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CHEMICAL COMPOSITION OF TOTAL SUSPENDED PARTICULATE MATTER (TSP) IN OBARETIN

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ABTRACT

Particulate matter was captured from five different sites in Obaretin, Ikpota-Okha LGA of Edo State using SKC Air Check gravimetric sampler Model 21-5000 serial no 20537 and a glass fiber filter between the months of December 2008 and April 2009. The glass fiber filters were analyzed for nine trace metals – Fe, Cu, Zn, Cd, Mn, Pd, Ni, Cr and Co (by Atomic Absorption spectrophotometric (AAS). The data obtained were subjected to factor analysis. The mean concentration of the various elements were: Fe2.56mg/m^3; Zn 0.034mg/m^3; Cu 0.1mg/m^3; Mn 0.166mg/m^3; Cd 0.0404mg/m^3; Pb 0.19mg/m^3; Cr 0.1mg/m^3. While the concentration of Ni and Co were below detection limits. The concentration of the trace metals obtained in this study fell within the purview of the occupational health and safety standard but higher than WHO limit. The element Cd was moderately enriched, when Fe was used as a reference element. Two components were obtained from the principal component analysis.

Running Title: Constituents of Aerosol Captured in Rural Community**.**

Key words: Trace metals, Enrichment Factor, Atomic Absorption Spectroscopy, Total Suspended Particulate Matter, Rural area.

INTRODUCTION

Rural dwellers are oblivious of the deleterious effect of particulate matter. Pollution resulting from suspended particulate matter and carbon monoxide may place an undue burden on the respiratory system and contribute to increased morbidity and mortality, especially among susceptible individuals in the general population (WHO, 1998). The major way of waste disposal in the rural area is by burning. Although, there is no single method of waste treatment or disposal that completely eliminate all risks to public and environment. Burning has been found to be the most effective way for destroying infectious and toxic components and for attenuating waste volume and weight (Tobin *et al*., 2014). Other human activities (anthropogenic sources) that generate particulate pollution include wood stoves, road construction and different artisans. Particulate matter of a small size in diameter are likely to be trapped in the bronchi. Smaller particulates end up in the alveoli, the thoracic or lower regions of the respiratory tract, where more harm can be done (Tobin *et al*., 2016; Ediagbonya *et al*., 2015; Ediagbonya *et al*., 2014). Air pollution, both natural and manmade affect climate (Fang, 2010).

Atmospheric particles have numerous effects. The most conspicuous of these is attenuation and distortion of visibility, they provide active surfaces upon which heterogeneous atmospheric chemical reactions can occur and nucleation bodies for the condensation of atmospheric water vapour, thereby exerting a significant influence upon weather and air pollution phenomena. Particulate matter has a net detrimental effect upon the environment or upon something of value in the environment (Martin *et al*.,2007). The severity of contamination by pollution increases with emission source strength and the atmospheric mixing of the pollutants (Obioh *et al*.,2005;Ediagbonya *et al*.,2013b). In terms of adverse effects on human health, particulate matter is perhaps the most important air pollutant. Though, much has been reported about particulate matter and its associated health problems, there is no established standard or guidelines as to the levels of particulate matter in the ambient air required to cause hazard. Mortality based epidemiological studies have linked air pollution episodes to health problems (Tobin et al.,2016; Anderson,2009; Zheming *et al*.,2016; Justino *et al*.,2006). Toxicological study has equally implicated particulate air pollution in adverse health effects (Palmer *et al*.,2006). The capture of particulate matter has not been reported in Obaretin (rural area). Particulate matter had been fingered as one of the major health problems in rural area (Manfred, et al., 2004: Brook, et al., 2013).

