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ENRICHMENT FACTOR OF ATMOSPHERIC TRACE METAL USING ZIRCONIUM TITANIUM IRON AND COPPER AS REFERENCE ELEMENT

T. F. Ediagbonya*
DEPT. OF CHEMICAL SCIENCE, ONDO STATE UNIVERSITY OF SCIENCE &TECHNOLOGY, OKITIPUPA, ONDO STATE. NIGERIA
E-mail addresses: *tf.ediagbonya@gmail.com*

ABSTRACT
Twelve (12) elements (Cl, K, Ca, Ti, V, Fe, Ni, Cu, Zn, Ba, Sr, and Zr) were detected in total suspended particulate matter (TSP), inhalable particulate matter(PM_{10}) and respirable particulate matter($PM_{2.5}$)collected at a receptor site located in University of Benin Teaching Hospital (UBTH).X-ray fluorescence was used to determine the trace metal in the particulate matter and the enrichment factors were computed using Iron (Fe), Titanium (Ti), Zirconium (Zr) and Copper (Cu) as reference elements. The measured metals in the glass filter paper were found to be in the range of Argon(Ar), 0.00-0.01mg/m³; Potassium(K), 0.03-0.18mg/m³; Calcium(Ca), 0.01 0.14mg/m³; Titanium (Ti), 0.01-04mg/m³; Iron (Fe), 0.00-0.02mg/m3, Zinc(Zn), 0.00-0.04mg/m³; Strontium(Sr), 0.02-0.21mg/m³; Barium(Ba), 0.08-0.16mg/m³; Nickel(Ni), 0.02- .07mg/m³; Copper(Cu), 0.08-3.10mg/m³; Zirconium(Zr), 0.01-0.27mg/m³; Vanadium(V), 0.00- .00mg/m³; Chlorine(Cl), 0.03-0.09mg/m³ in Total Suspended Particulate Matter (TSP), in inhalable particulate matter Argon(Ar), 0.00-0.01mg/m³; Potassium (K), 0.00-0.13mg/m³; Calcium (Ca), 0.00-0.11mg/m³; Titanium (Ti), 0.03-0.07mg/m³; Iron(Fe), 0.00-0.03mg/m³; Zinc(Zn), 0.00-0.03mg/m³; Strontium(Sr), 0.01-0.02mg/m³; Barium(Ba), 0.13-0.16mg/m³; Nickel(Ni), 0.02-0.14mg/m³; Copper(Cu), 0.20-1.12mg/m³; Zirconium(Zr), 0.01-0.22mg/m³; Vanadium(V), 0.00-0.05mg/m³; Chlorine(Cl), 0.03-0.07mg/m³, while in respirable particulate matter, the measured metals in the glass filter paper were found to be in the range of Argon(Ar), 0.00-0.00mg/m³; Potassium (K), 0.06-0.22mg/m³; Calcium (Ca), 0.01-0.07mg/m³; Titanium (Ti), 0.02-0.03mg/m³; Iron(Fe), 0.00-0.01mg/m³; Zinc(Zn), 0.01-0.02mg/m³; Strontium(Sr), 0.01-0.02mg/m³; Barium(Ba), 0.01-0.01mg/m³; Nickel(Ni), 0.03-0.51mg/m³; Copper(Cu), 0.15-0.19mg/m³; Zirconium(Zr), 0.00-0.01mg/m³; Vanadium(V), 0.00-0.00mg/m³; Chlorine (Cl), 0.03-0.08mg/m³·Copper (Cu) was highly enriched in all the locations when Iron was used as a reference element while Zirconium(Zr) was highly enriched when Iron was used as reference element but poorly enriched in all the locations when Cu was as a reference element. The enrichment values of the various element when Iron was as a reference element are shown in this order: Cu >Zr>Ba>Cl>Ni>Zn>Sr>Ti>K>Ca>V

Keywords: *Enrichment factor, X-ray fluorescence, Trace metal, TSP, PM_{10}, $PM_{2.5}$*

1. INTRODUCTION
Enrichment factors (EFs) were spawned in the early seventies to discriminate between oceanic, terrestrial and potentially other elemental sources in the atmosphere of remote regions. Other sources of elements or processes such as volcanic and biological mobilization, vapor phase condensation, terrestrial material and high temperature dispersion had been second-guessed [1-2]. The application of EFs has been wide spread; is being used in various environmental medium such as air, soil and water in order to evaluate the influence of anthropogenic activities on these various media. Plethora of studies had been done within the country and outside the country on soil, water and air using enrichment factor to assess the impact of human activities on these various media [3-12]. Presently, no work has been done on comparing the various reference element in computing the enrichment factor. The various assumptions to the Enrichment Factor(EF) concept are, the low variability in concentration for the reference elements relative to the elements of interest [13], the similarity in regional distribution patterns for various reference elements, and the conservation

