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Full Length Research Paper

EDXRF elemental assay of airborne particulates: A case study of an iron and steel smelting industry, Lagos, Nigeria

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The unregulated activities of a scrap iron and steel smelting industry in Lagos, Nigeria necessitated the sampling of particulate matter (PM_{10} and $PM_{2.5}$) particles from various sections of the industry. The samples were analyzed using polarized energy dispersive x-ray fluorescence (EDXRF) technique which allowed the simultaneous detection of over 25 elements in each of the samples. The mass concentration levels ranged from 86 to 8765 µg/m^3 for PM_{10} and 10 to 462 µg/m^3 for $PM_{2.5}$. The highest concentrations of 8765 and 462 µg/m^3 for PM_{10} and $PM_{2.5}$, respectively, were observed at one of the electric arc-furnaces (EAF-2). This was attributed to the scrap smelting and additives used. The observed high concentrations of PM_{10} lead (Pb) at various sites, when compared with exposure limit of between 1.0 and 5.0 µg/m^3 set by Occupational safety and Health Administration (OSHA) and United State Environmental Protection Agency (US EPA) is emphasized. For zinc (Zn), the measured levels exceeded the OSHA workplace occupational exposure limit set at 1 mg/m^3 for an 8-h workday over a 40-h work week and that set by the National Institute for Occupational Safety and Health (NIOSH) for up to a 10-h workday over 40-h workweek. These results suggest the need for immediate repair or replacement of the emission control devices.

Key words: PM_{10}, $PM_{2.5}$, polarized EDXRF, toxicity potential, electric arc-furnace, turboquant.

INTRODUCTION

Industries, through their various processes, generate toxic pollutants. Some of these pollutants are in particulate form, while others are not. In developed countries, environmental protection agencies ensure that industries install and maintain pollution abatement technologies, so as to reduce concentrations of the pollutants to conform to set-down guidelines. However, in developing countries, environmental protection agencies are hardly effective, in that very little efforts are geared towards pollution control devices, if they exist at all. The consequence of the ineffectiveness is that industries emit these pollutants into the workplace and neighbourhood environments. Unfortunately in these countries, industries are are sometimes located in residential and commercial areas partly due to lack of proper enforcement of urban planning bye-laws. Both the populace in the vicinity of such industries and the workers in the industries get exposed to the pollutants as they spend large fraction of their lives within the polluted environment (Akeredolu, 1989). Various studies evaluating the mass concentrations as well as the elemental composition of airborne particulate matter in workplace environments have been reported (Akeredolu et al., 1994; Obiajunwa et al., 2002; Cambra et al., 1999).

In Nigeria, there has been a remarkable advancement in industrial progress within the last two decades. This rapid rate of industrialization has not been matched with proper planning for environmental pollution problems that are usually associated with such development (Adejumo et al., 1994). The activities of the scrap iron and steel smelting industry has been on the high side due to increasing importation of used vehicles into the country. This has contributed to high and unregulated degradation of ambient air quality. Several studies evaluating the

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mass and composition of particulate matter (PM_{10}) and total suspended particles (TSP) in the ambient air of urban environments have been described (Olise et al., 2007). Most of these studies were carried out in vehicular traffic prone areas, and the rest were in cement Industries. Lagos, Nigeria is a rapidly growing city, with a population of about 9 million people, according to the Nigerian population census of 2007. The city also has a rapidly growing number of both large and small scale industrial establishments. The industries form major contributors to the environmental pollution problem in the city. The national and state environmental protection agencies are struggling to set up guidelines to limit emissions from the industries.