Objectives of this study are to analyse nine trace metals in the glass fibre filter that captured the particles in the air using Atomic Absorption spectroscopy and also to identify these elements which are abnormally enriched in the atmosphere and compare the trace metal with regulatory limits. Some of these constituent of particulate pollution is well known to cause chronic and acute poisoning of important organs in the body, cancer, dermatitis and ulcers of the skin benign pneumoconiosis, manganese poisoning and cause damage of mucous membranes and silicosis. (Beeleen *et al*., 2014; Beelen *et al*., 2008; Fissher *et al*., 2015; Tobin *et al*., 2016; NIOSH, 2002; IARC, 1997; Parke *al*., 1999).These metals enter the atmosphere from both anthropogenic and biogenic sources.

MATERIALS AND METHODS

Sampling Site

Sampling was done in Obaretin in Ikpoba-Okha L.G.A Edo State in Niger Delta region of Nigeria. The rural community is sparsely distributed with a population estimate of few thousands of inhabitants; the settlement is situated along the main road that is Nodal Settlement. There are thick rubber plantations and industrial farms all located behind the community.

The rural dwellers engage themselves in farming, hunting, rubber tapping and intra-transportation due to the accessibility of the community to the main road. Also, the people engage in cassava processing, smoking of fishes, and their major way of waste disposal is by burning. The main road that led to the community is untarred. Other human activities in this locality include paving of roads and different artisans such as vulcanizes, carpentry etc. All these activities aforementioned are veritable generators of particulates to the environment.

The major human activities in this region that generate cumbersome pollution are the particulate generate from bike, vehicle exhaust, and bush burning and re-suspended particle from the untilled road.

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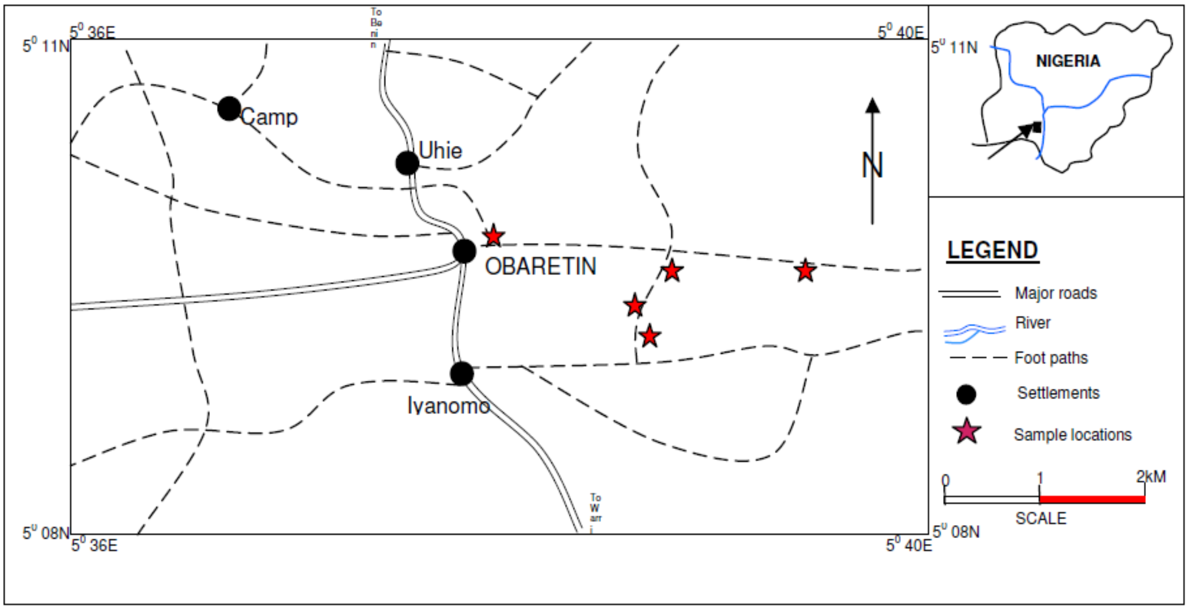