* Corresponding author, tel: +234-806-960-66577

of crustal element ratios through various compartments of the ecosystem [14]. In a more advanced version which involves the use of the enrichment factor formula, the values are in addition normalized to a "conservative" element [2]. "Conservative" or "reference" elements are those for which the concentration in the sample medium will practically exclusively be influenced by crustal sources. Most popularly used elements for the enrichment factor computation are: Al, Fe, Li, Sc, Ti, Si and Zr, and the elements for which the interference factor (IF), is minute are: Si, Al, Fe, Ti [2, 7, 15-17] or which are surmised to be practically not given off by human activities (Li, Sc, Zr). The resulting formula is where "Q" is the chosen reference element (e.g., Al). Al (and Na for an oceanic source) have been used originally [2] for the purpose of comparing the chemical composition of atmospheric particulate material collected at the various locations to the composition of the crust (or the ocean). These authors suggested that if this ratio is close to unity for any element this element may have a crustal or oceanic, and thus natural, source. It had been reported that Sb, Se, Br, Pb, Zn and Cu have very high enrichment factor(EF) and these high value of enrichment factor was adduced to vapor-phase condensation or a high-temperature dispersion source (volcanism or anthropogenic emissions) because of their high volatility. Since that time, enrichment factors (EFs) have increasingly been used to identify geogenic and anthropogenic element sources in environmental sciences [18-22]. When EFs are calculated, elements such as Ti, Al and Fe quite typically give very low values around 10 or less, while elements such as Cd, Se, Pb, Sb, Hg, Ag, Zn, As, Cu, Sn have EFs between hundreds and thousands [23-25]. This was then taken as proof of a major influence of anthropogenic activities on the concentration of these elements in the atmosphere at the sampling site. Cd gives by far the highest average EFs, followed by Cu, Pb, then Rb and this had also reported by other authors [15, 5].It had also been reported that the enrichment of particle and trace metals in the atmosphere had engendered serious health effect [26]. It had also been reported elsewhere that organometallic compounds play an important role in the general enrichment of certain elements at the surface of the earth [27]

The objectives of this work are; using x-ray fluorescence to determine the spatial distribution of the trace metals in total suspended particulate matter(TSPM), inhalable particle and respirable particle, calculate the enrichment factor using Zirconium (Zr) , Titanium (Ti), Iron (Fe) and Copper (Cu) as reference elements, compare difference between Zirconium (Zr) , Titanium (Ti), Iron (Fe) and Copper (Cu) when used as reference element in total suspended particulate matter(TSPM) inhalable particulate matter respirable particulate matter and compare the mean value of the trace metal with available occupational exposure value limit.

2. MATERIALS AND METHODS

2.1 Background to the Study Area

The study was carried out at the University of Benin Teaching Hospital (UBTH) Benin City, Nigeria. The teaching hospital comprises several departments which include: Surgery, Orthopedics and Trauma, internal medicine, child health, obstetrics and gynecology, mental health and community health, radiology, pathology, family medicine and dentistry. There is also general practice clinic (GPC) and store and supply and the Account Department, Accident and Emergency (A & E) units which are an out patient's arrangement. Burning of waste product, the use firewood by food vendors, photocopier and vehicular movement, the use of rug in office, and printers are veritable sources of particle. Fig 1 shows the map of the various sampling locations.

2.2 Sampler and Analytical Procedure for Total Suspended Particulate Matter

Sampler and analytical procedure SKC air check XR 5000 high volume gravimetric sampler Model 210-5000 serial No. 20537. The sampling unit consists of a gas pump with an in built flow rate meter and a filter holder manifold connected to the sampling pump by a Teflon tube. Airborne particulate matter was collected on a What man glass fiber filter paper. The in-built gas flow meter has a rating of 1000 to 5000ml/mm of air samples. Before sampling, all unloaded glass fiber filters were dried in a desiccators at room temperature and their initial weights were taken. The particulates were collected on the pre-weighed filter by pumping 2000ml/min (2L/min) volume of air through it for eight hours, after sampling, the loaded filters were again desiccated and re-weighed to determine the final weight. The concentration of the total suspended particulates in the air was determined from the difference in weight of the filter paper after and before sampling, the duration of the sampling and the flow rate [29, 30]. The sampler was placed at heights of 1.5m above ground level to coincide with the breathing zone of human.