The production of steel in an electric-arc furnace (EAF) is a batch process, and the input material is typically 100% scrap. Scrap, alloying agents and fluxing materials are loaded into the cylindrical, refractory-lined EAF. The current through the graphite electrodes generates heat which subsequently melts the scraps. The emitted dust is principally iron, and silica oxides and lime. The concentrations of the trace metals such as chromium, copper, manganese, nickel, lead, zinc, etc are significant (US EPA, 1995). Several works by different authors in this area have linked several health problems to exposure to some of these pollutants. These include increased allergy, asthma, cardiovascular and cardio-pulmonary diseases. Where exposure is prolonged, cases of different forms of cancer have been reported (Erhabor et al., 1992; Odu et al., 1993). Some heavy metal pollutants have also been implicated in certain disorders of the nervous system (Kagawa, 1984). Though standards and guidelines on allowable concentrations of these pollutants have been set by environmental protection agencies, there is no consensus on whether there is any threshold concentration below which a pollutant has no detrimental effect on human health. It is therefore very important to monitor the level of pollutants from industries, especially in the work-place environment.

This research monitors airborne particulate matter in working area of an iron and steel smelting industry in Lagos, Nigeria. Samples were collected and analyzed for 25 major, minor and trace elements with a view to assessing the impact of the factory operations on the factory workers as well as the factory's immediate environment.

EXPERIMENTAL

Sampling

The airborne particulate matter samples were collected at five major production sections of the iron and steel smelting industry [two electric arc-furnaces (EAF-1 and 2), continuous casting (Cont. Cast.), rolling mill, and quality control laboratory (Qual. Control)]. The sampling locations were selected to reflect locations where workers spend most of their working hours, and the samples were collected at a height of about 1.6 m above the floor.

Measurements of PM_{10} and $PM_{2.5}$ fractions of particulate matter were carried out using a low-volume Gent Stacked Filter Unit PM_{10} sampler. The stacked filter unit contains two filters, a fine filter (for particles with aerodynamic diameter $d_{ae} \leq 2.5\mu m$) and a coarse filter (for particles with aerodynamic diameter $2.5\mu m \leq d_{ae} \leq 10\mu m$). The sampler operated at a flow rate of between 16 - 17 litres per minute. The sampling times were between 4 and 24 h depending on the activities in each of the production sections. The variations in the sampling time depended on the particulate load in the production sections at the time of sampling. After sampling, the exposed filters were unloaded from the filter unit and pre-conditioned for 24 h before reweighing to determine the particulate matter weight deposited on the filter. In all, 220 samples of both fractions were collected during the campaign over a period of 1 year covering both the wet and dry seasons. All the samples were collected during the working days, at least once a month from each production section and offices. The sampling was done for each location at the same fixed point throughout the sampling periods.

Analytical techniques

The mass concentrations of the PM_{10} and $PM_{2.5}$ fractions of the particulate matter were determined by gravimetric analysis. Concentration of each fraction of the suspended particulate matter in the ambient air was determined by dividing the difference between the filter weight after and before sampling, W_A and W_B, respectively, by the total volume of air sampled, V.

$$C_{SPM} = \frac{\Delta W}{V} = \frac{W_A - W_B}{V} \quad (1)$$

Toxicity potentials (TP) were calculated for each site (Tables 1 and 3) for both PM_{10} and $PM_{2.5}$ fractions of the suspended particulate matter.

$$TP_I = \frac{C_I}{TLV_I} \quad (2)$$

where TP_I is the toxicity potential, C_I the concentration (µg/m^3), and TLV_I is the threshold limit value for the size fraction *I*. TLV_I was set equal to the US EPA standard.

The elemental concentrations of the samples were determined using the polarized EDXRF (SPECTRO LAB2000) spectrometer. The analysis time per sample was 25 min for the determination of trace elements, which allowed the simultaneous detection of analytes from sodium (Na) to uranium (U) in all the samples. The detection limit for each element is of the order of a few ng/cm^2. Micromatter standard reference samples (Micromatter, US) were used for the system calibration. A check on the calibration was done by analyzing the standard CRM128 (Fly ash on artificial filter) of the Bureau of Community Reference (BCR). The samples were quantified using TURBOQUANT, a brand name for a SPECTRO method.

