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ED-XRF ANALYSIS OF WET DEPOSITION AROUND METAL RECYCLING PLANT

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ABSTRACT

The study investigated the compositions of air emissions from a steel recycling factory with a view to assessing the impact of emissions from the factory on elemental deposition in the immediate environment of the factory. Wet atmospheric depositions samples were collected in four geographic directions and at varying distances from the factory. The collected samples were filtered; oven dried and subjected to elemental determination using energy dispersive x-ray fluorescence (ED-XRF) technique. Results showed that maximum elemental depositions occurred between 0.4 – 0.6 km away from the factory in the north-east direction, with potassium being the most dominant element. Generally, the concentrations of elements decreased with increasing distance from the factory except for potassium whose trend suggested that other sources such as bush burning might also be contributing to its concentration. The possibilities of bio- accumulation and uptake of heavy metals by crops planted in the neighbourhood of the factory most especially in the north-eastern direction exist. The study concluded that emissions from the factory be treated before their release into the environment.

Keywords: Atmospheric deposition; Bio-accumulation; Elemental ratio; Steel recycling; Energy dispersive x-ray fluorescence

INTRODUCTION

In metal recycling, scrap metals from different sources are gathered, sheared and melted in a furnace to produce metallic materials such as iron rods for light construction works. In some cases, additives are added. In Nigeria, there have been an increasing number of scrap metal recycling factories over the past one decade. While these factories get their scrap metals from different sources, their major source is the damaged auto parts which abound in the country. Although, the steel recycling factories have the advantage of provide jobs and reducing solid waste management issues; there is however a concern about air emissions from the factories. The major sources of air emissions are the furnaces where the metals are melted and the utilities such as electric power generators. Pollutants which are usually emitted into the environment from furnaces and utilities such as electric power generators will include particulate matters which are usually composed of trace and heavy metals (Fridell *et al.,* 2008; Fakinle *et al.,* 2013).

Whether by intrinsic properties or in combination with other substances heavy metals have been known to exert varying degree of toxicity depending on their concentrations (Gilmour et al 1996; Lu et a., 2008). They constitute one of the most dangerous groups of anthropogenic environmental pollutants due to their potential toxicity and their persistence in the soils and biological systems (Ogunkunle and Fatoba, 2014). Exposure to heavy metal emissions via respiration and other means have been reported to have diverse adverse effects on human health (Wallenborn *et al.,* 2009; Jomova and Valko, 2011; Jaishankar *et al.,* 2015; Valko *et al,* 2016). Some of the particulate heavy metals are strong triggers for carcinogenesis, teratogenesis and mutagenesis (Hetland *et al.,* 2001; Ken *et al.,* 2002). Apart from humans, soils (Ogunkunle and Fatoba, 2014; Olowoyo *et al.,* 2015), vegetations (Pourrut *et al.,* 2011; Shahid *et al.,* 2014; Olowoyo *et al.,* 2015 and aquatic lives (Duce *et al.,* 2009) are affected by presence of heavy metals. The contamination of soil by heavy metals can be problematic because they do not degrade easily (Emmanuel *et al.,* 2009) and this always results in several soil dysfunctions leading to concerns about the environmental quality. Metal contaminated soil poses risks to humans and animals through

ingestion of plants that have bio-accumulated toxic metals from contaminated soil (Turner, 2009). Evaluation of the levels of heavy metal deposition is consequently of vital importance.

When pollutants get into the atmosphere, they may spend days, weeks, months or even years depending on their size and residence time before getting deposited. The process of how contaminants travel in the atmosphere has become a subject of significant scientific research. Quite a number of studies have pointed to importance of atmospheric deposition whether wet or dry as a major pathway through which pollutants are removed from the atmosphere (Duce *et al.,* 2009; Huston *et al.,* 2009; Maina *et al.,* 2013). Urban storm water is an important pathway for the transport of pollutants generated by anthropogenic activities. Substances present on particles, such as most heavy metals generally have relatively short residence times (days to a few weeks) and their removal, either by wet or dry deposition to the soil surface, will generally be on a local to regional scale (Duce *et al,* 2009). Measurement of atmospheric depositions is thus a good approach for determination of pollutants and how far they have been transported by atmospheric processes.