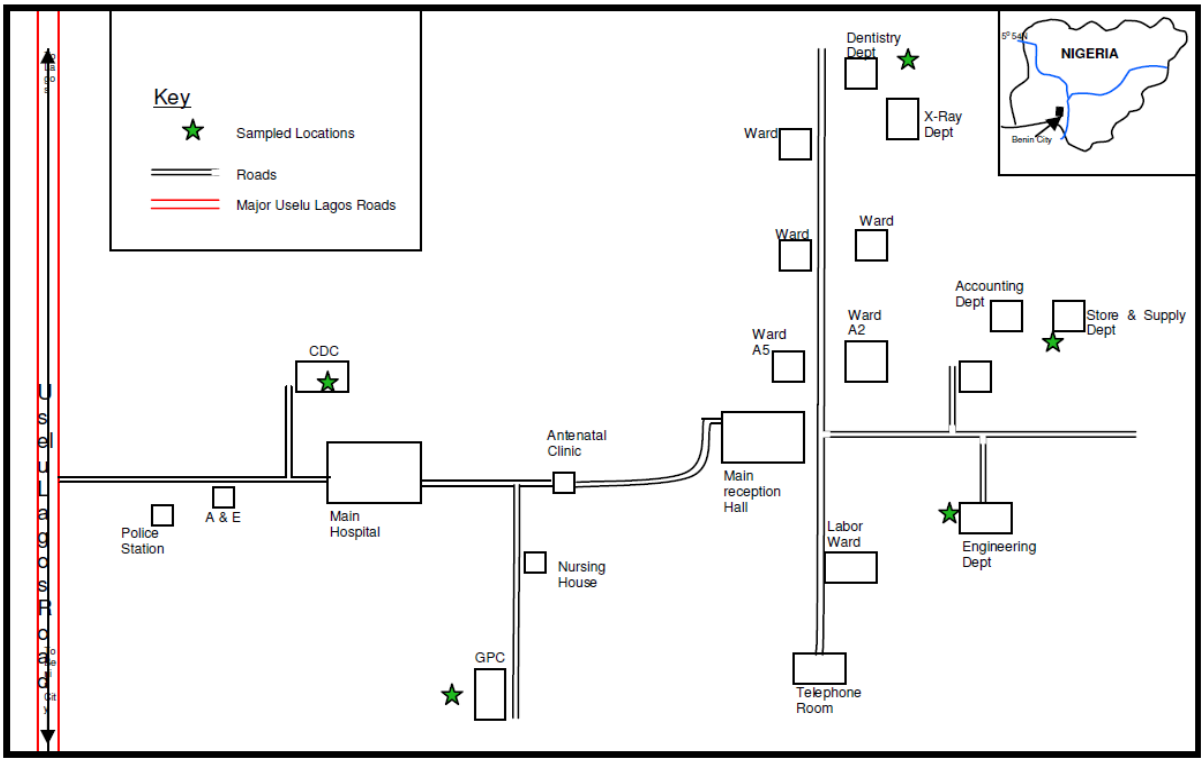

Figure 1: Shows the various sampling locations in UBTH

2.3 Sampler and Analytical Procedure for Respirable Particulate Matter and Inhalable Particulate matter

SKC Air check XR5000 High volume Gravimetric sampler Model 210-5000 serial No. 20537 and the I.O.M multi fraction dust sampler (Institute of Occupational Medicine) were used in this study. The sampling train was made of an air mover, a flow measuring device and a sample collection. A flow of air was created by the air mover which allowed the capture of contaminants in the air into the sample collection. The collection mechanism was made of cassette cover front plate, two-orings, cassette rear front and the sampler body which was connected to a vacuum pump with a Teflon tube. The inbuilt flow meter has a rating of 1000 ml/min to 5000 ml/min of air samples which was calibrated into 2000 ml/min (2 l.min).Before sampling, the unit was carefully calibrated against a standard meter to determine the quantity of air flows and all unloaded glass fiber filter and the foam were dried in the desiccator at room temperature. The respirable foam was affixed to 25 mm diameter filter for inhalable dust sampling with a flexible sample head to determine the respirable particle. The filter and cassette rear were pre-weighed to determine the initial respirable dust, while the filter, foam and whole cassette together were pre-weighed to determine the initial inhalable dust. After sampling, the filter, foam, with the whole cassette together were re-weighed to determine the inhalable fractions. The respirable fraction was determined by weighing the cassette rear and the filter only. These particles were collected at a flow rate of 21/min for eight hours and the sampler was placed between heights of 1.5-2 m to reflect the breathing zone of man. The difference between the final weight and the initial weight was the amount of respirable and inhalable dust collected [29, 30].

2.4 Sample Preparation and Measurement for XRF Analysis

The elemental analysis of the glass fibre filter paper was performed using the Energy Dispersive X-ray Fluorescence (EDXRF) spectrometer. The glass fibre filter paper was inserted directly into the instrument. The sample on the glass fibre filter was irradiated with a beam of X-rays. This primary radiation interacts with the elements in the sample to produce vacancies in the inner atomic shells, which then de-excite to produce characteristic secondary X-ray radiation. The wavelengths detected indicate which types of elements are present, and the quantity was determined from the intensity of the X-rays at each

characteristic wavelength [28].Each glass fiber filter paper was irradiated for 1000 seconds at fixed condition of 25 kV and 50 μA. The X-Ray Detector is a Model XR-100CR, high-performance thermoelectrically cooled Si-PIN photodiode, with a preamplifier. The analysis was carried in Obafemi Awolowo University Ile-Ife.

