

## Contamination Assessment of Heavy Metals in Road Dust of the University of Nigeria, Enugu Campus, Southeastern Nigeria

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**Received date:** 15 November 2018, **Accepted date:** 20 December 2018, **Online date:** 31 December 2018

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### Abstract

Heavy metals concentration in the environment is increasingly becoming a health concern in the world for humans and a disruptor of the ecosystem. This is particularly observable in street dust of urban cities and settlements with high density traffic. Road dust samples were analyzed for determination of concentrations of the environmentally sensitive elements, Co, Cr, Cd, Ni, Pb, Fe, Mn and Zn in fraction of dust smaller than 100 µm. The dust particles were collected during the dry season along the road in office complexes, construction sites, residential, business centers and classroom areas representing different activities across the University of Nigeria Campus located in an urban city, Enugu, southeast Nigeria. The road dust was collected near the curb and 1 m from the curb on the road. The dust samples were measured for their heavy metal concentration and contamination levels. The assessment of heavy metal pollution was based on such geochemical models as single pollution indices (Contamination Factor and enrichment factor), integrated pollution index (degree of contamination (Dc)) and Pearson moment correlation in order to determine their possible source and spatial distribution. The results obtained after acid digestion and metal determination with an atomic absorption spectrophotometer gave the following mean values for Co, Mn, Zn, Ni and Fe: 11.53, 99.92, 221, 44.23 and 216 mg kg<sup>-1</sup> respectively from samples near the curb and 12.37, 92.25, 248.87, 43.62 and 197.5 mg kg<sup>-1</sup> respectively from samples 1 m from the curb. The mean values for the physico-chemical parameters obtained which include electrical conductivity (EC), pH and total organic matter (TOM) are 304µS/cm, 7.13, and 6.9% respectively from samples near the curb and 408µS/cm, 7.33 and 5.57% respectively for samples 1 m from the curb. The general pattern of occurrence of heavy metals on the two road positions follows a similar order of Zn>Fe>Mn>Ni>Co>Pb>Cd>Cr. The highest levels of Cr, Zn and Ni were found in the high traffic density areas, and strong positive correlations were found between these metals. These results suggest diverse origin of pollution sources which include human activities, vehicular emissions and lithogenic occurrences of the metals from road construction currently in some of the sites sampled.

**Key words:** Heavy metals, Road deposited sediments, Geo-statistical analysis, Nigeria, Atomic Absorption Spectroscopy.

### INTRODUCTION

Surfaces such as pavements and road surfaces in urban environments usually contain an accumulation of fine solid particles on them. These particles deposited on these surfaces are called road deposited sediments (RDS); also commonly referred to as street dust or road dust. Road deposited sediments are usually a complex mixture of fine solid particles and pollutants obtained from a wide range of urban and industrial sources and processes. Their sources are either as a result of human activities in nature (vehicle tyre and body wear, vehicle exhaust emissions brake-lining material, road salt, atmospheric deposition, building and construction materials or soil material particles, litter obtained from plant and leaf and atmospheric deposition (HOPKE *et al.*, 1980; BACKWITH *et al.*, 1986; XIE *et al.*, 1999; LECOANET *et al.*, 2003; ROBERTSON *et al.*, 2003). The potential health risks and high levels of heavy metal pollution measured in a number of cities of the world have generated a lot of interest in heavy metal pollutions in RDS. Roadways and automobiles are presently considered as the largest sources of heavy metals in the urban environment. The most common heavy metals released from road travel are Zn, Cu and Pb. These account for at least 90 percent of the total metal pollution in road runoff. The accumulation of road dust along pavements in urban environments have the potential to provide considerable loading of heavy metals to receiving waters and water bodies (YISA *et al.*, 2012). These metals are not biodegradable in the environment. This is one of the most important properties of these pollutants which differentiate them from other toxic pollutants. (SEZIFE *et al.*, 2013). The possibility for bioaccumulation and bio-magnification is another problem associated with them. This causes an exposure for organisms to higher concentrations of these contaminants than is present in the environment alone. As a result of direct uptake from the surroundings across body walls through respiration and from food, these toxic metals accumulate in organisms (O'NEIL., 1990). Roads are known as the second largest non-point source of creating pollution in urban environment (FAKAYODE & OLU-OWOLABI., 2003). Road and highway surfaces are impervious, and serve as temporary sinks for various types of pollutants that are washed off during rainfall to the surrounding environment (CHARLESWORTH, *et al.*, 2003; VIRAD *et al.*, 2004; ROBERTSON & TAYLOR., 2007). Road surfaces receive varying amount

