Trace Metal Levelsin Suspended Particles of Street Dust in Eket, AkwaIbom State, Nigeria

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Abstract:*This research assessed the levels of some trace metals in suspended particles of street dust from four locations with high anthropogenic activities in Eket. Similar analyses were carried out in AfahaOffiong (control) with little or no activities. The results revealed that levels of the metals were higher in the four locations than in the control. Physicochemical parameter analyses gave variable results between the four locations and the control. Correlation between the trace metals indicated high positive values at p < 0.05. Negative values were observed between sand and silt at p = 0.05. Negative values were equally seen between pH and SO_4^{2-} and between electrical conductivity and NO_3^-at p = 0.05. Principal component analysis revealed human activities as the major factor for the presence of these metals at the different locations studied. Cr, Cu, Zn and Pb were mainly from lubricants, incinerator and vehicular emissions while Cd originated from industrial sources. Obviously, street dust receives varying inputs of trace metals from different mobile or stationary sources namely, vehicular emission, industrial and power generating plants, oil burning, waste incineration, construction and demolition activities as well as other human activities which could be detrimental to the environment and living organisms.*

Keywords:*Trace metals, street dust, anthropogenic activities, Eket, environment, Pollution*

I. Introduction

Street dust is one of the most common pollutants in the rapid urbanization and industrialization context in the world. Street dust is referred to as solid particles that accumulate on urban street and it originates from the interaction of solid,liquid and gaseous materials which are produced fromdifferent sources and deposited on streets[1]. According to Banerjee[1], thecomposition and quantity of chemical matrix of street dustare indicators of environmental pollution. Street dust receives varying inputs of trace metals from mobile or stationary sources such as vehicular emission, industrial plants, power generation plants, oil burning, waste incineration, construction and demolition activities[2]. Accordingly, street dust is known to contain elevated levels of trace metals due to the effects of human activities such as traffic (vehicle exhaust, tire wears, break lining wear), industrial activities (coal combustion, metallurgy, auto repair and chemical engineering), road construction (asphalt, concrete) and road paint[3]. Lead (Pb), for example is known to come from the use of leaded gasoline, whereas Cu, Zn and Cd are known to originate from tyre abrasion, lubricants, industrial and incinerator emissions. The source of Ni and Cr in street dust is believed to be due to corrosion and eroding of some motor vehicle parts[4, 5]. The phenomenon contributes significantly to the pollution of urban environment.

Pollution of urban environment has been reported in many countries with activities that generate toxic organic and inorganic pollutants, especially trace metals[6]. It is therefore, an important issue in urban areas[7]. These toxic metals can remain in urban environments for a long time. Their entrance into the human body can likely occur through direct inhalation, ingestion and skin contact[8]. The amount of dust particles inhaled, ingested and through dermal contact by humans is usually dependent on the grain size of the particles[9]. The particles with diameters below 100 µm in street dust are inclined to be suspended in the air and move in the wind stream; these are also called suspended particles[10].

Long-term exposure to an urban dust environment that contains elevated levels of trace metals would cause chronic damage through ingestion via the hand to mouth pathway, inhalation and dermal contact[6]. More people now dwell in urban areas; therefore, the changes in the urban environment are crucially important for the dwellers. Metal pollution of urban dust is one of the fastest growing types of environmental pollution and is raising serious concern because of the health risks[11]. Urban dust is an important reservoir of trace metal contaminants in urban environment[12]. Urban dust has been reported as a special type of environmental medium that contains toxic organic and inorganic pollutants, especially high levels of trace metals in many countries[13]. Indeed, according to Zhenget al[14],metals in dust can enter the human body through inhalation, ingestion and dermal contact and accumulate in the adipose tissues or deposit in the circulation system, causing respiratory and cardiovascular disease and even mortality.