Fig. 1: Obaretin showing sampling locations

Table 1 Monitoring sites and their co-ordinates

SN	Site Code	Co-Ordinates	Site Descriptions
1	RHA	N06°09' 43.3" E005° 38' 49.2"	Mud house detached, kitchen unceiled roof. Rural House A(RHA)
2	RHB	N06° 09'46.9"E005° 38'44.7"	Mud house detached, kitchen unceiled roof. Rural House B(RHB)
3	RHC	N06°09' 46.9"E005° 38' 48.1"	Mud house detached, kitchen unceiled roof Rural House C(RHC)
4	RHD	N06° 09' 40.0"E005°38' 53.8"	Mud house detached, kitchen unceiled roof Rural House D(RHD)
5	RHE	N06° 09' 35.8"E005° 38'30.4"	Mud house detached, kitchen unceiled roof. Rural House E(RHE)

Sample Collection

SKC Air Check XR5000 high volume, Gravimetric sampler model 210-5000, High volume Gravimetric sampler model 210-5000 serial No. 20537 with a Whatman glass fibre filter were used to capture the particles. The particles were collected at a flow rate of 2l/min for eight hours and the sampler was placed between the heights of 1.5-2m of human. The Whatman glass fibres used were conditioned in a controlled room temperature for at least 24hrs before pre-and post-weighing. The sampling was done from Dec. 2008-April 2009.

Sample Digestion and Measurement

The trace metals Pb, Cd, Ni, Cu, Co, Fe, Zn, Cr and Mn were determined by AAS (Thermo electron corporation Atomic Absorption spectrometry, S. Series) A portion of the effective filter and the respirable foam were digested separately with 20mL 1:1 HNO_3 in a beaker and covered with a watch glass which was concentrated to about 50ml on a hot plate at 150-1800C 10ml of 1:1 HNO3 was added to repeat it. The extract was filtered through a 541 filter paper, the filter paper and the beaker was washed with 0.25M HNO_3. The filtrate was transferred and weighted into 50ml volumetric flask. The chemicals and reagents used for analysis were analar grade.

Data Analysis

The results got from this work were subjected to descriptive statistics and enrichment factor computation. In this work, Iron was chosen as the reference element during the computation of enrichment factor (Ediagbonya *et al.*, 2013a). Enrichment factor (EF) is given by:

$$EF = \left(\frac{C_1}{C_{Fe}}\right)_{TSP} \Big/ \left(\frac{C_1}{C_{Fe}}\right)_{crust}$$

Where C_1 is the concentration of the element considered in the TSP of the crust and C_{Fe} is the concentration of the reference element (Fe). The elemental concentration in the crust used in this study was got from (Wedephol, 1969). An enrichment factor close to 1 indicates that the relative concentration of a given element is identical to that which is present in the soil. An enrichment factor greater than 1 indicates that the element is more abundant in the air relative to that found in the soil, while values less than 1 suggests a depletion of the element in the air over that found in soil.

RESULTS AND DISCUSSION

Tables 1 and 2 show the mean concentration of the trace metal composition of the various locations in rural areas and the descriptive statistic of the trace metals concentration and the Enrichment factor. High intakes of cobalt, zinc, cadmium, copper and manganese interfere with iron absorption in the human body, which can lead to anemia (WHO, 2003). From Table 2, the mean concentration of the trace metal of Iron in TSP is 2.56mg/m^3. The concentration of Iron in TSP obtained in this study fell below the occupational exposure value limit for each element for 8hrs (5mg/m^3). The value obtained in this study can be compared to the values obtained in some parts of the country and other parts of world. According to (Okuo and Ndiokwere,2005) (Warri), the mean was 2.69mg/m^3, in other location by (Okuo and Okolo,2011) (Benin City),the rang of Iron was ;0.00246mg/m^3--0.00582mg/m^3. However, the levels of Iron in TSP in other parts of the world are; the mean value was 0.0027mg/m^3 (Khartoum) (Habbani *et al*.,2002); mean value 0.00091mg/m^3 (Birmili *et al*.,2006); mean value 0.000094mg/m^3 (Cong et al.,2007); 0.0023837mg/m^3 (China) (Ruojie *et al*.,2015); (Simon et al.,2004) had a mean concentration of 0.038903mg/m^3 (Santa Cruz). Copper released into the environment usually attaches to particles made of organic matter, clay, soil, or s everyone must absorb small amounts of copper every day because