of heavy metals by the process of atmospheric deposition, sedimentation, impaction and interception (LI *et al.*, 2001). In urban environments, the top soils and road deposited sediments (RDS) or road dust are indicators of heavy metal contamination from atmospheric deposition. Industries, traffic, mining activities, smelters and construction are some of the main anthropogenic sources of heavy metal pollution. The traffic source includes vehicles (tyre wear, brake linings, fuel combustion, etc.) and road infrastructure (pavement wear, corrosion of galvanized steel crash barriers, etc.) (PAGOTTO *et al.*, 2001). It has been reported that the pollutants such as As, Cd, Cr, Cu, Ni, Pb and Zn due to heavy traffic are at high concentrations on road surfaces, roadside soils and particulate matter which affect the environmental air quality (CULBARD *et al.*, 1988). It has been estimated that the annual amount of dust emitted into the air by Nigerian motor vehicles was 612,000 tonnes and 187,000 tonnes for unpaved and paved roads, respectively (EGWUATU., 1998). Road deposited sediments (RDS) play a key role in road traffic pollution assessment and comprise a complex mix of particulates and contaminants derived from the road traffic environment which are of serious concern for environmental health supervisors. Most of the previous RDS studies have been based on samples collected within 1 m from the curb along roads or from road side soils (FAKAYODE & OLU-OWOLABI., 2003; ZHU, *et al.*, 2008; BANERJEE., 2003; HJORTENKRANS *et al.*, 2006; RASTMANESH *et al.*, 2010). Only a limited number of studies have looked at carriageway positions further from the curb. The present study considered areas beyond the curb which revealed that larger proportion of particles below 150 µm are found towards center of the road compared to near the curb where larger particles are dominant (BECKWITH *et al.*, 1986; SERIFE *et al.*, 2003; LECOANET *et al.*, 2003; IMPERATOR *et al.*, 2003; DE MIGUEL., 1990; LU *et al.*, 2010; HERNGREN *et al.*, 2006). Similarly, heavy metal concentrations in RDS were higher in the centre of the road and decreased towards the road gutter - confirming their higher association with the smaller particle size fraction (HARRISON *et al.*, 1985; DELETIC & ORR., 2005). Although some previous studies have focused on some major cities in Nigeria, there is scanty information on pollution build-up and heavy metal concentrations around the selected study area in spite of its social relevance. The objectives of this study therefore are to assess heavy metal contamination in road dust collected near the curb and 1 m from the curb on the road network and to conduct a contamination assessment of the road dust using geochemical models.

### 1.1 Location, geomorphology and geology of the study area

Enugu is located in a tropical rain forest zone with a derived savannah. The city has a tropical savanna climate. Enugu's climate is humid and this humidity is at its highest between the months of March and November. For the whole of Enugu State, the mean daily temperature is 26.7 °C (80.1 °F). As in the rest of West Africa, the rainy season and dry season are the only weather periods that recur in Enugu. The average annual rainfall in Enugu is around 2,000 millimetres (79 in), which arrives intermittently and becomes very heavy during the rainy season. Other weather conditions affecting the city include Harmattan, a dusty trade wind lasting a few weeks in the months of December and January).

Having been subject to weathering and erosion for long periods, the characteristics landscape of this area is extensive level plains interrupted by steep valleys and low hills. These features form a major landscape of the metropolis. Enugu's hills at the extreme may reach an elevation of 1,000 metres (3,300 ft). However, the topography in Enugu metropolis ranges from 15 to 75 m (UMA & OTEZE., 1999). The general relief comprises gently undulating plain with low hills and steep valleys. The topography within the city is much gentle when compared to the Western part which shows high relief with undulating hills. Much of the population of the area is located within the city.