As noted by Li et al[15], and several other authors, there is a growing need for the investigation of trace metal levels in urban street dust. Urban street dust can be a potential risk to humans as its small particle size and suspension in wind can lead to the possibility of direct and indirect exposures. Exposures to metal contaminated dust may cause human health issues through skin contact and hand to mouth activities, particularly through the unintentional uptake by children in playgrounds and streets. Numerous studies on trace metals have been conducted in bulk dust samples. Information about trace metal levels in suspended particles (i.e. the fraction below 100 µm) in street dust is limited, especially in developing countries like Nigeria. So, there is every need to study the sources and levels of some trace metals in suspended particles of street dust in Eket, AkwaIbom State.

II. Materials and Methods

Study area: Eket Local Government Area (LGA) of AkwaIbom State, Nigeria is geographically situated at coordinates of 4^0 39′ 10″ N, 7^0 56′ 37″ E. The climate of the area is humid and most of the rainfall occurs between the months of April and October. Eket LGA is bounded by NsitUbium to the North, Onna to the West, EsitEket to the East and Ibeno to the South. The area covers a landscape of about 83 m^2 and the projected population is 288,980[16]. Eket is blessed with abundant deposit of crude oil and clay as well as forest resources such as timber and palm produce. The area is also noted for sea food production and farm crops which ranges from yam, cassava, coco-yam, plantain to maize and vegetables. The area is the thriving hub of a new oil and gas business, with more than 250 companies providing support services such as catering, flights and exports[16].

Samples collection: Dust samples were randomly collected from four locations (Atabong Park, UruaNka, Marina junction and Onna Head Bridge) in Eket where all kinds of anthropogenic activities are carried out. These four sample locations were designated as AP, UN, MJ and OB, respectively. At each sample location, dust samples were randomly collected from four spots using plastic brush and scoop, and then mixed thoroughly to obtain a composite sample. Powder free gloves were worn during samples collection. Samples were equally collected from AfahaOffiong, the headquarters of NsitIbom LGA where there are little or no human activities, to serve as the control. The control location was designated as AO. The randomly collected samples in each of the five sample locations (including the control), were pooled together to obtain five composite samples. The samples were collected between December 2016 and January 2017. Map of Eket showing the sample locations is presented in Figure 1.

Samples preparation: Suspended particles are the fractions below 100 µm in dust. The dust samples were dried at room temperature, crushed using mortar and pestle, and then sieved through a 100 µm nylon mesh to remove extraneous matter such as pieces of brick, paving stone and other debris.
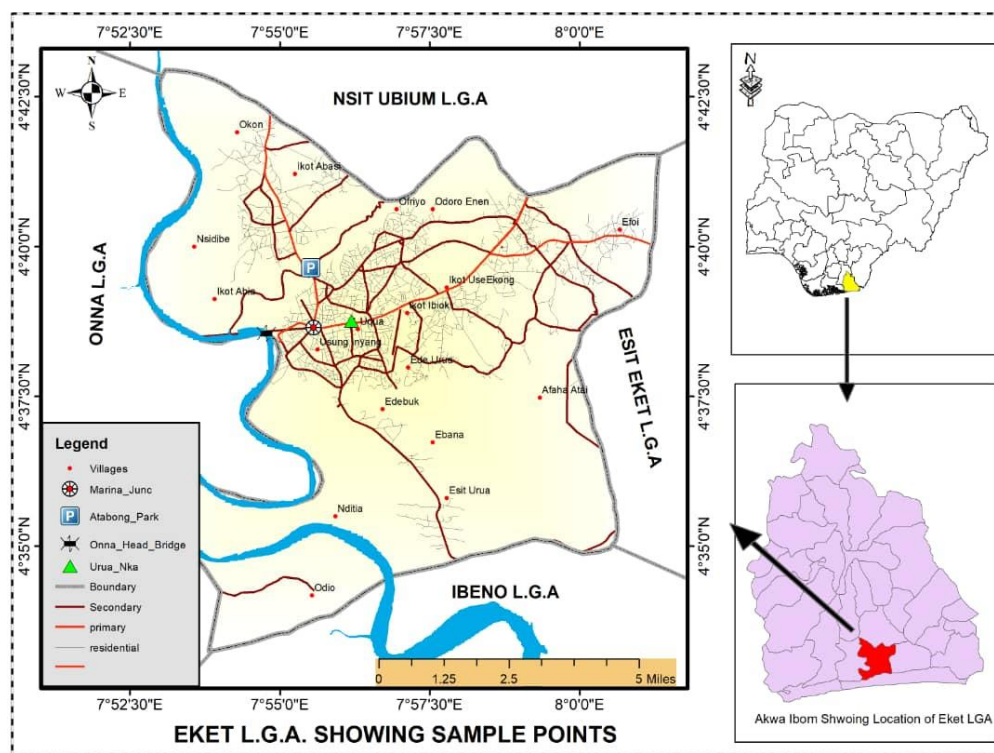