RESULTS AND DISCUSSION

PM_{10} and $PM_{2.5}$ mass concentrations

The mass concentration levels ranged from 86 to 8765

Table 1. Average PM_{10} and $PM_{2.5}$ mass concentrations and the sampling sites toxicity potentials.

Site	$PM_{2.5}$		PM_{10}	
	Conc. (µg/m^3)	TP	Conc. (µg/m^3)	TP
EAF-1	171.4	2.6	2244	34.4
EAF-2	156.0	2.4	4975	76.5
Continuous Casting	147.7	2.3	3314	51.0
Rolling Mill	92.8	1.4	687	10.6
Quality Control Lab	31.9	0.5	127	2.0

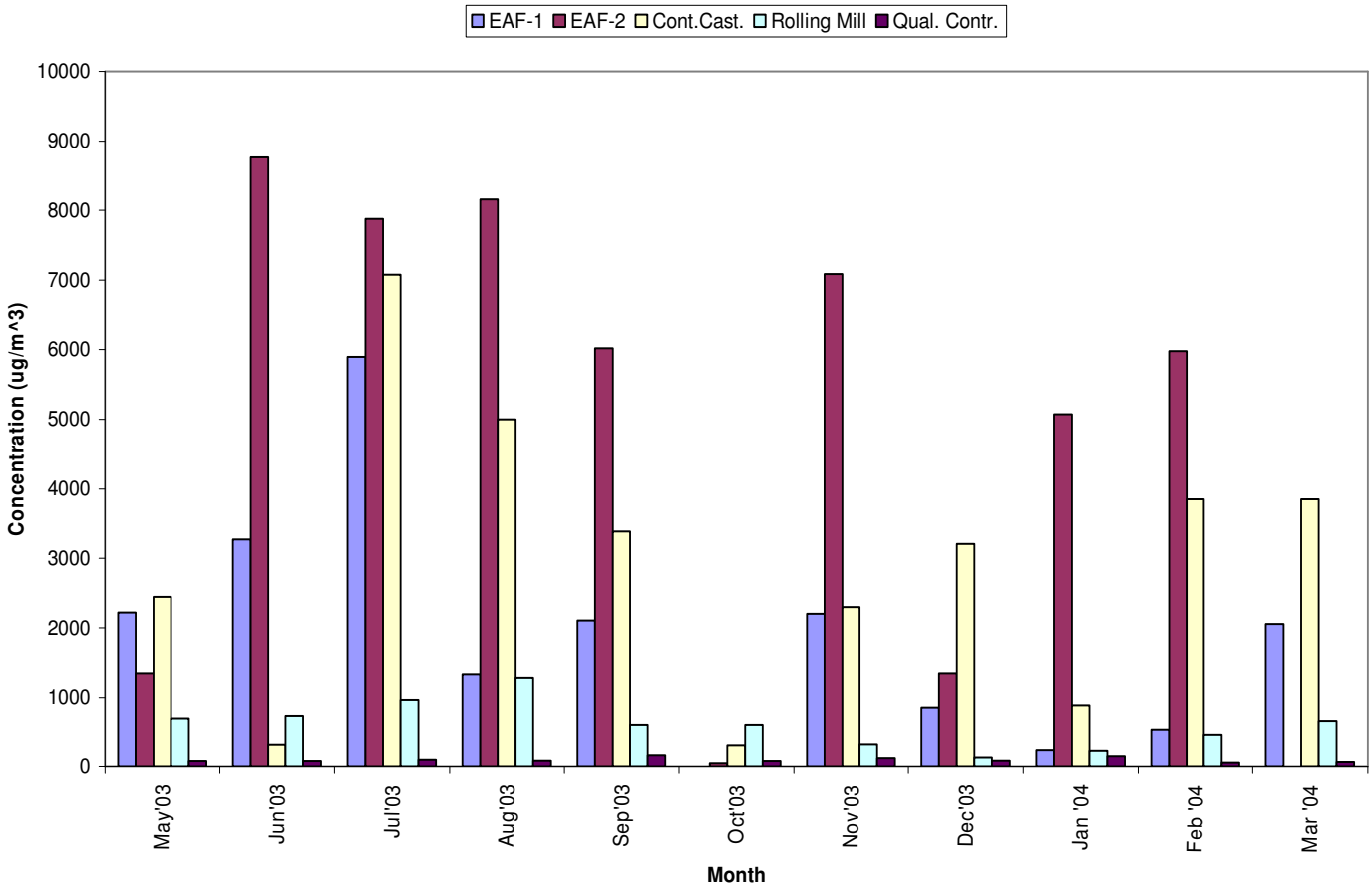

Figure 1. Average mass concentration of PM_{10} particles in the five production sections of the scrap Iron and Steel Smelter.

µg/m^3 for PM_{10} and 10 to 462 µg/m^3 for $PM_{2.5}$ as shown in Figures 1 and 2. The lowest concentration levels of 86 and 10 µg/m^3 for PM_{10} and $PM_{2.5}$, respectively were observed at the Quality Control Laboratory while the highest concentrations of 8255 and 462 µg/m^3 for PM_{10} and $PM_{2.5}$, respectively were observed at the EAF-2. It was observed that the $PM_{2.5}$ fraction sampled at EAF-1 and EAF-2 is lowest in July, 2003 for EAF-1 and in June, 2003 for EAF-2. The same fraction was highest in January, 2004 and October, 2003 for EAF-1 and EAF-2, respectively. This might be as a result of particle sizes emitted when the furnaces are in the charging stage. Sampling did not take place in October 2003 at EAF-1 and in March 2004 at EAF-2 and this explains their non-inclusion in Figures 1 and 2. The dust loadings at the other sampling sites within the same industry were also high. This was found to be due mostly to electric arc furnace emissions (Michand, 1993). The emission control device in this industry was not functioning at the time of the sampling. We observed that the effect of seasonal variation was not significant because high mass concentration recorded between May, 2003 to August, 2003, which was the wet season in Nigeria, was not as a result of seasonal change but due to the nature, quantity of