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copper is essential for good health. High levels of copper can be harmful. Breathing high levels of copper can cause irritation of your nose and throat. Ingesting high levels of copper can cause nausea, vomiting, and diarrhea. Very-high doses of copper can cause damage to your liver and kidneys, and can even cause death. (ATSDR, 2004). The Occupational Safety and Health Administration (OSHA,2008) requires that levels of copper in the air in workplaces not exceed 0.1 mg of copper fumes per cubic meter of air (0.1 mg/m^3) and 1.0 mg/m^3 for copper dusts. Table 2 shows the mean concentrations of the trace metal Copper. The mean concentration of Copper in TSP was 0.122 mg/m^3. The concentration of Copper in TSP obtained in this study fell within the purview of the occupational exposure value limit for each element for 8hrs (0.1mg/m^3). The value obtained in this study can be compared to the values obtained in some parts of the country and other parts of world. According to (Okuo and Ndiokwere,2005) the mean value of Copper in TSP was;0.1mg/m^3 (Warri) (Obioh *et al.*,2005*)* had a range of Copper 0.00018mg/m^3---0.00321mg/m^3(Lagos)(Obioh *et al.*,2005*)*. However, the mean of Copper concentration in total suspended particulate matter (TSP) 0.0002mg/m^3 (Khartoum) (Habbani *et al*.,2012); 0.000000024mg/m^3 (Birmili et al.,2006); 0.00000031mg/m^3 (Tibtan Plateum) (Cong *et al*.,2007); 0.0000283mg/m^3 (China) (Ruojie et al.,2015); 0.0002mg/m^3 (Atlanta) (Thomas and Richard,2012) has reported by other countries. The mean of Lead in air is usually below 0.00015 mg/m^3 at non-urban sites. Urban air lead levels are typically between 0.00015 and 0.0005 mg/m^3 in most western cities (Habbani *et al*., 2002; Birmili *et al*., 2006; Cong *et al*., 2007; Ruojie *et al*., 2015). Additional routes of exposure must not be neglected, such as Lead in dust, a cause of special concern for children. Critical effects to be considered in the adult organism include elevation of free erythrocyte protoporphyrin, whereas for children cognitive deficit, hearing impairment and disturbed vitamin D metabolism (Rosen,1980;IARC,1997;Manderly,1994) are taken as the decisive effects Currently measured "baseline" blood lead levels of minimal anthropogenic origin are probably in the range10–30 μg/various international expert groups have determined that the earliest adverse effects of Lead in populations of young children begin at 100–150 μg/l. From Table 2, the mean concentration of Lead in total suspended particulate matter (TSP) was 0.119mg/m^3. The concentration of Lead in TSP obtained in this study violated Occupational Health and Safety Administration limit(OSHA) for each element for 8hrs (0.05mg/m^3), also higher than the WHO limit(0.0005mg/m^3). The value obtained in this study can be compared to the values obtained in some parts of the country and other parts of the world. According to (Okuo and Ndiokwere, 2005) (Warri), the mean value of lead in TSP was; 8.72mg/m^3, in other location by (Okuo and Okolo, 2011) (Benin City) the range of lead was; 0.00121mg/m^3-0.002419mg/m^3; Obioh *et al*., 2005(Lagos) had a range of lead 0.00108mg/m^3---0.00958mg/m^3. However,the mean of lead in TSP in westernized world the mean 0.000049mg/m^3 (Khartoum) (Habbani *et al*.,2002; 0.00000047mg/m^3 (Birmili et al.,2006); 0.00043mg/m^3 (Tibetan Plateum) (Cong *et al*.,2007); 0.0000467mg/m^3 (China) (Ruojie *et al*.,2015). Natural emissions of zinc and