Figure 1: Map of Eket showing the sampling locations

Samples digestion: An exact amount (0.5 g) of the samples was taken in a volumetric flask, 100 mL of distilled water added and followed by the addition 0.5 mL of trioxonitrate (v) acid (HNO_3) and 5 mL of hydrochloric acid (HCl). The resulting sample solution was heated on a hot plate in a well-ventilated hood until the volume reduces to 20 mL. The solution was then cooled and filtered into a 100 mL volumetric flask and the filtrate made up to the 100 mL mark using distilled water[17]. These procedures were repeated for the other samples. Trace metals (Cd, Cu, Pb, Zn and Cr) levels in the final solutions were determined using Perkin-Elmer Analyst 300 atomic absorption spectrophotometer (AAS).

Physicochemical parameters (pH, electrical conductivity, particle size distribution (sand, silt, clay), SO_4^{2-}, NO_3^-, Cl^-, acidity and alkalinity) in the dust samples were determined using standard procedures. Particle size distribution was determined using hydrometer method. Accurate weights (50 g) of the air dried dust samples were taken in a mechanical stirrer cup, distilled water added and a total of 20 mL of sodium hexametaphosphate was also added, the cup was inserted into the mechanical stirrer, the stirrer blade lowered into the suspension and then stirred for 10 minutes. The cup was later removed and the content poured into a measuring cylinder and made up to 1000 mL mark with distilled water and the temperature noted. The mixture was suspended by turning the cylinder end to end several times vigorously and the time taken immediately. The hydrometer was carefully placed into the suspension and the reading taken. Readings were also taken after one and two hours and the temperatures noted. The pH of each sample was determined using the pH meter. The pH meter was calibrated using two pH standard solutions (pH 4 and pH 10). A total of 20 g of the prepared dust sample were taken in a 50 cm^3 beaker, 20 mL of distilled water added and allowed to stand for 30 minutes while stirring occasionally with a glass rod. The pH electrode was immersed in the partly settled suspension and the reading recorded. The electrical conductivity of each sample was determined using the conductivity meter. The meter was switched on and the conductivity electrode was immersed into the partly settled suspension. The "CND" button was pressed and the reading recorded.

For the determinations of nitrate and sulphate, the dust samples were digested by the wet digestion method in which 1.0 g powdered sample concentrated with 5 mL of $HClO_4$ and 10 mL of HNO_3 were treated in a digestion flask and the filtered and diluted digest used for the determinations[18]. Nitrate was determined by the Brucinecolometric method in which 10 mL aliquot of the dust extract were transferred into a 25 mL volumetric flask and 2 mL of Brucine reagent were added and then 10 mL of concentrated sulphuric acid, H_2SO_4 were rapidly added. The flask was set in cold water for about 5 minutes and the contents made up to the mark and the absorbance was measured at 470 nm[19]. Sulphate was determined by the turbidimetric method in which 10 mL of the sample aliquot was transferred into a 25 mL volumetric flask and diluted with distilled water to bring the volume to approximately 20 mL. Gelatin $BaCl_2$ (1 mL) reagent was added and the solution made up to the mark with distilled water. The solution was thoroughly mixed and allowed to stand for 30 minutes. The percentage transmittance (%T) and absorbance were measured at 420 nm within 30 minutes. The contents in the flask were properly shaken before pouring into the photo test tubes[20].