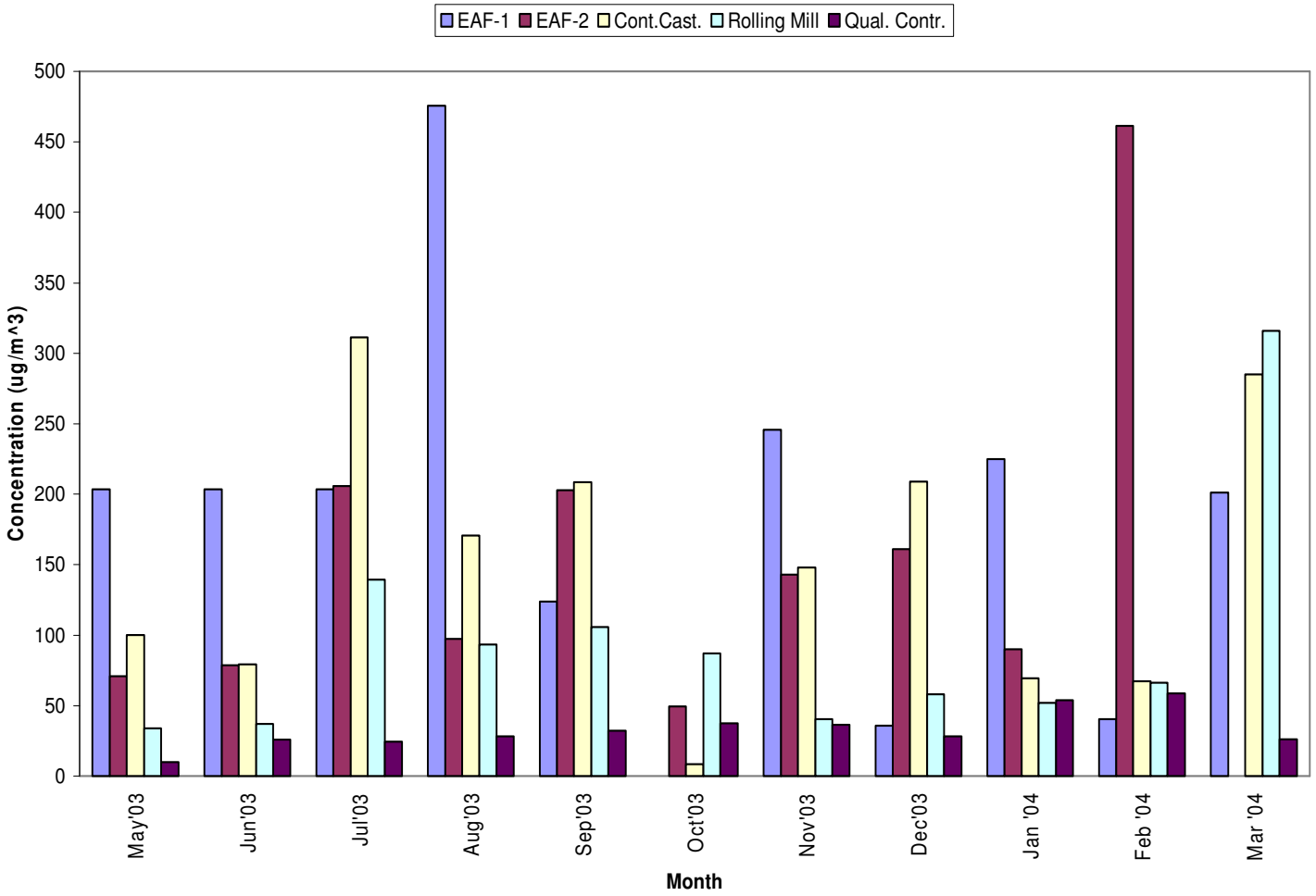

Figure 2. Average mass concentration of $PM_{2.5}$ particles in the five production sections of the scrap Iron and Steel Smelter.

of scrap and the additives used during the process of production. Mass concentrations were unexpectedly observed to be very high at the continuous casting section. This can be attributed to the downwind location of this section to the EAF-1 and 2 where most of the particles are emitted. Also, it was observed that the measurements in EAF-1 and 2 especially for $PM_{2.5}$ exceeded the US EPA 24-h average standard of 65 $\mu g/m^3$ with average annual mass concentrations exceeding annual standard of 15 $\mu g/m^3$ in all the sites (EPG, 1992; ECEE, 2001). The suspended particulate matter (SPM) at every sampling site was also higher than the ambient air quality standard of 250 $\mu g/m^3$ set by the Nigerian Federal Environmental Protection Agency.

Elemental Concentrations of PM_{10} and $PM_{2.5}$ fractions

Table 2 shows average elemental concentrations for PM_{10} and $PM_{2.5}$ fraction in all the samples and also the detection limit for each element. The EDXRF technique allowed the simultaneous detection of Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Rb, Br, Sr, Cd, Sn, Sb, Cs, Ba, Pb, and Bi in all the samples. Of particular interest are the concentrations of PM_{10} and $PM_{2.5}$ Pb at various sites. The concentration of PM_{10} lead (Pb) ranged from 0.4 to 160.2 $\mu g/m^3$ with the highest and lowest values, respectively observed at EAF-2 and quality control lab. Also the concentration of $PM_{2.5}$ Pb ranged from 0.1 to 9.7 $\mu g/m^3$ with the lowest value at the quality control lab and the highest value at the continuous casting section. Four elements: Mg, Mn, Fe and Zn have relatively higher concentrations in all the sections and show same trend of higher values in the PM_{10} compared with the $PM_{2.5}$ particle fractions. However, aluminium (Al) was observed to have lower concentration in the PM_{10} fraction compared with the $PM_{2.5}$ fraction at the continuous casting section only while the cesium (Cs) concentration values were consistently lower in the PM_{10} fractions compared with the $PM_{2.5}$ fraction. Vanadium (V) and nickel (Ni) were observed to be consistently low for the mass fractions for all the sections.