2.5 Data Analysis

During this study the enrichment factor was computed using Iron (Fe) Titanium (Ti), Zirconium (Zr) and Copper as reference element. In previous studies iron was used as reference element [15, 16]. The reference crustal ratio was taken from [13]. An enrichment factor close to 1 indicates that the relation concentration of a given element is identical to that which is present in soil. An enrichment factor greater than 1 indicates the element is more abundant in the air relative to that found in soil. While value less than 1 suggest a depletion of the element in the air over that found in soil.

The enrichment factor (EF) was computed using this formula

$$EF = \left(\frac{Q_1}{Q_{Fe}}\right)_{TSP} \Bigg/ \left(\frac{Q_1}{Q_{Fe}}\right)_{crust} \quad (1)$$

In (1), Q_1 is the concentration of the element is considered in the TSP of the crust and Q_{Fe} is the concentration of the reference element (Fe).

3. RESULTS AND DISCUSSION

Table 1, 2 and 3 show the mean concentration of heavy metals in total suspended particulate matter (TSPM), inhalable particulate matter (PM_{10}) and respirable particulate matter ($PM_{2.5}$).The results of the enrichment values computation for total suspended particulate matter(TSPM), inhalable particulate matter (PM_{10}) and respirable particulate matter ($PM_{2.5}$) are summarized in Table 4, 5, 6, 7 and 8. The most abundant element was Cu in both size fractions. The high value of Cu can be adduced to high level of windblown dust and combustion in the locations. The particulate matter concentration had been reported [29, 30].

From Table 1, K, Ca, Ti, Zn, Sr, Cu. Zr and Cl showed significant spatial variation ($p<0.05$); while Ar, Fe, Ba, Ni and V didn't show spatial variation ($p>0.05$). For K, the different location showed significant spatial variation; except outpatients and store, dentistry and community which did not show any spatial variation. For Ca, the different location showed significant spatial variation; except dentistry and community health and community health and store. For Ti, the different location showed no significant spatial variation; except in outpatients and account. For Fe, the different location showed no significant spatial variation. For Zn, there is no significant spatial variation in dentistry and community health, there is no significant spatial variation in outpatients and store but there is significant spatial variation in account. For Sr there is no significant spatial variation in the different locations except in dentistry. For Ba there is no significant spatial variation in all the different locations. For Ni there is no significant spatial variation in all the different locations. For Cu there is no significant spatial variation in the different locations except in community health. For Zr, there is no significant spatial variation in the different locations except in outpatients and store. For V, there is no significant spatial variation in all the different locations. For Cl, there is significant spatial variation in outpatients and store, there is no significant spatial variation in account, dentistry, community health and store. The trace metal obtained in this study can be compared with other studies done within and outside the country [23, 31-36].

Table 1: Concentration of heavy metals in total suspended particulate matter(mg/m³)

TSP	Outpatients	Account	Dentistry	Community Health	Store	p-value
Ar	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.00 ± 0.00^{a}	0.127
K	0.18 ± 0.01^{a}	0.03 ± 0.00^{b}	0.10 ± 0.01^{c}	0.10 ± 0.00^{c}	0.14 ± 0.02^{a}	0.000
Ca	0.14 ± 0.01^{a}	0.01 ± 0.00^{b}	0.08 ± 0.01^{c}	0.08 ± 0.01^{cd}	0.11 ± 0.00^{d}	0.000
Ti	0.04 ± 0.00^{a}	0.01 ± 0.00^{b}	0.02 ± 0.00^{c}	0.03 ± 0.00^{c}	0.03 ± 0.01^{ac}	0.000
Fe	0.02 ± 0.02^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.310
Zn	0.04 ± 0.00^{a}	0.00 ± 0.00^{b}	0.02 ± 0.00^{c}	0.03 ± 0.00^{cd}	0.03 ± 0.00^{ad}	0.000
Sr	0.02 ± 0.00^{a}	0.02 ± 0.00^{a}	0.21 ± 0.01^{b}	0.02 ± 0.00^{a}	0.02 ± 0.00^{a}	0.000
Ba	0.16 ± 0.02^{a}	0.08 ± 0.06^{a}	0.15 ± 0.02^{a}	0.14 ± 0.02^{a}	0.13 ± 0.01^{a}	0.105

TSP	Outpatients	Account	Dentistry	Community Health	Store	p-value
Ni	0.04 ± 0.00^{a}	0.03 ± 0.01^{a}	0.07 ± 0.09^{a}	0.02 ± 0.00^{a}	0.02 ± 0.00^{a}	0.578
Cu	0.10 ± 0.13^{a}	0.08 ± 0.01^{a}	0.08 ± 0.11^{a}	3.10 ± 1.06^{b}	0.26 ± 0.11^{a}	0.000
Zr	0.10 ± 0.00^{a}	0.14 ± 0.02^{ab}	0.15 ± 0.03^{ab}	0.24 ± 0.01^{ab}	0.27 ± 0.11^{b}	0.013
V	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.136
Cl	0.09 ± 0.01^{a}	0.03 ± 0.01^{b}	0.07 ± 0.01^{ab}	0.03 ± 0.01^{b}	0.04 ± 0.02^{b}	0.001

Mean with different superscript is statistically significant @p<0.05, "a" means no significance difference when it appears in two difference locations but" a and b" mean significance difference in difference locations.