Among the available analytical procedures, the multi-elemental capability of the Energy Dispersive X-Ray Fluorescence (ED-XRF) technique and its suitability for aerosol studies has been demonstrated by researchers (Adejumo *et al.,* 1994; Omatola *et al,* 2009; RTI, 2009). XRF technology provides one of the simplest, most accurate and cost effective analytical methods for the determination of the chemical composition of wide varieties of substances including solid and liquid samples (John et al., 2001). To be specific, it has found useful applications in the investigation of mineral compositions of soils and construction materials. It is also used for research in archaeology, geochemistry and forensic sciences. Other advantages of XRF include; its ability to detect concentration limits at the sub-ppm level as well as measurement of concentrations of up to 100% easily and simultaneously (Jenkins, 1999). It is a reliable and non-destructive technique that does not require complex sample preparation procedures.

Majority of atmospheric deposition studies in Nigeria have focused on cement industries (Adejumo *et al.,* 1994; Maina *et al.,* 2013; Ogunkunle and Fatoba, 2014) and traffic related pollutions. Also, the study areas for air pollution measurements have been largely skewed towards highly populated and industrialized regions of the country. However, there has been tremendous increase in the number of metal recycling plants in Nigeria over the past decades some of which are located in the near rural areas that are originally alien to pollution from industrial sources. This may not be unconnected with availability of scrap metals from used automobiles with short life span which have now flooded the Nigerian market.

The primary purpose of this paper is to characterize qualitatively and quantitatively the wet atmospheric deposition of some trace and heavy elements around a metal recycling factory in Ile-Ife, Nigeria and to look at their spatial spread along four geographic directions. Information about atmospheric deposition for this region is not presently available.

METHODOLOGY

Description of study area.

The study area is a scrap metal recycling factory in Ife Central Local Government Area, Osun State of Nigeria (Figures 1a-c). Ile-Ife, an ancient town in Osun State, South-Western Nigeria is located between coordinates 7°28'N and 4°34'E. It has four Local Governments two of which are located at the heart of Ile-Ife town. The two Local Government Areas within the heart of the agrarian society have a total population of about 355,818 people according to 2006 population census figures which was that last official head count in the country. While the study area is not essentially a rural settlement, it lacks the features of an urban city which is often characterized by proliferation of industries.

Sampling

Wet atmospheric depositions were collected within and outside the metal recycling factory using deposition gauges fashioned after a British Standard deposit gauge (BS1747). Each comprised a cylindrical jar 15 cm high, 20 cm in diameter half filled with distilled water and mounted on 1.2 m high iron tripod with a concrete

slab base to avoid being blown away by wind. The deposition gauges were changed weekly and the measurements were taken for 2 months at the factory premises and at various distances (0-1.2km) around and away from the factory. The distance 0.0- 0.2 km represented locations within the factory while others represented distances away from the factory. The deposition sample was filtered in order to collect the particulate matter on a pre-weighed filter paper. The wet filter paper was dried to a constant weight at 105°C and reweighed.

Analytical Technique

Elemental analysis of the samples were done at the Center for Energy Research and Development, Obafemi Awolowo University, Ile-Ife Nigeria using Energy Dispersive X-Ray Fluorescence Spectroscopy (EDXRF) system link Analytical XR model coupled with computer based MCA which controls the sample holder and data acquisition. The X-ray beam was produced from a tube with Ag anode. Si/Li semiconductor detector detects the characteristic X-ray from the sample at 90° relative to the incident rays. Calibration of the system was done using single element standards provided by the manufacturer. Samples for EDXRF analysis were mounted on disposable XRF sample holders and measured for 1200 s with an accelerating voltage of 25.0 kV and a current of 0.050 mA. The analysis was carried out at these settings because the elements of interest have their characteristic X-rays within the energy range selected. The elements that were determined include K, Ca, Ti, V, Mn, Fe, Ni, Cr, Cu and Zn.