For the determination of chloride (Cl^-), exact amounts (2.5 g) of the samples were taken in a conical flask, 50 mL of distilled water added. The flask was then shaken on a mechanical stirrer for 2 hours. The mixture was filtered after 2 hours and 25 mL of the filtrate were transferred into another conical flask and 1 mL of potassium dicrohromate was added. The resulting solution was titrated with 0.026N $AgNO_3$ to a pink end point and titre value recorded[18] (AOAC, 2007). For the determination of exchangeable acidity, exact amount (2.5 g) of the dust sample was taken in a shaking bottle and 50 mL of 1 N KCl added. The solution was placed on a mechanical stirrer and shaken for one hour and then filtered and the extract used for the determination by titrating with 0.02 N NaOH to a permanent pink endpoint.

III. Results and Discussions

Physicochemical parameters: Physicochemical parameters of dust such as pH, electrical conductivity, particle size distribution, chloride, sulphate, nitrate, exchange acidity and alkalinity are useful indicators of dust quality. The results for the Physicochemical parameter analyses of the dust samples are as presented in Tables 1. From the table, pH ranged from 6.20 in sample from location AP to 6.50 in sample from location MJ. The control sample (AO) had the pH of 6.60. The pH serves as useful index for availability of nutrients, the potency of toxic substances present in the dust and the physical properties of the soil. The availability of trace metals is pH dependent, so the solubility of metal cations generally increases with a decrease in pH. The pH values obtained in this study are slightly higher than those reported by Osakwe[21], but are in agreement with those reported by Chaudhari[22].The electrical conductivity ranged from 3.51 sm^{-1} in sample from location AP to 3.69 sm^{-1} in sample from location OB, with the control sample (AO) having the electrical conductivity of 3.32 sm^{-1}. Electrical conductivity offers quick and convenient way for determining the total amount of ionisable salts in soil. Electrical conductivity may be ascribed to the presence of salts, trace metal ions or ionisable materials in the dust. The values of electrical conductivity obtained in this study were higher than those reported by Chaudhari[22]. For particle size distribution, sand ranged from 83.21 to 95.38%, silt ranged from 2.62 to 9.52%

and clay ranged from 1.50 to 11.10%. In the control, sand, silt and clay were 95.38%, 2.66% and 2.20% respectively. The texture class of the dust samples was sandy. Sand size fraction was the highest, followed by silt and then clay. This proportion shows that the dust particles were coarse.

SO_4^{2-} levels in the studied locations ranged from 1287.21 to 2044.40 mg/kg, with the control having SO_4^{2-} level of 605.76 mg/kg. $SO_4^{2-}$are naturally occurring anions found in soil; about 95% of the sulphur contents in soil are contained in organic matter. Most fuels that are burnt for heat, power and transportation contain some sulphur. The sulphur escapes as sulphur dioxide which later dissolves in rain water and reaches the soil as sulphate-sulphur.NO_3^-ranged from 589.01 to 708.42 mg/kg in the studied locations, with control having the NO_3^- level of 719.82 mg/kg. Nitrate-nitrogen occurs in various dissolved forms as dissolved molecular nitrogen, inorganic nitrogen (as ammonia nitrite and nitrate) and organic nitrogen (as amino acid and proteins). The major source of nitrate in the dust samples could be bacteria and cynobacteria which fix atmospheric nitrogen emitted from fossil fuel combustion. The nitrate (NO_3^-) levels in the investigated dust samples can enhance plantgrowth; improve quality of yield, seed and fruit productions.