The Occupational Safety and Health Administration (OSHA) 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. The trace metal concentrations obtained in this study fell within the purview of the regulatory limit of the Occupational Safety and Health Administration (OSHA) [37].

From Table 2, Ar, K, Ca, Ti, Fe, Zn, Sr, Ni, Cu, Zr, V showed significant spatial variation ($p<0.05$); while Ba, and Cl showed no significant spatial variation. For Ar there is no significant spatial variation in all the different locations. For K, there is significant spatial variation in the different locations except in outpatients and store. For Ca, there is significant spatial variation in outpatients, dentistry and store; while there is no significant spatial variation in the other locations. For Ti, there is no significant spatial variation in the different locations; except in outpatients. For Fe there is no significant spatial variation in dentistry, community health and store but there is significant spatial variation in outpatients and account. For Zn there is no significant spatial variation in account, dentistry, community health and store; but there is significant spatial variation in outpatients, account, dentistry and community health; but no significant spatial variation in outpatients and store. For Sr, there is significant spatial variation in account and dentistry; in account and store; while there is no significant spatial variation in outpatients, dentistry, community health, and store; there is also no significant spatial variation in outpatients, account and community health. For Ba, there is no significant spatial variation in all the different locations. For Ni, there is no significant spatial variation in the different locations except in store. For Cu, there is no significant spatial variation in the different locations except in outpatients. For Zr there is significant spatial variation in outpatients and accounts; in accounts and store; while there is no significant spatial variation in the other different locations. For V, there is no significant spatial variation in the different locations except in store. For Cl, there is no significant spatial variation in all the different locations. The values obtained in this study can be compared to other favorably with other studies done within the country and westernized world [6, 38-40].

Table 3 shows that for respirable particulate matter, K, Ca, Fe, Zn, Ba, Ni, and Zr, showed significant spatial variation ($p<0.05$) while Ar, Ti, Sr, Cu, V, and Cl showed no significant spatial variation. For Ar there is no significant spatial variation in all the different locations. For K, there is no significant spatial variation in all the different locations. For Ca, there is no significant spatial variation in outpatients, accounts and dentistry; in community health and store; while there is significant spatial variation in the other locations. For Ti, there is no significant spatial variation in all the different locations.

Table 2: Concentration of heavy metal in inhalable particulate matter (PM_{10})(mg/m^3)

Inhalable	Outpatients	Account	Dentistry	Community Health	Store	p-value
Ar	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.00 ± 0.00^{a}	0.031
K	0.00 ± 0.00^{a}	0.13 ± 0.01^{b}	0.10 ± 0.02^{c}	0.09 ± 0.01^{c}	0.01 ± 0.00^{a}	0.000
Ca	0.11 ± 0.00^{a}	0.10 ± 0.01^{ab}	0.07 ± 0.01^{bc}	0.06 ± 0.01^{c}	0.00 ± 0.00^{d}	0.000
Ti	0.07 ± 0.01^{a}	0.03 ± 0.01^{b}	0.03 ± 0.01^{b}	0.03 ± 0.01^{b}	0.03 ± 0.00^{b}	0.020
Fe	0.03 ± 0.00^{a}	0.01 ± 0.00^{b}	0.00 ± 0.00^{c}	0.00 ± 0.00^{c}	0.00 ± 0.00^{c}	0.000
Zn	0.00 ± 0.00^{a}	0.03 ± 0.00^{b}	0.02 ± 0.01^{b}	0.02 ± 0.00^{b}	0.01 ± 0.00^{ab}	0.001
Sr	0.02 ± 0.00^{ab}	0.02 ± 0.00^{a}	0.01 ± 0.00^{b}	0.01 ± 0.00^{ab}	0.01 ± 0.00^{b}	0.011
Ba	0.15 ± 0.04^{a}	0.14 ± 0.03^{a}	0.16 ± 0.05^{a}	0.14 ± 0.02^{a}	0.13 ± 0.02^{a}	0.763

Inhalable	Outpatients	Account	Dentistry	Community Health	Store	p-value
Ni	0.04 ± 0.01^{a}	0.04 ± 0.01^{a}	0.02 ± 0.00^{a}	0.02 ± 0.00^{a}	0.14 ± 0.02^{b}	0.000
Cu	1.12 ± 0.10^{a}	0.23 ± 0.11^{b}	0.21 ± 0.10^{b}	0.22 ± 0.11^{b}	0.20 ± 0.02^{b}	0.000
Zr	0.01 ± 0.00^{a}	0.22 ± 0.11^{b}	0.13 ± 0.02^{ab}	0.16 ± 0.04^{ab}	0.01 ± 0.00^{a}	0.002
V	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.50 ± 0.20^{b}	0.000
Cl	0.03 ± 0.01^{a}	0.07 ± 0.01^{a}	0.04 ± 0.01^{a}	0.04 ± 0.01^{a}	0.07 ± 0.03^{a}	0.096