RESULTS AND DISCUSSION

The results of ED-XRF analysis of wet depositions collected around the metal recycling factory are summarized in Tables 1- 4. The mean concentrations of the elements in the north-eastern direction (Table 1) over 0.0 - 1.2 km radius from the factory ranged between 41.472 - 95.30; 11.03 - 23.81; 20.18 -52.09; 17.42-56.58; 22.84 - 53.53; 31.92- 40.73; 18.80 - 28.92 and 28.13 - 40.96 μg/cm^2 for K, Ca, Ti, Mn, Fe, Ni, Cu and Zn, respectively while the corresponding concentrations of the elements in the wet deposition samples collected in the south-eastern direction (Table 2) ranged between 31.00 - 49.31; 11.03- 23.81; 20.18- 52.09; 17.42- 56.58; 22.84 - 53.53; 31.92- 40.73; 18.80- 28.92 and 28.13- 45.03 μg/cm^2, respectively. The ED-XRF analysis of the samples collected in the south-western direction of the factory gave concentrations of K, Ca, Fe, Ni, Cu and Zn ranging between 22.94 - 34.53; 2.90 - 5.22; 0.24 - 1.89; 9.37 - 31.57; 13.24 - 18.62 and 11.38 - 18.06 μg/cm^2, respectively while the range of concentrations of the elements for samples collected from the north-western direction were 21.73- 28.24; 0.21- 2.90; 0.11- 0.91; 8.01- 29.93; 9.51- 16.97 and 9.39 - 17.53 μg/cm^2.

Table 1: Concentration of element in wet deposition along north-eastern direction (μg/cm^2)

km	K	Ca	Ti	V	Mn	Fe	Ni	Cr	Cu	Zn
0.0-0.2	49.03±2.51	20.17±3.12	41.35±24.15	5.81±0.15	46.32±3.61	43.24±2.37	38.23±5.71	4.00±1.23	27.17±3.55	39.41±2.79
0.2-0.4	52.52±10.11	23.81±3.25	48.73±4.42	5.92±1.92	56.58±4.14	51.00±3.22	40.73±3.01	4.15±0.17	28.28±2.57	40.96±3.28
0.4-0.6	95.30±14.05	14.91±1.96	52.09±4.55	0.33±0.03	40.01±3.19	53.53±3.38	39.76±2.50	9.50±1.87	28.92±1.89	45.03±3.52
0.6-0.8	45.67±10.31	14.29±2.22	41.37±3.65	0.17±0.01	35.74±4.98	42.55±2.69	38.97±2.50	1.07±0.01	27.37±1.76	40.337±3.27
0.8-1.0	70.13±7.91	11.13±1.94	25.18±1.93	ND	18.98±1.95	23.53±1.98	32.87±2.65	ND	22.06±2.15	30.68±2.71
1.0-1.2	41.47±7.52	11.03±2.00	20.18±2.19	ND	17.42±1.98	22.84±1.48	31.92±2.44	ND	18.80±1.77	28.13±2.16

Table 2: Concentration of element in wet deposition along south-eastern direction (μg/cm^2)

km	K	Ca	Ti	V	Mn	Fe	Ni	Cr	Cu	Zn
0.0-0.2	31.00±6.77	10.74±1.96	15.72±2.01	0.12±0.02	15.16±1.92	20.44±1.36	31.60±2.04	ND	18.12±178	27.39±2.33
0.2-0.4	39.16±7.84	9.78±2.10	11.73±1.73	ND	11.85±1.87	19.51±2.04	30.43±2.39	ND	17.90±1.62	18.77±1.23
0.4-0.6	33.64±9.15	9.29±1.89	11.50±1.81	ND	10.52±0.79	17.07±1.92	28.03±1.79	ND	17.84±1.22	17.67±1.15
0.6-0.8	49.31±8.14	8.61±1.46	10.17±1.92	ND	10.44±1.58	14.71±1.58	27.97±2.25	ND	16.72±1.26	11.50±0.80
0.8-1.0	34.64±6.78	8.03±2.96	8.84±0.83	ND	8.23±1.68	10.12±1.32	26.55±2.13	ND	16.69±1.55	9.00±1.30
1.0-1.2	31.00±2.96	6.00±1.04	7.99±0.51	ND	6.73±1.88	8.15±2.35	20.01±1.32	ND	16.00±1.89	8.97±1.26