Chloride ions (Cl^-)in the dust samples ranged from 2.22 mg/kg in location UN to 4.43 mg/kg in location AP, with control having the value of 2.77 mg/kg of Cl^-. Chloride ions account for nearly all the chlorine available in the street dusts and remain mainly in the soil solution that so plants can take up. Cl^- is an essential micronutrient available in small quantities for certain photochemical reactions during photosynthesis. The chloride ion levels in this study posse no toxicity problems because of it low levels in the dust samples. The exchange acidity ranged from 0.81 to 1.20mg/kg in samples from the studied locations. In the control, it was 1.40 mg/kg. Exchange acidity is the amount of hydrogen and aluminium that can be replaced from the adsorption complex by a neutral salt solution. Alkalinity levels in the samples ranged from103.00 to 350.00 mg/kg. Alkalinity level in the control was 120.30 mg/kg.

Trace metal levels in dust samples: The levels of the analysed trace metals in this study are presented in Table 2. Variable levels of the metals were observed across all the sample locations. Generally, the levels of all the analysed metals were low in the control samples (AO) compared with samples from the four locations (AP, UN, MJ and OB). Cd levels in each sample location were lower than the value of 115.27 mg/kg and higher than 9.11mg/kg reported by Babatundeet al[23] and Jagtapet al[24], respectively, except that of the control which was lower than 9.11mg/kg. As noted by Jagtapet al[24], the source of Cd in soil could be the wearing of automobile tyres, lubricants, mining and metallurgical activities. The observed Cd levels across all the sample locations were above the maximum permissible level of 3.0 and 0.14 mg/kg set by WHO and United State Environment Protection Agency (USEPA), respectively, except that of the control which was below 3.0 mg/kg. Cu levels were lower than those reported by Chatterjjee and Banerjee[25] and Al-Khashman[2]. Cu levels in samples from all the locations were below the maximum permissible levels of 100 and 270 mg/kg set out by WHO and USEPA, respectively. The possible source of Cu in street dust could be corrosion of metallic parts of cars derived from engine wear, thrust bearing, brushing and bearing. The sequence of the observed Cu levels in samples from all locations was in the order: AP > UN > OB > MJ > AO. The mean Pb level recorded in samples from location AP was found to be comparatively higher than those reported by Liang et al[26]; Bichi and Bello[27]; Mojolagbeet al[28] and Osakwe[21]. It was equally higher than the maximum permissible level of 100 mg/kg set by WHO, but lower than 300 mg/kg set by USEPA. As noted by Liang et al[26], the major sources of Pb pollution are exhaust gases of petrol engines and the atmospheric fallout from the combustion of fossil fuels. The observed Pb levels in locations UN, MJ, OB and AO were below the maximum permissible levels of 100 and 300 mg/kg set by WHO and USEPA, respectively.The sequence of the Pb levels in samples from all locations was in the order: AP > UN > MJ > OB > AO.

The observed Zn levels were lower than those reported by Chatterjjee and Banerjee[25] as well as the maximum permissible levels of 300 and 200 mg/kg set by WHO and USEPA, respectively. According to Chatterjjee and Banerjee[25], the main source of Zn could be attrition of motor vehicles, metal fabrication works and lubricating oil The sequence of the Zn levels in samples from all locations was in the order: AP > MJ > UN > OB > AO. The observed Cr levels in this study were significantly lower than the Cr levels of 54.0 mg/kg and 26.0 mg/kg reported by Chatterjjee and Banerjee[25]and Shi et al[29], respectively. The sequence of the observed Cr levels in samples from all locations follows the order: AP > UN > MJ > OB > AO. The observed Cr levels across all the sample locations were below the maximum permissible levels of 100 and 11 mg/kg set by WHO and USEPA, respectively.