Enugu is located within the Anambra sedimentary basin of southeastern Nigeria (Fig.1). Enugu Metropolis lies between latitudes 6° 23' N and 6° 29' N and longitudes 7° 29' E and 7° 32' E. Precambrian basement rocks in this region are overlain by sediments of Cretaceous and Tertiary age. Highlands surrounding Enugu for the most part are underlain by sandstone, while lowlands are underlain by shales which include the Asata-Nkporo shales and the Enugu shales. The Enugu Shale outcrops occur in the plains east of the North-South trending escarpment (EZEIGBO & EZEANYIM., 1993). Most of the Enugu metropolis is underlain by the Enugu shale.

**Table 1:** Description of sampling sites

Site No	Sampling Sites	Site code	Description of sampling sites
1	Main Entrance Gate	MEG	2 lane asphalt road, all vehicles slow down here while exiting and entering the University
2	Main Entrance, U-turn	MEU	A U-turn along the main entrance road
3	UBA	UBA	Location of a bank and a construction site
4	Roundabout, FS	RFS	Roundabout
5	Roundabout, Chapel	RCH	Roundabout
6	Parking lot, Auditorium	PLA	Parking lot of the main auditorium
7	Medical Centre	MDC	Road bend to the University medical centre
8	Staff Quarters	SQS	Sloppy road leading to the staff quarters
9	Staff Quarters	SQB	Road bend within the staff quarters
10	Staff Quarters	SQI	Road intersection leading out of the quarters
11	Abuja Road	ABJ	Long stretch of road leading to classrooms, business centres, hostels and offices.
12	St. Mulumba Church	SMC	Road bend by a Roman Catholic Church
13	Access Bank	ABK	Road Intersection by a bank and construction site.

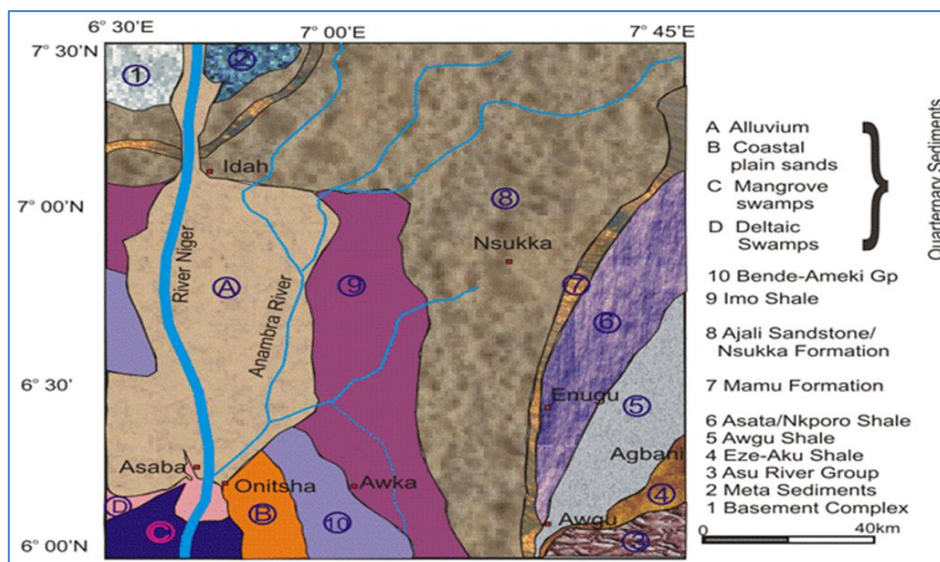


Figure 1. Geological map of the Anambra basin showing Enugu and environs



Figure 2. Map showing the University of Nigeria, Enugu Campus and sampling sites

## MATERIALS AND METHODS

This study is based on the paved road network within Enugu Campus of University of Nigeria, (UNEC) located inside Enugu town, behind Independence Layout (Figure 2). The Enugu Campus has just four faculties, namely: Business Administration, Environmental Studies, Law and Medical Sciences. It is a smaller campus, compared with Nsukka campus, which happens to be the main campus of University of Nigeria. Its land mass is 200 hectares. The sampling sites were 1 and 2 lanes of traffic with asphalt road surfaces, with low traffic densities. The surrounding land area is devoted to campus buildings, some farm land, foot paths, pavements and staff residential quarters.