Table 3: Concentration of element in wet deposition along south-western direction (μg/cm^2)

km	K	Ca	Ti	V	Mn	Fe	Ni	Cr	Cu	Zn
0.0-0.2	23.05±2.14	5.22±0.60	2.35±0.43	ND	5.12±1.48	1.89±0.12	31.57±2.58	ND	18.62±1.64	18.06±1.95
0.2-0.4	28.35±6.28	4.45±0.53	0.11±0.01	ND	4.52±0.45	0.9±0.06	29.48±2.86	ND	17.56±1.71	17.91±1.74
0.4-0.6	25.92±5.53	3.78±1.19	0.11±0.03	ND	1.50±0.01	0.85±0.053	27.49±2.18	ND	17.06±2.10	17.17±1.68
0.6-0.8	22.94±6.39	3.68±0.38	0.10±0.01	ND	ND	0.44±0.03	25.91±2.08	ND	16.47±1.95	15.33±1.73
0.8-1.0	31.00±2.80	3.58±0.48	ND	ND	ND	0.29±0.02	17.23±2.11	ND	16.10±1.61	13.99±1.42
1.0-1.2	34.53±6.25	2.90±0.89	ND	ND	ND	0.24±0.02	9.37±1.08	ND	13.24±2.13	11.38±0.81

Table 4: Concentration of element in wet deposition along north-western direction (μg/cm^2)

km	K	Ca	Ti	V	Mn	Fe	Ni	Cr	Cu	Zn
0.0-0.2	25.039±2.18	2.9	1.12±0.01	ND	3.23±0.09	0.91±0.01	29.93±1.91	ND	16.97±1.16	17.53±1.15
0.2-0.4	22.17±5.12	2.73	ND	ND	1.62±0.10	0.72±0.01	25.91±2.01	ND	16.40±1.58	13.63±0.91
0.4-0.6	28.24±2.50	1.98	ND	ND	ND	0.61±0.01	18.91±1.81	ND	16.34±1.76	11.38±0.81
0.6-0.8	21.73±2.00	1.31	ND	ND	ND	0.37±0.03	10.21±2.13	ND	13.21±0.91	10.63±0.74
0.8-1.0	26.91±2.62	0.21	ND	ND	ND	0.19±0.02	8.17±1.60	ND	10.21±1.13	10.09±1.16
1.0-1.2	27.25±6.19	0.21	ND	ND	ND	0.11±0.01	8.01±2.04	ND	9.51±3.12	9.39±1.27

With the exception of the north-eastern direction the maximum concentrations of all elements except K, in all other directions were generally at the maximum within the factory (0.0 – 0.2 km) as summarized in Tables 1- 4. These concentrations were observed to progressively thin out (decrease) with increasing distance from the factory in all directions. K and Ni were generally observed to have fairly higher concentrations around the factory in all directions more than any other elements while V and Cr had the least concentrations and were virtually not present in the wet atmospheric deposition samples collected except in the north-eastern direction. Even in the north-eastern direction, V and Cr were not detected in the samples collected at distances beyond 0.8 km.

The maximum values of the deposited elements were observed to occur between 0.4 - 0.6 km away in the north-eastern direction of the factory (Table 1). In Nigeria, there are two prevailing winds. The first is the north-east trade wind from the Sahara which is prevalent during the dry season while the second is the south westerly wind which dominates the rainy season. The present study was carried out in the rainy season; hence, it was not a coincidence that the flux of pollutants from the factory was observed to be towards north –eastern direction because of the prevalence of south westerly wind during this period. This may be responsible for the observed higher concentrations of the elements in the north-eastern direction than any other direction. It thus means that the flux may be higher in the South-Western direction in the dry season when north east trade wind from the Sahara is prevalent. With the exception of K; all other elements were observed to diminish in concentration after 0.6 km away from the factory; an indication that most of the pollutants were washed down by wet deposition before reaching 1 km radius. Since the maximum wet atmospheric deposition rate around the factory occurred between 0.4 -0.6 km in the north-eastern direction, the elemental balance in the soil around this region is likely to be influenced. The soils are expected to be richer in the elements present in the sample than soils at other locations around the factory.

The concentrations of K were observed to be generally high in all directions and there is no specific trend to associate it with the factory's activities. There is therefore the possibility of other sources contributing to the observed concentrations of K. Since the Ile – Ife town where the study area is located is an agrarian community; there is the possibility of bush burning. Bush and biomass burning have been reported to emit considerable amount of K (Lewis et al., 1988; Cheng et al., 2000). The elemental ratio K/Fe is sometimes used to indicate presence of pollutants from bush and biomass burning most especially for agricultural

purposes. A ratio K/Fe that is greater than 0.45 is reported to suggest a signature for bush and biomass burning (Lewis et al., 1988). Table 5 summarizes the elemental ratio K/Fe for all the wet atmospheric deposition samples collected at all directions and distances. In all cases, the ratio K/Fe was found to be greater than 0.45 an indication that bush and biomass burning might have contributed to the observed levels of K.