its compounds to air are mainly due to windborne soil particles, volcanic emissions, and forest fires. Volcanic release of zinc has been estimated to be around 35,800 tonnes/year (Garrette, 2000). Other natural sources of zinc in air are biogenic emissions and sea salt sprays with annual amounts estimated to be 8,100 and 440 metric tons, respectively (Raghunath *et al*., 1997). Anthropogenic releases of zinc and its compounds to the atmosphere are from dust and fumes from mining, zinc production facilities, processing of zinc-bearing raw materials (for example, lead smelters), brass works, coal and fuel combustion, refuse incineration, and iron and steel production (EPA, 1980; Burton et al., 2001; Nriagu, 1989). From Table 2 the mean concentration of Zinc in total suspended particulate matter (TSP) was 0.034mg/m^3. The concentration of Zinc in TSP obtained in this study fell below the Occupational Health and Safety Administration(OSHA) limit for each element for 8hrs (5mg/m^3).The value obtained in this study can be compared to the values obtained in some parts of the country and other parts of the world. According to Obioh *et al.*,2005 the range of Zinc was 0.00019mg/m^3--0.00552mg/m^3 (Lagos). The mean Zinc in TSP in westernized world; 0.000015mg/m^3 (Khartoum) (Habbani et al.,2002);0.00000091mg/m^3 (Birmili *etal*.,2006);0.000171mg/m^3 (China) (Ruojie et al.,2015). IARC has classified cadmium and cadmium compounds as Group 1 human carcinogens, having concluded that, there was sufficient evidence that cadmium can produce lung cancers in humans and animals exposed by inhalation (IARC, 1997). Because of the identified and controversial influence of Concomitant exposure to arsenic in the epidemiological study, however, no reliable unit risk can be derived to estimate the excess lifetime risk for lung cancer. Cadmium, whether absorbed by inhalation or via contaminated food, may give rise to various renal alterations. From Table 2, the mean concentration of cadmium in TSP was 0.0404mg/m^3. The concentration of cadmium in TSP obtained in this study violated the occupational exposure value limit for each element for 8hrs (0.005mg/m^3), also higher than the WHO limit (0.000005mg/m^3). The value obtained in this study can be compared to the values obtained in some parts of the country and other parts of the world. According to (Okuo and Ndiokwere,2005), the mean value of cadmium in TSP was; 0.552mg/m^3(Warri), in other location by (Okuo and Okolo,2011),the range of cadmium was;0.00003mg/m^3--0.00122mg/m^3(Benin) . However, the mean of Cadmium in TSP in westernized world; 0.00000005mg/m^3 (Birmili et al.,2006);0.0000009mg/m^3 (Santa Cruz) (Simone *et al*.,2004). Chromium is ubiquitous in nature. Available data, generally expressed as total chromium, show a concentration range of 5–200 mg/m^3.Chromium (III) is recognized as a trace element that is essential to both humans and animals. Chromium (VI) compounds are toxic and carcinogenic, but the various compounds have a wide range of potencies. (IARC, 1997) has stated that for chromium and certain chromium compounds there is sufficient evidence of carcinogenicity in humans (Group 1). From Table 2 the mean concentrations of chromium in total suspended particulate matter (TSP). The mean concentration range of chromium in TSP was 0.1mg/m^3. The concentration of chromium in TSP obtained in this study fell below of the occupational exposure value limit for each element for 8hrs (0.5mg/m^3), but higher than the WHO