### 2.3 Sample Collection

RDS samples were collected from thirteen (13) sites on the campus roads and for two transverse positions (near the curb; and from 1 m further away from the curb towards the center of the road) to characterize the influence of road-traffic on heavy metal deposition. A close inspection of the sites showed that the RDS particles originate primarily from the vehicles, road surface, atmospheric deposition and the surrounding land. The sites comprise a road bend, a roundabout, a U turn, a road intersection, a slope and a typical road section to represent a typical road layout. Samples were collected within a week in February 2017 to avoid temporal variation. Sampling plots comprising a 1 m<sup>2</sup> road surface area for both positions were initially cleaned by repeated sweeping. Then RDS samples were collected in a clean plastic dustpan after sweeping according to literature (FAKAYODE & OLU-OWOLABI.,2003; ROBERTSON & TAYLOR., 2007; KIM *et al.*, 1998). The sweeping technique was also kept consistent to avoid sample variability. During sampling, care was taken to minimize sweeping pressure so that (artificial) detachment of road material particles could be avoided. Samples were then transported back to the laboratory in sealed and well labeled plastic bags to avoid contamination.

### 2.4 Sample Pre-treatment and Analysis

After collection, samples were air-dried at room temperature and weighed prior to further analysis. Samples were dry-sieved using a 1 mm aperture metal sieve to remove large objects, litter, plants and leaves. The dried samples were further passed through a 230 mesh size (63 µm aperture) sieve to separate them. This size has some importance for metal concentrations as suggested by various researchers (SUTHERLAND., 2003). 1 gram of the RDS was weighed with an electronic balance. They were placed on a hot plate at 105°C in 50 cm<sup>3</sup> beakers and digested for 1hr 30 mins with 20cm<sup>3</sup> acid mixture of concentrated HNO<sub>3</sub>, HF and HClO<sub>4</sub> (4:4:1) by volume, in a fume cupboard. The digested samples were cooled and filtered with Whatman No. 1 filter paper. The filtrates were made up to 100 cm<sup>3</sup> with distilled water in a volumetric flask. A Buck Model 210 VGP atomic absorption spectrophotometer was used to analyze for Zn, Cu, Cd, Cr, Ni, Pb, and Fe. The sample pH in water was carried out using a glass electrode (LIDA Instruments), while electrical conductivity (EC) was determined using Sanxin, SX 723 model electrical conductivity meter, both in a 1:2 (w/v) sample/water suspension. Walkley-Black chromic acid oxidation method was used to determine the total organic matter (TOM) of the samples.

### 2.5 Statistical analysis

The following statistical methods were applied to obtain the heavy metal concentration and assessment of heavy metal pollution in the road dust samples.

- Descriptive statistics and Correlation analysis: SPSS 20.0
- Single Indices: Contamination Factor (Cf), Enrichment factor (EF)
- Integrated index: Degree of contamination (Dc).

## RESULTS AND DISCUSSION

### 3.1 Heavy Metal Concentration and physico-chemical Parameters

The results of metal concentrations of the RDS samples collected near the curb are as given in the tables that follow. In table 2, Cr was not detected in all the sites near the curb. Pb was detected only in site 1. This is not surprising since all the vehicles slow down at this point. Pb sources include exhaust emissions and road paint (SUDIP.,2011). Cd whose sources include exhaust emissions, brake wear and road surface wear was found in small quantities at sites 2 and 4 where vehicles slow down as their brakes are applied. The highest emission of Zn was in site 4. This is also expected at a roundabout as Zn sources include exhaust emission, tyre wear, brake wear, road surface and infrastructure wear. The maximum Ni levels occurred at road bend in the staff quarters, site 9. Since this site experiences very low traffic density, the Ni source could be from the road surface and infrastructure wear apart from brake wear (SUDIP., 2011). The mean value of the pH: 7.14, shows that the samples are within the neutral range. The mean value of the EC: 304.23  $\mu\text{S}/\text{cm}$  indicates that the samples are extremely saline (SMITH and GILLER.,1992). Also the mean value of the TOM of the samples at 6.96 % indicates a very high organic content. The abundance of these pollutants near the curb follow the sequence  $\text{Zn}>\text{Fe}>\text{Mn}>\text{Ni}>\text{Co}$ .