Pearson's correlation analysis of trace metals: Pearson's correlation analysis is a statistical analysis that gives information about the statistical relationship or association between two continuous variables. The results of Pearson's correlation coefficient carried out on the analysed trace metals are presented in Table 3. Usually, the content of trace metals originating from the same or similar source tend to have a significant correlation[30], so the correlation between the analysed trace metals in the samples can be considered as an indicator of whether the source of trace metals was the same or not. The correlation was carried out at 95% confidence level. Significant correlation was found between Cd and Cr (r = 0.956), Cu and Pb (r = 0.952) and between Pb and Cr (r = 0.921).

Based on this analysis, we can infer that metals with strong correlation originate from similar contamination sources due to the human activities such as traffic (vehicle exhaust, tire wears, break lining wear), industrial activities (coal combustion, metallurgy, auto repair and chemical engineering), road construction (asphalt, concrete) and road paint[3]. Lead (Pb), for example is known to come from the use of leaded gasoline, whereas Cu, Zn and Cd are known to originate from tyre abrasion, lubricants, industrial and incinerator emissions. The source of Ni and Cr in street dust is believed to be due to corrosion and eroding of some motor vehicle parts[31, 32].

Principal component analysis (PCA): Principal component analysis (PCA) is a statistical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components. In this study, PCA was computed using the covariance method described by Jolliffe[33]. Here, the data were transformed to a new coordinate system such that the greatest variance by some projection of the data comes to lie on the first coordinate (called the first principal component), the second greatest variance on the second coordinate, and so on.

PCA was used to identify the possible emission sources of trace metals in the study locations. The goal of PCA is to reduce the number of variables and detect the structure in the relationship between them. Factor analysis was conducted to understand the variance and association between the five trace metals. The three principal components extracted are presented in Table 4. From the table, it is seen that the extracted three components accounted for 96.93% of the total variance. Component 1 accounted for 74.66% while components 2 and 3 accounted for 16.83% and 5.44%, respectively. Accordingly, three trace metals (Cu, Pb and Cr) loaded well oncomponent 1. The values obtained for these three trace metals suggested anthropogenic influence to the pollutant load. According to reliable source, tyre, brake abrasions and vehicle exhaust contribute significant amounts of Cu, Pb and Cr into the environment. The elements of component 1 could therefore be attributed to vehicular emissions (both exhaust and non exhaust emissions).

Component 2 has Cd and Cr as the major components. This gives an indication of similar anthropogenic source of these metals. According to Shi et al[34], the source of Cd and Cr in street dust is believed to be the corrosion of vehicular parts. Thus component 2 could therefore be attributed to corrosion of vehicular parts. The high rate of corrosion and wear from old vehicles (as a result of the high patronage in imported used cars) plying these roads could have accounted for the significant levels of anthropogenic contributions of Cd and Cr in the road dust. Component 3 has Pb, Zn and Cr as the major components. Zn is a product of tyre abrasion, whereas Pb and Cr are products of vehicular emission.

Pearson's correlation analysis of physicochemical parameters: The Pearson's correlation coefficient of the physicochemical parameters in the dust samples are presented in Tables 5 and 6. Negative correlation was observed between sand and silt at $p = 0.05$. This implies that these parameters are affected by different factors in the opposite directions, that is, as one factor increases, the other decreases. Accordingly, negative correlations were equally seen between pH and SO_4^{2-} and between electrical conductivity and NO_3^- at $p = 0.05$.