The two particulate fractions are inhalable and the $PM_{2.5}$ fractions are particularly respirable, and are there-

Table 2. Average elemental concentrations (µg/m^3) of PM_{10} and $PM_{2.5}$.

Element	DL (ng/cm^2)	EAF-1		EAF-2		Cont. Cast		Rolling Mill		Qual. Control	
		PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$
Na	50	13.6	1.8	34.6	2.0	26.5	3.33	4.7	0.9	0.3	0.1
Mg	9	472.7	393.9	125.1	4.4	1120.5	1117.8	378.6	1.0	82.1	1.1
Al	5.4	42.9	34.3	20.0	0.6	71.2	124.5	2.8	0.5	10.3	0.4
Cl	0.9	31.7	9.1	49.6	8.0	36.4	6.6	7.1	1.0	0.7	0.1
K	28.2	34.7	4.9	83.7	5.4	60.3	10.5	9.0	2.8	1.6	0.7
Ca	5.2	7.4	0.5	32.3	1.3	12.7	7.6	2.9	2.8	1.1	0.2
Ti	1.6	0.4	0.0	1.8	0.0	1.0	0.4	0.1	0.0	0.0	0.0
V	3.1	0.0	0.0	0.1	0.0	0.1	0.0	0.1	0.0	0.0	0.0
Cr	4.4	3.6	0.3	6.4	0.1	5.9	0.9	1.1	0.1	0.3	0.0
Mn	9.6	53.4	4.5	132.8	3.0	95.3	11.2	13.0	0.6	2.0	0.1
Fe	12.3	527.4	38.2	1592.1	23.8	913.5	106.5	198	14.1	43.0	8.0
Ni	1.9	0.6	0.0	1.8	0.0	1.3	0.7	0.2	0.0	0.2	0.1
Cu	4.7	4.8	0.5	12.7	0.3	9.8	3.8	1.8	0.2	2.4	0.9
Zn	6.3	311.8	29.0	2817.5	20.9	481.5	39.8	39.0	3.7	1.6	0.5
Br	1.8	2.0	0.3	8.5	0.3	3.6	0.3	0.4	0.1	0.0	0.0
Rb	3.2	0.3	0.1	0.7	0.1	0.4	0.1	0.1	0.0	0.0	0.0
Sr	2.7	0.1	0.0	0.3	0.1	0.2	0.3	0.0	0.0	0.0	0.0
Cd	26	0.9	0.1	2.3	0.2	1.9	0.4	0.2	0.1	0.0	0.1
Sn	25	1.7	0.6	3.9	0.2	2.4	1.3	1.6	0.3	0.5	0.2
Sb	17	0.6	0.4	2.6	0.0	0.9	1.0	0.1	0.0	0.1	0.0
Cs	2.1	0.9	1.4	0.5	0.9	1.3	3.8	0.2	0.5	0.3	0.2
Ba	23	3.5	3.0	4.0	1.1	5.0	4.0	1.4	0.8	0.8	0.3
Pb	5.1	59.2	5.2	160.2	5.9	103.6	9.7	11.9	1.4	0.4	0.1
Bi	3.5	0.4	0.1	1.2	0.1	1.0	0.3	0.1	0.1	0.0	0.0