Mean with different superscript is statistically significant @p<0.05, "a" means no significance difference when it appears in two difference locations but "a and b" mean significance difference in difference locations

Table 3: Concentration of heavy metal in respirable suspended particulate matter($PM_{2.5}$) (mg/m^3)

Respirable outpatient		Account	Dentistry	Community Health	Store	P value
Ar	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.01 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.062
K	0.11 ± 0.01^{a}	0.06 ± 0.01^{a}	0.09 ± 0.02^{a}	0.22 ± 0.11^{a}	0.08 ± 0.01^{a}	0.030
Ca	0.07 ± 0.02^{a}	0.05 ± 0.02^{ab}	0.06 ± 0.02^{a}	0.01 ± 0.00^{b}	0.01 ± 0.00^{b}	0.002
Ti	0.03 ± 0.01^{a}	0.02 ± 0.00^{a}	0.02 ± 0.00^{a}	0.03 ± 0.01^{a}	0.02 ± 0.01^{a}	0.568
Fe	0.01 ± 0.00^{a}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.000
Zn	0.02 ± 0.00^{a}	0.01 ± 0.00^{ab}	0.01 ± 0.00^{b}	0.02 ± 0.00^{a}	0.02 ± 0.00^{a}	0.006
Sr	0.01 ± 0.00^{a}	0.02 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.051
Ba	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.126
Ni	0.03 ± 0.01^{a}	0.05 ± 0.01^{a}	0.04 ± 0.02^{a}	0.31 ± 0.12^{ab}	0.51 ± 0.32^{b}	0.009
Cu	0.15 ± 0.02^{a}	0.15 ± 0.03^{a}	0.17 ± 0.06^{a}	0.15 ± 0.06^{a}	0.19 ± 0.05^{a}	0.751
Zr	0.01 ± 0.00^{a}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.00 ± 0.00^{b}	0.000
V	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.00 ± 0.00^{a}	0.857
Cl	0.05 ± 0.02^{a}	0.03 ± 0.01^{a}	0.04 ± 0.03^{a}	0.08 ± 0.03^{a}	0.03 ± 0.02^{a}	0.080

Mean with different superscript is statistically significant @p<0.05, "a" means no significance difference when it appears in two difference locations but "a and b" mean significance difference in difference locations

For Fe, there is no significant spatial variation in account, dentistry, community health and store; while there is significant spatial variation in outpatients. For Zn there is no significant spatial variation in outpatients, account community health and store, except dentistry. For Sr, there is no significant spatial variation in all the different locations. For Ba, there is no significant spatial variation in all the different locations. For Ni there is no significant spatial variation in the different locations except store. For Cu, there is no significant spatial variation in all the different locations. For Zr there is significant spatial variation in outpatients; while there is no significant spatial variation in the other locations. For V, there is no significant spatial variation in all the different locations. For Cl, there is no significant spatial variation in all the different locations. The values obtained in this study in all the locations can be compared to other studies done within the country and other countries [4, 38, 41-44].

From Table 4, Cu had the highest enrichment value of 6910.07, when Iron was used as reference element and V was poorly enriched with an enrichment value of 2.50 in the Outpatient Department. Also, the highest value was recorded in Cu in both inhalable particulate and respirable particulate matter. An enrichment factor closes 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. However, Enrichment Factor is also carefully used most of the time when the raw data do not show a clear signal. The results obtained in this study can be compared to other studies favorably [4, 14, 23, 32]. The enrichment values obtained in this study when iron was used as a reference element are almost ten time most enrichment values in other location. From Table 5, Cu had the highest enrichment value of 158082.95, when Iron was used as reference element and Ca had lowest enrichment value of 38.38 in the Account Department. Also, the highest value was recorded in Cu in both inhalable particulate and respirable particulate matter. From Table 6, Cu had the highest enrichment value of 51, 838.88, when Iron was used as reference element and V had the lowest enrichment value of

16.90 in the Dentistry Department. Also, the highest value was recorded in Cu in both inhalable particulate and respirable particulate matter. From Table 7, Cu had the highest enrichment value of 1704437.5, when Iron was used as reference element and V had the lowest enrichment value of 11.24 in the Community Health Department when compared to other locations. Also, the highest value was recorded in Cu in both inhalable particulate and respirable particulate matter. From Table 8, Cu had the highest enrichment value of 84971.23, when Iron was used as reference element and V had the lowest enrichment value of 6.37 in the Store Department. Also, the highest value was recorded in Cu in both inhalable particulate and respirable particulate matter. From different reference elements Fe, Ti, Zr and Cu, the enrichment values show similar distribution patterns. The locations with low enrichment value reflect decrease in contamination level of the metal.