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limit (0.00000025mg/m^3). The value obtained in this study can be compared to the values obtained in some parts of the country and other parts of the world. According to (Okuo and Ndiokwere, 2005) the mean value of chromium in TSP was; 0.085mg/m^3 (Warri), (Obioh *et al*.,2005) had a range of Chromium 0.00011mg/m^3---0.00296mg/m^3 (Lagos and Ile-Ife). The mean of Chromium in TSP in other parts of the world: 0.000158mg/m^3 (Tibetan Plateau) (Ningning *et al*., 2012); 0.000421mg/m^3 (Santiago) (Morata *et al*.,2008);0.0000097mg/m^3 (Daihai) (Han et al., 2009). In urban and rural areas without significant manganese pollution, annual averages are mainly in the range of 0.00001–0.00007 mg/m^3; near foundries the level can rise to an annual average of 0.0002–0.0003 mg/m^3 and, where ferro- and silico-manganese industries are present, to more than 0.0005 mg/m^3, with individual 24-hour concentrations sometimes exceeding 0.001mg/m^3 (Pace *et al*., 1983; Iregron, 1990). The toxicity of manganese varies according to the route of exposure. By ingestion, manganese has relatively low toxicity at typical exposure level and it is considered a nutritionally essential trace element. By inhalation, however, manganese has been known since the early nineteenth century to be toxic to workers. Manganese is characterized as a major cause of psychiatric problem and movement disorders, with some general resemblance to Parkinson's disease in terms of difficulties in the final control of some movements, lack of facial expression, and involvement of underlying neuroanatomical (extrapyramidal) and neurochemical (dopaminergic) systems (Antonini *et al*.,2005). Respiratory effects such as pneumonitis, pneumonia and reproductive dysfunction such as reduced libido are also frequently reported features of occupational manganese intoxication. From Table 1 the mean concentration of Manganese in TSP was 0.163mg/m^3. The concentration of Manganese in TSP obtained in this study fell below the Occupational Health and Safety Administration (OSHA) for each element for 8hrs (5mg/m^3) but higher than the WHO limit(0.00015mg/m^3). The value obtained in this study can be compared to the values obtained in some parts of the country and other parts of the world. According to (Okuo and Ndiokwere, 2005), the mean value of Manganese in TSP was 0.0899mg/m^3 (Warri). The mean of Manganese in TSP in westernized world:0.000068mg/m^3 (Khartoum) (Habbani *et al*.,2002); 0.00000017mg/m^3 (Birmili *et al*.,2006); 0.001216mg/m^3 (Santa Cruz) (Simone *et al*.,2004); 0.0000301mg/m^3 (China) (Ruojie *et al*.,2015). From Table 2, Cd was highly enriched and Pb was moderately enriched. In essay to find a common metal source, factor analysis was carried out which includes correlation coefficient of metal concentration and principal component analysis with Varimax rotation and cluster analysis. Table 3 shows the correlation coefficient of the metal concentration, Zinc correlated positively well with lead, Cadmium correlated positively well with Copper while Lead correlated negatively with Copper, this means that Zinc and Lead could be from the source while Lead and Copper from different source. Fig 3. Shows the Hierarchical Cluster Analysis. This cluster confirms two major clusters arrangement of the trace metal concentration and distribution at five monitoring sites. Cluster comprises Site 5 which is a unique cluster while the second cluster is made up of Site 1 and Site 3. From Table 4, the rotated component matrix showed that from the two components extracted from PCA Cu and Cd loaded positively with the first component, while Fe loaded negatively with the first component suggesting incineration of waste as a major source of the trace metal. For the second component Zn and Pb loaded positively, suggesting vehicular related emission as a major source of the trace metal. From the PCA with varimax rotation, two components were extracted which explained 80.46% of the total variance. Figure 2 below shows the rotated component plot.