**Table 2.** Metal Concentrations ( $\text{mg kg}^{-1}$ ) and physico-chemical parameters near the curb

Site	Co	Mn	Zn	Ni	Fe	Cr	Cd	Pb	EC( $\mu\text{S}/\text{cm}$ )	pH	TOM(%)
1	16	177	187	0	177	0	0	20	308	6.56	6.25
2	13	158	259	4	198	0	2	0	261	8.42	1.79
3	45	147	325	19	132	0	0	0	381	7.20	2.95
4	0	127	465	0	242	0	3	0	323	8.05	4.39
5	0	57	206	2	212	0	0	0	233	8.20	4.92
6	0	58	128	86	267	0	0	0	238	7.46	7.63
7	18	68	186	29	196	0	0	0	241	5.00	2.43
8	0	111	194	43	160	0	0	0	288	6.34	11.74
9	24	94	196	93	316	0	0	0	296	6.05	9.95
10	8	46	155	87	244	0	0	0	412	6.78	12.84
11	3	77	178	90	294	0	0	0	254	6.60	9.60
12	0	76	165	35	179	0	0	0	288	6.09	8.33
13	23	103	238	87	202	0	0	0	432	9.20	7.69
Range	0 - 45	46-177	128- 465	0-93	132-316	0	0-3	0-20	233- 432	5.00-9.20	1.79-12.84
Mean	11.5	99.92	221.69	44.32± 38.89	216.85	0	0	0	304.23	7.14	6.96
± SD	± 13.61	± 41.89	± 88.52		± 53.35				± 66.23	± 1.12	± 3.54
EU Reg. Std.		1500	300	50		100	1 - 3	90-300			

(European Commission, 1986)

**Table 3.** Metal concentrations ( $\text{mg kg}^{-1}$ ) and physico-chemical parameters, 1 m from the curb

Site	Co	Mn	Zn	Ni	Fe	Cr	Cd	Pb	EC ( $\mu\text{S}/\text{cm}$ )	pH	TOM (%)
1	15	145	535	0	166	0	1	0	254	6.42	8.40
2	16	43	134	17	244	0	0	0	259	9.25	5.78
3	19	137	480	18	199	0	0	0	760	7.00	7.34
7	0	111	194	43	160	0	0	0	458	6.41	2.83
9	0	113	198	27	179	0	0	0	451	6.53	8.10
10	42	115	196	70	186	0	0	0	441	8.35	7.92
11	0	0	55	68	121	0	0	0	421	8.50	0.17
13	7	74	199	106	325	2	0	20	223	6.20	4.05
Range	0- 42	0-145	55-480	0-106	121-325	0-2	0	0-20	223-760	6.20-9.25	0.17-8.40
	12.36	92.25	248.88	43.63	197.50	0	0	0	408.38	7.33	5.57
	± 14.29	± 49.79	± 167.74	± 35.31	± 62.27				± 173.06	± 1.18	± 2.98
EU Reg. Std		1500	300	50		100	1 - 3	90-300			

(European Commission, 1986)

In Table 3 which shows the metal concentration of the road dust collected 1 meter away from the curb, Cr, Cd and Pb were each detected in only 1 sampling site, sites 13, 1 and 13 respectively. The detection of Cr and Pb at site 13 may not be unconnected to emissions from heavy duty vehicles moving to the construction site nearby. Zn had a high occurrence in all the sites with the maximum occurring at MEG, site 1. Vehicle brake linings and tire wear have been identified as possible sources of Zn by BAI *et al.*, 2008. Also Zinc compounds are used widely as anti-oxidants and as detergent/depressants enhancing agents for motor oil. The maximum Ni levels occurred at a road intersection by a construction site, ABK. This could be attributable to the road wear imposed on the road by heavy duty vehicles conveying materials to the construction site nearby.

The mean value of the pH: 7.33, shows that the samples are within the neutral range. The mean value of the EC: 408.38  $\mu\text{S}/\text{cm}$ , indicates that the samples are extremely saline (SMITH and GILLER.,1992). Also the mean value of the TOM of the samples at 6.96 % indicates a very high organic content. The abundance of these pollutants 1m away from the curb follow the sequence  $\text{Zn}>\text{Fe}>\text{Mn}>\text{Ni}>\text{Co}$ .