Table 4: Enrichment factor of various elements in outpatients using Fe, Ti , Zr, &Cu as reference elements

Outpatients	TSP				Inhalable				Respirable			
	Fe	Ti	Zr	Cu	Fe	Ti	Zr	Cu	Fe	Ti	Zr	Cu
K	15.01	0.69	0.01	0.00	0.14	0.01	0.00	0.00	26.00	0.72	0.03	0.00
Ca	12.71	0.58	0.00	0.00	6.40	0.27	0.03	0.00	17.71	0.49	0.02	0.00
Ti	21.82	1.00	0.01	0.00	23.58	1.00	0.12	0.00	36.33	1.00	0.04	0.00
Fe	1.00	0.05	0.00	0.00	1.00	0.04	0.01	0.00	1.00	0.03	0.00	0.00
Zn	1186.73	54.39	0.41	0.17	3.77	0.16	0.02	0.00	1713.36	47.16	2.04	0.06
Sr	298.20	13.67	0.10	0.04	147.69	6.26	0.75	0.00	449.55	12.37	0.54	0.02
Ba	1892.05	86.72	0.66	0.27	1180.03	50.05	5.96	0.02	389.11	10.71	0.46	0.01
Ni	1598.40	73.26	0.56	0.23	1018.98	43.22	5.14	0.02	3467.87	95.45	4.13	0.12
Cu	6910.07	316.72	2.41	1.00	52072.07	2208.75	262.88	1.00	29080.65	800.45	34.66	1.00
Zr	2873.00	131.68	1.00	0.42	198.08	8.40	1.00	0.00	838.99	23.09	1.00	0.03
V	2.50	0.11	0.00	0.00	0.38	0.02	0.00	0.00	2.77	0.08	0.00	0.00
Cl	1807.01	82.82	0.63	0.26	439.82	18.66	2.22	0.01	2485.36	68.41	2.96	0.09

Table 5: Enrichment factor of various elements in account using Fe, Ti, Zr, & Cu as reference elements

Account	TSP				Inhalable				Respirable			
	Fe	Ti	Zr	Cu	Fe	Ti	Zr	Cu	Fe	Ti	Zr	Cu
K	64.13	0.69	0.00	0.00	24.62	0.75	0.00	0.00	120.93	0.65	0.44	0.00
Ca	38.38	0.42	0.00	0.00	18.80	0.58	0.00	0.00	94.65	0.51	0.35	0.00
Ti	92.33	1.00	0.00	0.00	32.62	1.00	0.00	0.00	185.80	1.00	0.68	0.00
Fe	1.00	0.01	0.00	0.00	1.00	0.03	0.00	0.00	1.00	0.01	0.00	0.00
Zn	4792.41	51.91	0.04	0.03	1947.27	59.69	0.14	0.06	11614.49	62.51	42.60	0.05
Sr	7645.33	82.81	0.07	0.05	617.12	18.92	0.05	0.02	5098.26	27.44	18.70	0.02
Ba	28605.02	309.82	0.25	0.18	3564.51	109.26	0.26	0.10	3806.38	20.49	13.96	0.02
Ni	42113.75	456.14	0.37	0.27	3660.86	112.21	0.27	0.10	49096.43	264.25	180.07	0.20
Cu	158082.95	1712.21	1.38	1.00	34892.13	1069.53	2.59	1.00	248498.12	1337.49	911.41	1.00
Zr	114547.59	1240.68	1.00	0.72	13481.67	413.24	1.00	0.39	272.65	1.47	1.00	0.00
V	50.86	0.55	0.00	0.00	2.36	0.07	0.00	0.00	22.03	0.12	0.08	0.00
Cl	17604.87	190.68	0.15	0.11	2802.39	85.90	0.21	0.08	12475.42	67.15	45.76	0.05

Table 6: Enrichment factor of various elements in dentistry using Fe, Ti , Zr, &Cu as reference elements

Dentistry	TSP				Inhalable				Respirable			
	Fe	Ti	Zr	Cu	Fe	Ti	Zr	Cu	Fe	Ti	Zr	Cu
K	74.52	0.66	0.00	0.00	134.38	0.54	0.00	0.00	152.18	0.89	0.56	0.00
Ca	61.16	0.54	0.00	0.00	109.10	0.44	0.00	0.00	109.36	0.64	0.40	0.00
Ti	112.90	1.00	0.00	0.00	247.19	1.00	0.00	0.00	170.22	1.00	0.63	0.00
Fe	1.00	0.01	0.00	0.00	1.00	0.00	0.00	0.00	1.00	0.01	0.00	0.00
Zn	6238.16	55.26	0.16	0.12	11446.93	46.31	0.19	0.05	5520.64	32.43	20.28	0.02
Sr	26781.77	237.22	0.70	0.52	2967.90	12.01	0.05	0.01	2903.50	17.06	10.67	0.01
Ba	15128.61	134.00	0.40	0.29	31182.32	126.15	0.52	0.13	2994.58	17.59	11.00	0.01
Ni	25515.43	226.01	0.67	0.49	12326.15	49.86	0.21	0.05	29479.01	173.19	108.28	0.13
Cu	51838.88	459.17	1.36	1.00	239233.70	967.81	4.01	1.00	228267.28	1341.04	838.49	1.00
Zr	38170.72	338.10	1.00	0.74	59586.02	241.05	1.00	0.25	272.24	1.60	1.00	0.00
V	16.90	0.15	0.00	0.00	14.57	0.06	0.00	0.00	17.34	0.10	0.06	0.00
Cl	11546.62	102.28	0.30	0.22	11202.38	45.32	0.19	0.05	14969.27	87.94	54.99	0.07