Table 1: The mean concentration of trace metal in total suspended particulate matter during dry season in obaretin (mg/m^3)

Mean	Mean RHA	Mean RHB	Mean RHC	Mean RHD	Mean RHE
FE	1.450±0.495	3.500±2.869	1.300±0.721	4.450±0.3323	2.100±0.000
ZN	0.080±0.070	BDL	0.115±0.000	0.065±0.014	0.067±0.042
CU	0.120±0.057	0.163±0.106	0.130±0.070	0.105±0.078	0.093±0.075
MN	0.1633±0.0551	BDL	BDL	BDL	BDL
CD	0.04815±0.02270	0.04130±0.1952	0.04125±0.2595	0.04125±0.02595	0.02985±0.001619
PB	0.1250±0.0636	0.1100±0.0520	0.1100±0.0520	0.1250±0.0636	0.1250±0.0636
CR	0.200±0.000	BDL	BDL	BDL	0.20±0.000
NI	BDL	BDL	BDL	BDL	BDL
CO	BDL	BDL	BDL	BDL	BDL

BDL= Below Detection Limit

Table 2: Descriptive statistics of total suspended particulate matter (mg/m^3) and enrichment factor during dry season in obaretin

	Min	Max	Mean	SD	Enrichment Factor	OSHA Limit	WHO Limit
FE	1.300	4.450	2.560	1.368	1.000	5	-----------
ZN	0.000	0.080	0.034	0.035	0.158	5	-----------
CU	0.090	0.160	0.122	0.027	0.570	0.1	-----------
MN	0.160	0.163	0.160	0.009	0.033	5	0.00015
CD	0.0300	0.0480	0.0404	0.0066	550.190	0.005	0.000005
PB	0.1100	0.1250	0.1190	0.0082	10.840	0.05	0.0005
CR	0.000	0.200	0.100	0.141	0.413	0.5	0.00000025

Table 3: Correlation coefficient of trace metals in the total suspended particulate matter

	FE	ZN	CU	CD	PB
FE	1	-0.322	-0.505	-0.105	0.468
ZN	-0.322	1	-0.148	0.282	0.642
CU	-0.505	-0.148	1	0.733	-0.736
CD	-0.105	0.282	0.733	1	-0.099
PB	0.468	0.642	-0.736	-0.099	1

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Table 4: Principal component matrix of the trace metals in total suspended particulate matter

	Components	
	1	**2**
FE	-0.695	0.027
ZN	0.271	0.937
CU	0.907	-0.376
CD	0.773	0.218
PB	-0.486	0.861