### 3.2 Correlations among the heavy metal pollutants and physico-chemical parameters

The correlation analysis was done to determine linear relationships among the metals. Pb and Cd were considered as outliers and were not considered in the correlation analysis shown in table 4.

**Table 4.** Correlation Analysis of heavy metals concentration near the curb

		Co	Mn	Zn	Ni	Fe	EC	pH	TOM
Co	Pearson Correlation	1							
	Sig. (2-tailed)								
Mn	Pearson Correlation	.433	1						
	Sig. (2-tailed)	.140							
Zn	Pearson Correlation	.210	.506	1					
	Sig. (2-tailed)	.492	.077						
Ni	Pearson Correlation	-.001	-.557*	-.506	1				
	Sig. (2-tailed)	.997	.048	.078					
Fe	Pearson Correlation	-.297	-.459	-.178	.622*	1			
	Sig. (2-tailed)	.324	.115	.560	.023				
EC	Pearson Correlation	.487	.173	.270	.244	-.216	1		
	Sig. (2-tailed)	.091	.573	.372	.421	.478			
pH	Pearson Correlation	-.060	.191	.394	-.130	-.088	.314	1	
	Sig. (2-tailed)	.845	.532	.183	.671	.775	.297		
TOM	Pearson Correlation	-.341	-.439	-.494	.706**	.381	.256	-.219	1
	Sig. (2-tailed)	.254	.133	.086	.007	.199	.398	.471	

The result of the correlation analysis presented in table 4 shows that Mn is significantly correlated negatively with Ni at < 0.05 significance level; this indicates that these metal pollutants do not share common sources. Ni sources include brake wear, road surface wear and from road infrastructures (SUDIP., 2011). There are also significant correlations at < 0.05 significance level between Ni with Fe and TOM. This indicates that the retention of these metals in the RDS samples is enhanced by the TOM of the samples.

**Table 5.** Correlation Analysis of heavy metals and physico-chemical parameters 1 m from the curb

		Co	Mn	Zn	Ni	Fe	EC	pH	TOM
Co	Pearson Correlation	1							
	Sig. (2-tailed)								
Mn	Pearson Correlation	.338	1						
	Sig. (2-tailed)	.414							
Zn	Pearson Correlation	.255	.797*	1					
	Sig. (2-tailed)	.543	.018						
Ni	Pearson Correlation	-.006	-.429	-.572	1				
	Sig. (2-tailed)	.988	.289	.139					
Fe	Pearson Correlation	.114	-.023	-.026	.404	1			
	Sig. (2-tailed)	.788	.957	.951	.321				
EC	Pearson Correlation	.118	.327	.268	-.221	-.387	1		
	Sig. (2-tailed)	.780	.429	.521	.600	.344			
pH	Pearson Correlation	.384	-.619	-.497	-.014	-.152	-.059	1	
	Sig. (2-tailed)	.347	.102	.210	.973	.719	.890		
TOM	Pearson Correlation	.561	.769*	.633	-.515	.132	.115	-.181	1
	Sig. (2-tailed)	.148	.026	.092	.191	.755	.786	.668	

The result of the analysis for metals 1 m from the curb as shown in table 5 revealed that Mn is significantly correlated with Zn and TOM. Since Mn pollution is from natural sources, this result could only mean that the presence of these metals is enhanced by the TOM of the samples.

### 3.3 Pollution Indices/ Geochemical models

To assess the pollution level of the road dust samples, geochemical pollution indices were used such as Contamination factor, Degree of contamination and Enrichment factor. The bases for heavy metal pollution assessment using the geochemical models is as shown in Table 6.