Table 7: Enrichment factor of various elements in community health using Fe, Ti, Zr, &Cu as reference elements

Community Health	TSP				Inhalable				Respirable			
	Fe	Ti	Zr	Cu	Fe	Ti	Zr	Cu	Fe	Ti	Zr	Cu
K	68.72	0.65	0.00	0.00	103.67	0.61	0.00	0.00	269.40	1.42	2.12	0.00
Ca	56.51	0.53	0.00	0.00	75.51	0.44	0.00	0.00	9.29	0.05	0.07	0.00
Ti	105.94	1.00	0.00	0.00	171.09	1.00	0.00	0.00	189.88	1.00	1.49	0.00
Fe	1.00	0.01	0.00	0.00	1.00	0.01	0.00	0.00	1.00	0.01	0.01	0.00
Zn	6737.51	63.60	0.13	0.00	8687.64	50.78	0.15	0.04	8726.13	45.96	68.63	0.06
Sr	2230.64	21.05	0.04	0.00	2517.72	14.72	0.04	0.01	2204.82	11.61	17.34	0.01
Ba	13073.15	123.40	0.25	0.01	21865.18	127.80	0.37	0.11	1824.45	9.61	14.35	0.01
Ni	6310.49	59.56	0.12	0.00	9254.26	54.09	0.16	0.05	194185.34	1022.70	1527.24	1.27
Cu	1704437.46	16088.16	32.43	1.00	200070.32	1169.41	3.42	1.00	153323.70	807.50	1205.87	1.00
Zr	52549.45	496.01	1.00	0.03	58564.25	342.31	1.00	0.29	127.15	0.67	1.00	0.00
V	11.24	0.11	0.00	0.00	11.83	0.07	0.00	0.00	17.57	0.09	0.14	0.00
Cl	5292.42	49.96	0.10	0.00	9324.88	54.50	0.16	0.05	23696.99	124.80	186.37	0.15

Table 8: Enrichment factor of various elements in store using Fe, Ti, Zr, &Cu as reference elements

Store	TSP				Inhalable				Respirable			
	Fe	Ti	Zr	Cu	Fe	Ti	Zr	Cu	Fe	Ti	Zr	Cu
K	56.82	0.69	0.00	0.00	87.58	0.06	0.00	0.00	126.38	0.62	0.50	0.00
Ca	43.92	0.54	0.00	0.00	10.81	0.01	0.00	0.00	10.87	0.05	0.04	0.00
Ti	81.91	1.00	0.00	0.00	1454.62	1.00	0.06	0.00	204.82	1.00	0.80	0.00
Fe	1.00	0.01	0.00	0.00	1.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00
Zn	4529.54	55.30	0.13	0.05	44921.85	30.88	1.72	0.04	11599.95	56.63	45.52	0.05
Sr	1446.44	17.66	0.04	0.02	16047.34	11.03	0.61	0.01	3776.13	18.44	14.82	0.02
Ba	7284.75	88.93	0.20	0.09	131323.08	90.28	5.02	0.11	2936.60	14.34	11.52	0.01
Ni	3865.07	47.19	0.11	0.05	524641.88	360.67	20.06	0.43	388716.87	1897.85	1525.44	1.63
Cu	84971.23	1037.36	2.37	1.00	1225155.22	842.25	46.83	1.00	239079.83	1167.27	938.22	1.00
Zr	35874.67	437.97	1.00	0.42	26159.98	17.98	1.00	0.02	254.82	1.24	1.00	0.00
V	6.37	0.08	0.00	0.00	24580.77	16.90	0.94	0.02	17.49	0.09	0.07	0.00
Cl	3985.72	48.66	0.11	0.05	115752.62	79.58	4.42	0.09	10741.83	52.45	42.15	0.04

4. CONCLUSION

Twelve (12) elements (Cl, K, Ca, Ti, V, Fe, Ni, Cu, Zn, Ba, Sr, andZr) were detected in total suspended particulate matter (TSP), inhalable particulate matter (PM_{10}) and respirable particulate matter ($PM_{2.5}$) collected at a receptor site located in UBTH. Elemental

composition of the aerosols captured on the glass fibre filters in both locations intotal suspended particulate matter (TSP), inhalable particulate matter(PM_{10}) and respirable particulate matter($PM_{2.5}$) revealed that the most abundant element was Cu. Enrichment factor calculation revealed that some elements were highly enriched thus, indicating anthropogenic origin while pollution indices displayed different pollution classes for the elements. The most abundant element was Cu in both size fractions followed by Zr, Ba, Cl, Ni, Zn, Sr, Ti, K, Ca and V.

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