal waste and automobile activities. These element also show strong correlation within the group as illustrated in Figs. 3 (a-c). the second group, Th, Cr and V accounted for 20.1% of the total variance with an Engen value of 3.0. These elements are believed to have been from alloys in chemicals and other domestic waste. The third group is Zn and Co. these also show strong correlation as illustrated in Figs. 3(a-c) and Table 2(a) of the correlation matrix showing same source. The element may have been from metallic waste from rust metals. The forth and fifth elements are Sr, and Cd respectively. The elements independently may have come from washed down vulcanized products such as tyres, brake linings as well as chemicals from vehicle body parts and dye products in the environment that may have been transported.

	Road deposited sediments (RDS) n = 52			(RDS)F	BGD 1	Т	op soil N =	ρ soil N = 42			
	Min (ppm)	Max (ppm)	Mean (ppm)	Min (ppm)	Max (ppm)	Mean (ppm)		Min PPM	Max	Mean	
Cu	31	210	80.94	68	96	86.6	55	4	1125	119.74	10
Pb	40	440	100.92	121	402	195.2	65	9	2889	232.31	16
Zn	116	729	279.92	315	443	392	192	29	5022	533.10	173
Ni	10	28	14.87	15	21	19	2	2	52	13.71	10
Со	2	5	2.83	3	4	3.4	2	1	124	7.29	2
Mn	119	708	229.62	230	268	253	159	53	1327	425.29	217
Cd	0.5	1.2	0.74	0.5	1.2	0.78	.8	0.5	27.2	3.01	.8
V	23	44	30.56	28	40	34.8	44	17	108	53.67	23
Cr	32	64	45	43	57	48.8	57	15	90	45.26	24
As	0.0	4.0	1.1	0.0	3.2	09	.2	0.0	6.0	1.6	.2
PH	6.3	7.2	6,7	6.5	7	6.7	-	5.5	7.1	6.5	-
EC	100	1437	768.5	110	436	273	-	37	860	209.2	-
TDS	65	934	499.5	71.5	283.5	177.3	-	24.05	559	136	-

Table 1. Summary of trace elements concentration top soils and road deposited sediments (RDS) of Benin City

BDG: Back ground concentration of element for both topsoil (BDG2) and RDS (BDG1)

(a)									
	Cu	Pb	Zn	Ni	Со	Mn	Cd	V	Cr
Cu	1.00								
Pb	0.41	1.00							
Zn	0.27	0.17	1.00						
Ni	0.68	0.54	0.36	1.00					
Co	0.12	-0.01	0.93	0.07	1.00				
Mn	0.41	0.14	0.15	0.61	-0.01	1.00			
Cd	0.02	0.00	-0.06	0.08	0.00	0.04	1.00		
V	-0.11	0.01	-0.19	0.15	-0.22	0.51	-0.14	1.00	
Cr	0.20	0.34	0.07	0.66	-0.17	0.58	0.03	0.74	1.00
(b)									
	Cu	Pb	Zn	Ni	Со	Mn	Cd	V	Cr
Cu	1.00								
Pb	0.32	1.00							
Zn	0.48	0.54	1.00						
Ni	0.68	0.31	0.49	1.00					
Co	0.33	0.27	0.59	0.42	1.00				
Mn	0.26	0.40	0.87	0.28	0.58	1.00			
Cd	-0.19	-0.04	0.34	-0.06	0.39	0.40	1.00		
V	0.30	0.35	0.45	0.39	0.47	0.34	0.17	1.00	
Cr	0.42	0.43	0.38	0.49	0.18	0.33	0.04	0.66	1.00
				Significant	Level: 0.50	)			

 Table 2. (a and b) Correlation Matrix showing inter-elemental relationships for top soils and RDS