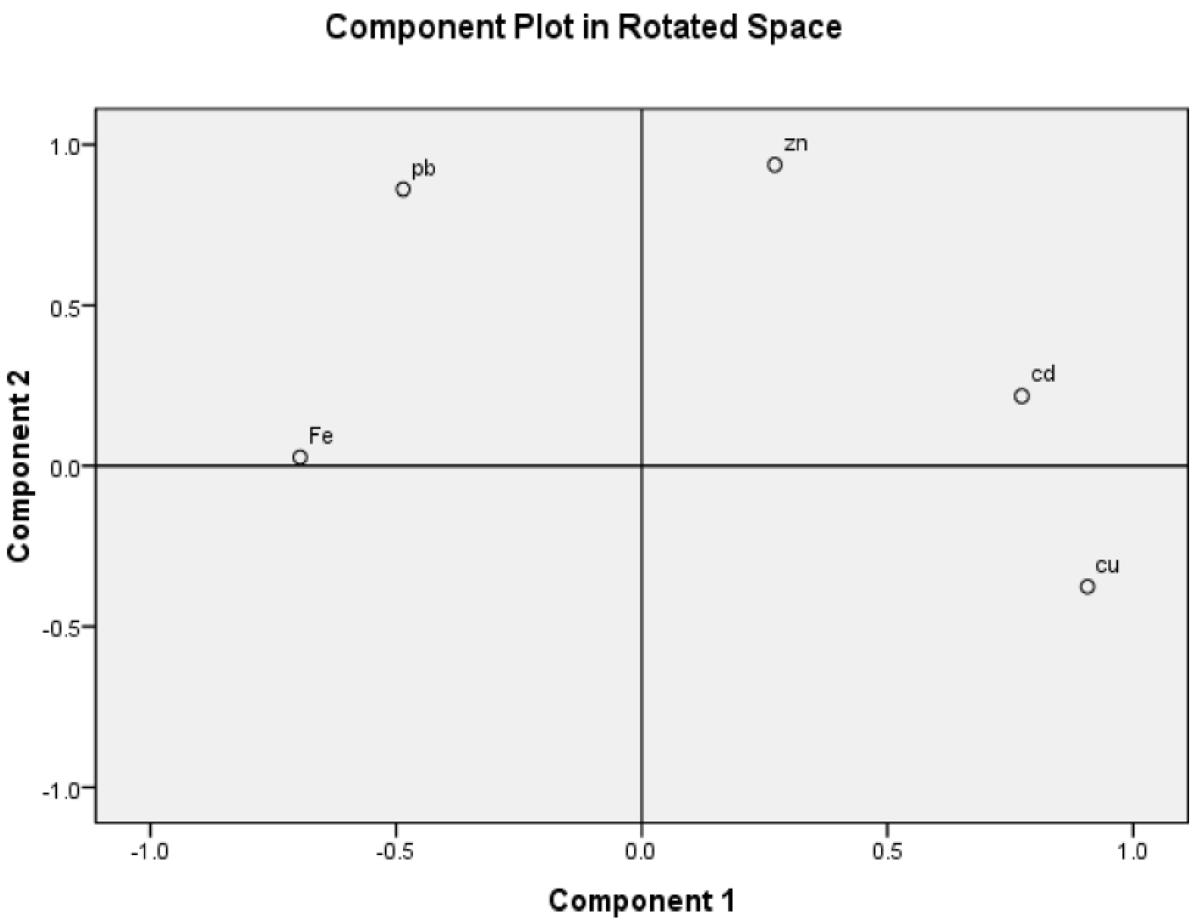

Figure 2: Rotated Component Plot

Figure 2: Rotated component plot

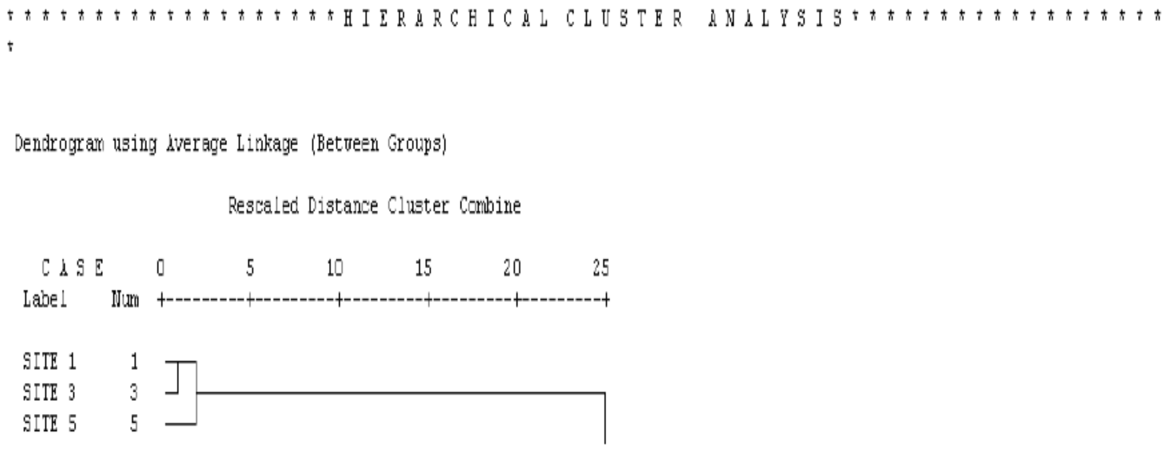

Fig 3: Dendrogram Showing sites cluster of total suspended particulate matter in Obaretin

Glass fibre filters used to capture the total suspended particulate matter were analyzed using AAS. The trace metal values obtained in this study were relatively high compared to other studies in other parts of the world. These high concentrations could be attributable to the various activities in the locality, such farming, rubber tapping, rural or intra-transportation, burning, paving of roads and activities from artisans such as panel beating, vulcanizes etc. From the principal component, two major components were obtained suggesting biomass burning and vehicular related emission as a major source of pollution in the locality. However, Zinc correlated positively well with Lead, Cadmium correlated positively well with Copper while Lead correlated negatively with Copper.

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