Table 1: Physicochemical parameters of street dust sample across the sample locations

Sample location	pH	EC (sm⁻¹)	Sand (%)	Silt (%)	Clay (%)	SO₄²⁻ (mg/kg)	NO₃⁻ (mg/kg)	Cl⁻ (mg/kg)	Acidity (mg/kg)	Alkalinity (mg/kg)
AP	6.20	3.51	89.38	5.52	5.10	2044.40	708.42	4.43	1.20	202.00
UN	6.30	3.63	83.38	9.52	3.20	1738.65	600.07	2.22	1.10	103.00
MJ	6.50	3.54	95.38	2.62	1.50	1590.08	624.21	3.88	0.81	350.00
OB	6.40	3.69	83.21	5.69	11.10	1287.21	589.01	3.32	1.i0	261.00
AO	6.60	3.32	95.38	2.66	2.20	605.72	719.82	2.77	1.40	120.30

AP = Atabong Park, UN = UruaNka , MJ = Marina Junction, OB = Onna Head bridge, AO = AfahaOffiong (control), EC = Electrical conductivity

Table 2: Levels of some trace metals (mg/kg) in street dust samples across the sample locations

Metals	AP	UN	MJ	OB	AO	WHO	USEPA
Cd	24.60 ± 0.6	24.40 ± 0.72	24.20 ± 0.87	22.80 ± 2.22	2.04 ± 0.01	0.48	3
Cu	10.20 ± 1.22	6.80 ± 0.35	0.80 ± 0.17	2.80 ± 0.69	0.20 ± 0.01	100	270
Pb	120.80± 1.25	82.40 ± 2.16	39.60 ± 2.16	27.80 ± 2.70	1.12 ± 0.01	100	300
Zn	62.80 ± 0.95	33.00 ± 1.25	36.20 ± 3.27	27.10 ± 2.66	3.00 ± 0.01	300	200
Cr	1.20 ± 0.10	1.00 ± 0.20	0.80 ± 0.16	0.40 ± 0.10	0.30 ± 0.01	100	11

Above are means ± standard deviation of triplicate analyses. AP – Atabong Park, UN– UruaNka, MJ – Marina junction, OB – Onna head bridge, AO – AfahaOffiong

Table 3: Pearson correlation coefficient of trace metal in street dust

Cd		Cu	Pb	Zn	Cr
Cd	1				
Cu	0.55	1			
Pb	0.77	0.95	1		
Zn	0.66	0.76	0.79	1	
Cr	0.96	0.77	0.92	0.79	1

IV. Conclusion

Based on the analyses and results, it was observed that suspended particles of street dust samples in Eket contain variables levels of the analysed trace metals in all the sample locations due to uncontrolled anthropogenic activities. The levels of these metals were higher than those in the control. Accordingly, physicochemical parameter analyses gave variable results between the study locations and the control. Street dust could receive varying inputs of trace metals from different mobile or stationary sources such as vehicular emission, industrial plant, power generating plant, oil burning, waste incineration, construction and demolition activities, which could be detrimental to human health (living organisms) and the environment. The study has been able to establish the levels and sources of the analysed trace metals in the dust samples, thereby contributing effectively to knowledge in the area of Environmental Chemistry.

Table 4: Extracted principal component by PCA

Element	Component		
	1	2	3
Cd	0.13	0.97	0.13
Cu	0.93	0.16	0.31
Pb	0.81	0.25	0.51
Zn	0.46	0.19	0.85
Cr	0.51	0.62	0.53
Variance (%)	4.66	16.88	5.44
Cumulative (%	74.66	91.49	96.93

Table 5: Pearson's correlation coefficient between physicochemical parameters (particle size distribution) in street dust

	Sand	Silt	Clay
Sand	1		
Silt	-0.871*	1	
Clay	-0.692	0.260	1

*Correlation is significant at the 0.05 level (1-tailed).

Table 6: Pearson's correlation coefficient between physicochemical parametersin street dust

	pH	EC	SO_4^2	NO_3	Cl^-	Acidity	Alkalinity
pH	1						
EC	-.526	1					
SO_4^2	-.875*	.548	1				
NO_3	.121	-.885*	-.240	1			
Cl^-	-.300	-.023	.463	.311	1		
Acidity	0.82	-.571	-.504	.657	-.291	1	
Alkalinity	.129	.311	.230	-.323	.662	-.78	1

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