The degree of metal contamination in the soils of the study area was also determined using the calculated geo-accumulation index (Igeo), with the formula expressed as,  $I_{neo}=Log_2Cn/1.5B_n$  and a classification of (0 - 6) (Muller, 1979). This method has been adopted by several workers in the assessment of the degree of metal accumulation in the soils and sediments (Singh et al., 1997, Singh, 2001). The geo-accumulation indices (Igeo) map was used for the interpretation of the top soils which is Shown in Figs. 5(a-d). Four of the metallic ions were used to evaluate the degree of contamination of the environment, they include; Pb, Zn, Ni and Cu for the top soils. The evaluation of these results on the basis of the Igeo classification carried out in the study area for the top soils indicates that Cu was graded to be uncontaminated to moderately contaminated (1.43 - 3.82) in some locations, Ni was classified to be uncontaminated to moderately contaminated (1.12 - 2.54). Pb was classified to be moderately contaminated to heavily contaminated (1.98 - 4.49) in some locations as well. However, Zn was the only metallic ion that was seen to have high contamination index of Zn in all the area study for the topsoil (3.57 - 6.11). This may be connected to greater influence of urbanization and its corresponding environmental poor practices being experienced in Benin City. The contamination index for the different locations in the study area revealed that the heavily built-up areas, places close to high waste dump, market environment, Abattoir as well as motor parks were noticed to be with high level of metallic ion contamination. These selected metallic ions all have almost the same trend of metal enrichment with the core city center as it is been imaged in the geochemical maps.

	Topsoils						Road Deposited Sediments					
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5		
Cu	.759	235	200	.003	083	.422	.364	206	642	109		
Pb	.610	009	358	408	193	.663	.183	369	.207	160		
Zn	.346	633	.649	079	.007	.893	231	086	182	046		
Ni	.925	.045	064	018	.037	.426	.384	111	694	059		
Со	.224	617	.698	103	.015	.684	015	.534	127	150		
Mn	.638	.336	.169	.469	.116	.797	465	.080	030	.032		
Cd	.228	148	095	035	.931	.422	.364	206	642	109		
V	.152	.858	.376	.007	.028	.663	.183	369	.207	160		
Cr	.605	.665	.163	130	.085	.893	231	086	182	046		
Eigen total value	4.434	3.146	1.775	1.328	.987	4.476	2.179	1.889	1.468	1.192		
% Variance	29.558	20.973	11.836	8.855	6.583	29.839	14.526	12.591	9.787	7.949		
% Cum Variance	29.558	50.532	62.368	71.223	77.806	29.839	44.365	56.956	66.743	74.692		

Table 3. R-mode factor analysis for metallic ions in the topsoil and road deposited sediment in the study area



(c) Scatter plots of V vs. Cr in topsoil

(d) Scatter plots of Cu vs. Ni in RDS



(e) Scatter plots of Zn vs. Mn in RDS

Fig. 3(a-e). Relationship plot between some of the trace elements in the Benin city top soils and RDS



Fig. 4(a-g). Geochemical map of elemental concentration in Top soil of the study area, a: Cu, b: Pb, c:Zn, d: Ni, e: As, f: Cr, g: Cd



Fig. 5(a-d). Geo-accumulation index map of Benin City topsoil; (a) Pb, (b) Zn, (c) Ni, (d) Cu