**Table 6.** Description of Contamination Factor ( $C_f$ ), Degree of Contamination ( $C_{deg}$ ) and Enrichment Factor ( $EF$ )

Description of Contamination Factor ( $C_f$ )		Description of Degree of Contamination ( $C_{deg}$ )		Description of Enrichment Factor ( $EF$ )	
Value	RDS Quality	Value	RDS Quality	Value	RDS Quality
$C_f < 1$	Low contamination factor indicating low contamination	$C_{deg} < 8$	Low degree of contamination	$EF < 2$	Deficiency to minimal enrichment
$1 \leq C_f < 3$	Moderate contamination factor	$8 \leq C_{deg} < 16$	Moderate degree of contamination	$2 < EF < 5$	Moderate enrichment
$3 \leq C_f < 6$	Considerable contamination factor	$16 \leq C_{deg} < 32$	Considerable degree of contamination	$5 < EF < 20$	Significant enrichment
$6 \leq C_f$	Very high contamination factor	$32 \leq C_{deg}$	Very high degree of contamination	$20 < EF < 40$	Very high enrichment
-	-	-	-	$40 < EF$	Extremely high enrichment

#### 3.3.1 Contamination factor (Degree of Contamination)

To assess the extent of contamination of heavy metals in RDS, contamination factor and degree of contamination have been used (RASTMANESH *et al.*, 2010; MULLER., 1969). The  $C_f$  is the single element index which is determined by the relationship:

$$C_f^i = C_{o-i}^i \div C_n^i \quad (1)$$

where  $C_f^i$  is the contamination factor of the element of interest,  $C_{o-i}^i$  is the concentration of the element in the sample,  $C_n^i$  is the background concentration. In this study, the continental crustal averages have been used (TAYLOR., 1964).  $C_f^i$  is defined according to four categories as shown in Tables 2 presents the



description for the various regimes of Degree of Contamination. The sum of the contamination factors of all the elements in the sample gives the degree of contamination as indicated in equation 2:

$$C_{deg} = \sum C_f^i \quad (2)$$

The contamination factor (Degree of Contamination of heavy metals near the curb and 1 meter away from the curb is presented in Table 7 below. The result of the contamination factors of the heavy metals near the curb in Table 7 shows moderate contamination factors for Co, Mn, Ni and Fe. Zinc however showed moderate to very high contamination factors in all the sites. The result of the degree of contamination shows low degree of contamination for Co, Mn, Ni and Fe. Zinc however showed a very high degree of contamination.

**Table 7.** Contamination factor or degree of contamination

Contamination Factors of metals near the curb						Contamination factors of metals 1 m from the curb					
Site	Co	Mn	Zn	Ni	Fe	Site	Co	Mn	Zn	Ni	Fe
1	0.64	0.19	2.67	0	0.003	1	0.60	0.15	7.64	0	0.003
2	0.52	0.17	3.70	0.05	0.004	2	0.64	0.05	1.90	0.23	0.004
3	1.8	0.15	4.64	0.25	0.002	3	0.76	0.14	6.86	0.24	0.004
4	0	0.13	6.64	0	0.004	4	0	0.12	2.77	0.57	0.003
5	0	0.06	2.94	0.03	0.004	5	0	0.12	2.83	0.36	0.003
6	0	0.06	1.83	1.15	0.005	6	1.68	0.12	2.80	0.93	0.003
7	0.72	0.07	2.66	0.39	0.003	7	0	0	0.79	0.91	0.002
8	0	0.11	2.77	0.57	0.003	8	0.28	0.08	2.84	1.41	0.006
9	0.96	0.10	2.80	1.24	0.006	Degree of Contamination	<b>3.96</b>	<b>0.78</b>	<b>28.44</b>	<b>4.65</b>	<b>0.028</b>
10	0.32	0.05	2.21	1.16	0.004						
11	0.12	0.08	2.54	1.2	0.005						
12	0	0.08	2.36	0.47	0.003						
13	0.92	0.11	3.40	1.16	0.004						
Degree of Contamination	<b>6</b>	<b>1.37</b>	<b>41.17</b>	<b>7.67</b>	<b>0.05</b>						

Similarly, the result of the contamination factors of metals 1m from the curb also shows low to moderate contamination factors for Co, Mn, Ni and Fe. Zn, on the other hand showed low to very high contamination factors in all the sites. The degree of contamination result shows that Co, Mn, Ni and Fe have low degrees of contamination while Zn had a considerable degree of contamination.