fore likely to get into the respiratory system and get absorbed into the blood. Some of the heavy metals especially Pb from workplace air have occupational exposure limit of between 1.0 to 5.0 µg/m^3 set by Occupational safety and Health Administration (OSHA), while United State Environmental Protection Agency (US EPA) set occupational limit at 1.5 µg/m^3, 8-h working day and 40-h work week (US EPA, 1995). For zinc (Zn), the OSHA workplace occupational exposure limit was set at 1 mg/m^3 for an 8-h workday over a 40-h work week and National Institute for Occupational Safety and Health (NIOSH) has set the same standards for up to a 10-h workday over 40-h workweek. A worker at EAF-1 section, working 12 h per day, was exposed to average $PM_{2.5}$ and PM_{10} of about 15.6 and 178 µg/m^3 for Pb, respectively and to 87 and 6.4 mg /m^3 for Zn, respectively. Likewise, for a worker at EAF-2 with the same 12 h per day was exposed to 17.7 µg/m^3 $PM_{2.5}$ Pb and 480 µg/m^3 PM_{10} Pb and 62.8 µg/m^3 $PM_{2.5}$ Zn and 8.5 mg/m^3 PM_{10} Zn. All these exceeded the limit when compared with the above set standards.

Toxicity potential (TP) calculated for average PM_{10} and $PM_{2.5}$ mass concentrations at these sites were much higher than 1, except for $PM_{2.5}$ of the quality control laboratory (Table 1). This was also reflected in PM_{10} and $PM_{2.5}$ Pb toxicity potential for each of the site except at quality control laboratory (Table 3).The implication of this is that workers were being exposed to excessive level of this toxic pollutant. Table 4 shows the comparison between this work $PM_{2.5}$ elemental concentration in the EAF sections with that of US (AISI, 2000). The concentrations of elements: Fe, Zn, Mn and Pb were observed to be higher than those of AISI, 2000 except for Fe in EAF-2. The EAF-2 was about 10 years old while EAF-1 was about 30 years. Other elements: Cr, Cu and Ni were observed to be relatively low, and this may be attributed to the nature of scraps. The scraps used by the smelting

Table 3. PM_{10} and $PM_{2.5}$ Pb toxicity potential for each site.

Site	$PM_{2.5}$ Pb	TP	PM_{10} Pb	TP
EAF-1	5.2	3.47	59.2	39.47
EAF-2	5.9	3.93	160.2	106.8
Continuous Casting	9.7	6.47	103.6	69.07
Rolling Mill	1.4	0.93	11.9	7.93
Quality Control Lab	0.1	0.07	0.4	0.27

Table 4. Comparison of this work $PM_{2.5}$ average elemental concentration in EAF ($\mu g/m^3$) with literature.

Element	EAF		
	AISI, 2000	EAF-1 (TW)	EAF-2 (TW)
Fe	29	38	24
Zn	16	29	21
Mn	4	5	3
Pb	2	5	6
Cr	1.3	0.3	0.1
Cu	2.7	0.5	0.3
Ni	0.3	0	0

TW: This work.

industry are majorly iron and steel.

Conclusion

This study has shown the extent of air particulate pollution in the workplace of a scrap iron and steel smelting industry in Lagos, Nigeria. It was observed that there were high mass concentrations in some of the production sections especially in the electric arc-furnaces. The elements Cr, Mn, Fe, Cu, Zn, and Pb measured in PM_{10} and $PM_{2.5}$ fractions of the particulates were found to be high in the electric-arc furnace section as a result of the scrap and additives used in the process and the rate of emission are relatively high when compared with other production sections within the industry. This has led to the observed high elemental concentrations of some of the elements which have been implicated as having serious health impacts on human life. It was also observed that emitted pollutants from the furnaces are blown in the direction of continuous casting section because of its downwind location, which makes the measured elemental concentrations at that section higher than expected.

It can be inferred from this work that if the emission of the pollutants are left unabated, the workers' health are likely to be at risk. The high levels of PM_{10} and $PM_{2.5}$ particulate fractions with the concomitant high level of heavy metals are likely to lead to impairment of the workers' lung functions, (Kelsall et al., 1997; Pagano et al., 1998). Thus it is recommended that the emission control devices should be repaired to control the emissions from the production processes. Also, regular air quality monitoring should be carried out both by the industry and the government agents who are responsible for ambient air quality standards.

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