#### 3.2 Geochemistry of the Road deposited sediments (RDS)

Concentration of the metals in the RDS ranges from Cu (31 - 210 ppm), Pb (40 - 440 ppm), Zn (116- 729 ppm), Ni (10 – 28 ppm), Co (2 – 5 ppm), Mn (119 – 708 ppm), Cd (0.5 – 1.2 ppm, V (23 - 44 ppm), Cr (32 - 64 ppm), The results also indicate the following order of decrease in the magnitude of metal concentration in the analyzed RDS samples: Zn > Mn >Pb > Cu > Cr > V > Ni > Co > Cd. While that of the filling station samples of RDS are as follows, Cu ranges from (68–96ppm), Pb (121–402 ppm), Zn (315- 443ppm), Ni (15 – 21 ppm), Co (3 –4 ppm) Mn (230 – 268 ppm), Cd (0.5 – 1.2 ppm), V (28 – 40 ppm), and Cr (43 – 57 ppm). The results also indicate the following order of decrease in the magnitude of metal concentration in the analyzed road deposited sediments samples (RDS); Zn > Pb > Mn > Cu > Cr > V > Ni > Co > Cd. From the geochemical results, high concentration of Cu, Pb and Zn in samples fall in locations within the ever busy Akpakpava road as well as the New Lagos road with high traffic activities. Also, high concentration of other elements in RDS are found mainly along the high traffic density areas of the city compared to light or medium traffic density roads Figs. 6(a-f). The geochemical result of the road deposited sediment when compared with the back ground sample (BGD), which was collected from an isolated area without any influence of vehicular activities at the outskirt of the study area, it was found to have very low concentration of the observed elements than all other sample location in the study area (Table 1). This shows that urban and its related activities have great influence on the elevation of element in the study area, which include commercial activities, domestic waste, machine shops, exhaust emission, wear and tear of vulcanized rubber tires. The correlation matrix of inter-elemental relationship for the data showed a strong direct relationship between Ni and Cu, (0.68), Zn and Pb (0.54), Mn and Co (0.58), Co and Zn (0.59), Mn and Zn (0.87), Cr and V (0.66), Cr and Mn (0.58), Sr and Zn (0.73), and Sr and Co (0.54), as illustrated in (Table 2b) and Figs. 3(d & e). The correlation of these elements is an indication of possible relationship between them, while Cd and Sb are poorly correlated with all other elements, suggesting their presence in the samples may have been influenced by different geochemical factors.



Fig. 6(a-f). Geochemical map of elemental concentration in Road dust of the study area; (a) Cr, (b) Pb, (c) Cu, (d), Ni, (e)Zn, (f) Mn

Also for the geo-accumulation index evaluation selected element of RDS, Co (0.43 - 0.82), was graded to be practically uncontaminated in all the locations. Cu was graded to be moderately contaminated (3.06 - 3.89) in all locations and roads. Ni was graded to be uncontaminated to moderately contaminated (1.12 - 1.57). Pb was graded to be moderately to heavily contaminated (3.24 - 4.28) in some locations, while Zn was graded to be heavily contaminated  $(4 \cdot 13 - 4.92)$  in all the locations.

The contamination index of the various elements used for the different locations in the study area revealed that most of the areas with high elevated metal are mainly on the major roads with high traffic activities as compared with the minor roads with light traffic. Also areas with heavy traffic, near filling stations and near market had the highest level of metal concentration. The high presence of Cu, Pb and Zn concentration may be connected to vehicular and human activity, such as wear and tear of vulcanized vehicle tires, corrosion of galvanized automobile parts, and emission of carbon monoxide through leaded gasoline as well as erosion of other industrial and domestic waste on the road. The Igeo maps for Pb, Zn and Ni of the road deposited sediments are shown in Fig. 7(a-c).



Fig. 7(a-c). Geo-accumulation index map of (a) Pb, (b) Ni, (c) Zn in Benin city road deposited sediment

#### 4. CONCLUSION

This reseach has been able to establish information about the metallic ion concentration of some selected metals in both the topsoils and road deposited sediments in Benin City. The reseach revealed that topsoils and roaddust in Benin metropolis are contaminated with metallic ions such as Cu, Zn and Pb, which are seen to be relatively high in some areas especially in core city center with high human and vehicle related activities when compared with other locations in the study area values and the back ground value. The geochemical maps of the different metallic ions in topsoils and road deposited sediment within Benin city were plotted using GIS methods. Pb, Zn, Cu and Mn, showed strong positive association with one another, which indicate that they are of similar trend of metallic ions contamination in the study area. Several high concentration spots were identified in the geochemical maps. Most of the spots with high concentration of metallic ions where seen to be of areas with high human activities, abattoirs, erosion deposition areas, areas close to waste dump sites, motor parks and mechanic workshops. Further pollution level evaluation revealed that Zn, Pband Ni enrichment in these media have attained significant pollution status, far exceeding their background level in almost all of the location from the Igeo values. All of these, human activities are responsible for the current level of heavy metal distribution and enrichment of the study area.

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# **COMPETING INTERESTS**

Authors have declared that there are no competing interest exits.

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