### 3.3.2 Enrichment Factor

Furthermore, in order to differentiate heavy metals originating from human activities from those of natural sources, the enrichment factor geochemical model was used. Enrichment Factor (EF) of an element in the studied samples is based on the standardization of a measured element against a reference element. A reference element is often the one characterized by low occurrence variability. This is determined by the relationship:

$$EF_X = [X_S / E_{S(ref)}] \div [X_C / E_{C(ref)}] \quad (3)$$

where  $EF_X$  is the enrichment factor for the element X,  $X_S$  is the concentration of element of interest in sample,  $E_{S(ref)}$  is the concentration of the reference element used for normalization in the sample,  $X_C$  is the concentration of the element in the crust and  $E_{C(ref)}$  is the concentration of the reference element used for normalization in the crust (TAYLOR, 1964). Five contamination categories are recognized on the basis of the enrichment factor as shown in table 2.

Similarly, the enrichment factors of metals near the curb and one metre (1m) away from the curb is presented in table 8 below. The results of the EF calculations in table 8 revealed the enrichment level of some of the metals in the RDS samples. The enrichment factors of Cr (0 - 519) and Ni (0 - 330) obtained in all the sites near the curb showed minimal to extremely high enrichment. The EF values of Mn showed significant to extremely high enrichment: Mn (12 - 48). Zn however showed extremely high enrichments in all the sites. Their mean values were Co (150), Mn (28), Zn (890) and Ni (158). The elements with the EF values higher than 10, are considered to be mainly of anthropogenic sources. Hence, EF can also be assumed to be an indicator of natural and anthropogenic sources of heavy metals (HAN, *et al.*, 2006).

**Table 8.** Enrichment factors of metals in the study area

Enrichment factors of metals near the curb						Enrichment factors of metals 1 m from the curb					
Site	Co	Mn	Zn	Ni	Fe	Site	Co	Mn	Zn	Ni	Fe
1	184	48	719	0	1	1	190	43	2257	0	1
2	150	43	995	14	1	2	203	13	565	66	1
3	519	40	1249	67	1	3	241	41	2025	70	1
4	0	34	1787	0	1	4	0	33	819	167	1
5	0	15	792	7	1	5	0	34	835	105	1
6	0	16	492	305	1	6	532	34	827	273	1
7	208	18	715	103	1	7	0	0	232	265	1
8	0	30	746	153	1	8	89	22	840	413	1
9	277	25	753	330	1	Range	0-532	0-43	232-2257	0-413	1
10	92	12	596	309	1						
11	35	21	684	319	1						
12	0	21	634	124	1						
13	265	28	915	309	1						
Range	0 - 519	12 - 48	492-1787	0-330	1						

The mean EF's of the metals decreased in the order Zn > Ni > Co > Mn. The result of the enrichment factors of metals 1m from the curb in also shown in table 8 revealed minimal to extremely high enrichment of the following metals Co, Mn, and Ni. Zn showed extremely high enrichment in all the sampling sites. Their mean values which are all greater than 10 suggest that the enrichment of these metals is from anthropogenic sources (HAN, *et al.*, 2006). Fossil fuel combustion, traffic emissions and industrial processes are considered as the major pollution sources of heavy metal pollutants in the atmosphere (MEZA-FIGUEROA *et al.*, 2007).

## CONCLUSION

The concentrations and emission pattern of heavy metals in the road network within the University of Nigeria Enugu campus have been studied. Cr, Pb and Cd were considered as outliers. Their emission was limited to 1 or 2 sites. This means that there is no significant contamination on the roads in the campus by these metals. There was a higher occurrence of Zn and Co away from the curb than near the curb. They showed higher concentrations near the curb than 1 m away from the curb. These may be as a result of the manual sweeping of the roads towards the curb by the sanitation officers. The contamination factor and degree of contamination results showed that Zn has very high value in all the sites and position. The metals also showed higher enrichment 1 m from the curb than near the curb suggesting enrichment from diverse origins of pollution sources which include human activities, vehicular emissions and lithogenic occurrences of the metals.

## ACKNOWLEDGEMENT

The authors wish to acknowledge the support of the Project Development Institute (PRODA), Enugu, Nigeria and the Federal University of Technology, Owerri, Imo State Nigeria, towards the completion of this work. We acknowledge with thanks the research grant received from the Centre for Research and Development (CRID), Tertiary Education Trust Fund of the Federal University of Technology, Owerri.

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