Table 5: Elemental ratio of K/Fe

km	NE	SE	SW	NW
0.0-0.2	1.131	1.52	12.2	27.5
0.2-0.4	1.02	2.01	31.5	30.8
0.4-0.6	1.78	1.97	51.8	46.3
0.6-0.8	1.07	3.35	52.1	58.7
0.8-1.0	2.98	3.42	106.9	141.63
1.0-1.2	1.81	3.8	143.9	247.7

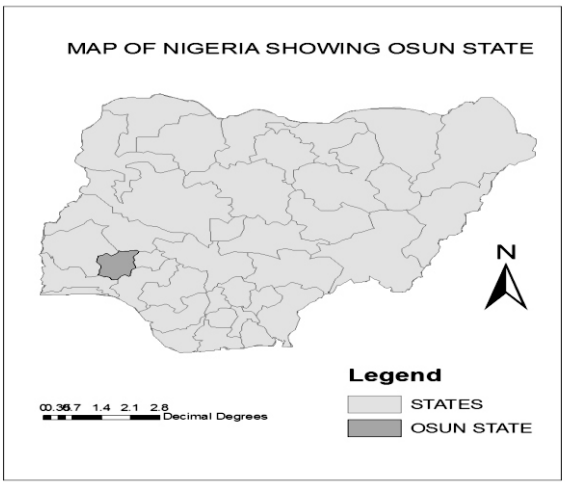

Figure 1a: Map of Nigeria showing Osun State

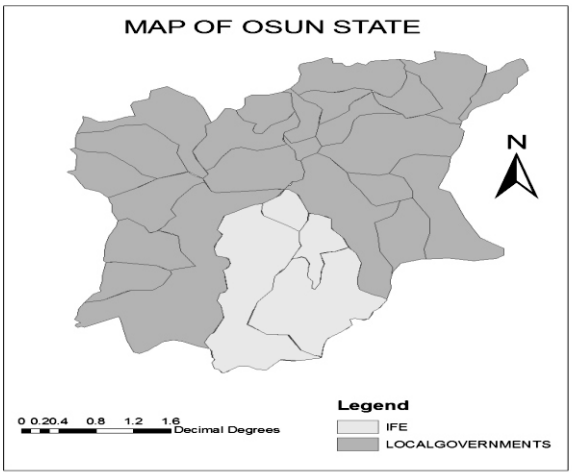

Figure 1b: Map of Osun State showing Ile-Ife

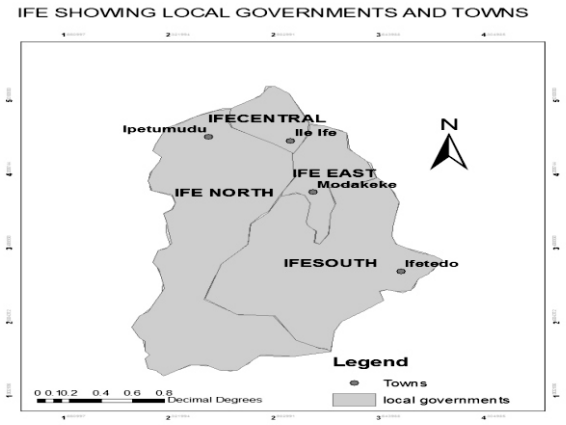

Figure 1c: Map of Local Governments in Ile-Ife (Ajala and Olayiwola, 2013)

CONCLUSION

In this study, ED-XRF analysis of wet atmospheric deposition samples was carried out in order to ascertain the elemental compositions and the spatial spread of air emissions from a steel recycling factory in Ile-Ife, Nigeria a town originally alien to industrial pollutions. Maximum concentrations of all elements were obtained between 0.4 - 0.6 km in the north-eastern direction of the factory. The study concluded that the deposition of elements at this distance will influence the soil elemental balance. Heavy metals in soils are known to bio-accumulate in plants; hence, humans can take up such elements through consumption of crops grown in such areas. With the exception of potassium, the concentrations of all elements were observed to decrease progressively with increasing distance from the factory. Among all the elements investigated, K was observed to have the highest concentrations and these were with no particular trend. The elemental ratio K/Fe having values greater than 0.45 in all cases suggested that in addition to the factory's activities; bush burning as an agricultural practice might also be contributing to the observed levels of K in the study area.

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