EDXRF ELEMENTAL ASSAY OF AIRBORNE PARTICULATES: A CASE STUDY OF AN IRON AND STEEL SMELTING INDUSTRY, LAGOS, NIGERIA*

O.K. OWOADE[1,+], F.S. OLISE[1], I.B. OBIOH[2], H.B. OLANIYI[1] and E. BOLZACCHINI[3]

1. Environmental Research Laboratory (ERL), Physics Department, Obafemi Awolowo University, Ile-Ife, Nigeria.
2. Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria.
3. Universita Milano-Bicocca, Dipartimento di Scienze-Ambientali, Pizza della Scienza, Milano, Italy.

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Abstract

The unregulated activities of a scrap iron and steel smelting industry in Lagos, Nigeria necessitated the sampling of PM_{10} and $PM_{2.5}$ particulates 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 all the samples. The mass concentration levels ranged from 86 μg/m³ to 8255 μg/m³ for PM_{10} and 10 μg/m³ to 462 μg/m³ for $PM_{2.5}$. The highest concentrations of 8255 μg/m³ and 462 μg/m³ for PM_{10} and $PM_{2.5}$ respectively were observed at one of the electric arc-furnaces (EAF-2). This was observed to be as a result of the scrap and additives used here and of the highest rate of emission. The observed higher concentrations of PM_{10} Pb at various sites when compared with the USEPA standard of 1.5 μg/m³ suggest immediate repair or replacement of the emission control devices.

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

1. Introduction

Industries, through their various processes, generate toxic pollutants. Some of these pollutants are gaseous, while others are in particulate form. 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, not investing on 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 sometimes located in residential and commercial areas. This is partly due to lack of proper enforcement of urban planning bye-laws which state clear-cut demarcation between residential and industrial areas. 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; Adepetu *et al.*, 1988). Various studies evaluating the mass concentrations as well as the elemental composition of airborne particulate matter in workplace environments have been reported (Potts *et al.*, 1999; Rodriquez, 2001; Querol *et al.*, 2001; Borbely-kiss, 1999). The inhalable and alveolar particulate fractions ($\leq$ 10 μm) will enter the respiratory system until deep into the lungs (EN481 standard). In 1999, the European Council set air quality standards for PM_{10} mass concentration and in the Daughter Directive (Directive 1999/30/EC); the request for a first characterization of $PM_{2.5}$ was added. The EU standard fixes, for 2010, an annual PM_{10} (particles with aerodynamic diameter d_{ae}<10μm) mean limits value of 20μg/m³ and a daily PM_{10} values of 50μg/m³ which should not be exceeded more than 7 days/year. The application of these limit values will take place through an intermediate stage (2005-2010) with more permissive limit values (40 μg/m³ PM_{10} annual value and 50 μg/m³ PM_{10} daily mean not to be exceeded more than 35 days/ year).

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

+ *corresponding author* (email: oowoade2001@yahoo.com)

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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 led to high and unregulated reduction of ambient air quality standards. Several studies evaluating the mass concentration, the composition of PM_{10} and total suspended particulates (TSP) in the ambient air of urban environments have been described (Ogunsola, 1995; Adejumo, 1994; Oluyemi, 1996; Olisemeke, 2002 and Olise, 2004). Most of this studies were carried out in vehicular traffic prone areas with the rest few in cement industries. Lagos, Nigeria is one of the very fast growing cities, with a population of about twelve million people, by WHO statistics. The city also has a fast growing number of industrial establishments. Some of the industries are small scale, while others are large-scale. 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 percent 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 processing time of a batch ranges from 1.5 to 5 hours to produce carbon steel and from 5 to 10 hours to produce alloyed steel. 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 and the dusts are therefore considered hazardous. 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, cardio-vascular and cardio-pulmonary diseases. If 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. Though standards and guidelines on allowable concentrations of these pollutants have been set by environmental protection agencies, there is no consensus agreement 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. In this work, the ambient air was sampled for airborne particulate matter in an iron and steel smelting industry, Lagos at an altitude of 38 m above the sea level. This is located on latitude 6.58°N and longitude 3.33°E. The industry was divided into two main sections: Enamelware and Rolling mill which also house the EAF and the continuous casting sections.

2. Experimental

Sampling

The airborne particulate matter samples were collected in the various production sections of an iron and steel smelting industry. The sampling locations were selected to reflect where workers spend most of their working hours and the samples were collected at the respirable height of about 1.6 m. Five major locations (two electric arc-furnaces, continuous casting, rolling mill, and quality control laboratory) were identified as areas where major activities of the production take place.

Measurements of PM_{10} and $PM_{2.5}$ fractions of particulate matter were carried out using a low-volume PM_{10} sampler. The filter unit contains two filters, each for a different fraction of the particulate matter. The sampler operated at a flow rate of between 16-17 litre per minute, to select particles with aerodynamic diameter less than 10μm. After sampling, the exposed filters were unloaded from the filter unit and pre-conditioned for 24 hours 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 one year. Two sets of weather (rain and dry season) were considered during the sampling. All the samples were collected during the working days, at least once a month from each production section and offices. The sampling took place in each location at the same 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.

$$C_{SPM} = \frac{\Delta W}{V} = \frac{W_A - W_B}{V} \qquad 1$$

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

$$TP_I = \frac{C_I}{TLV_I} \qquad 2$$

where TP_I is the toxicity potential, C_I the concentration (μg/m³), and TLV_I is the threshold limit value for size fraction I. was set equal to the US EPA standard.

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

	$PM_{2.5}$		PM_{10}	
Site	Conc. (µg/m³)	TP	Conc. (µg/m³)	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

The elemental concentrations of the samples were determined using the polarized EDXRF (SPECTRO LAB2000) spectrometer. The analysis time per sample was 25 minutes for the determination of trace elements, which allowed the simultaneous detection of analytes from Na to U in all the samples. Based on its high flexibility the accuracy is between 10 to 20%. The detection limit for each element is of the order of a few ng/cm². Micromatter standard reference samples (Micromatter, US) were used for the quantitative calibration of the system. 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.

3. Results and Discussion

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

The mass concentration levels ranged from 86 µg/m³ to 8255 µg/m³ for PM_{10} and 10 µg/m³ to 462 µg/m³ for $PM_{2.5}$. The lowest concentration levels of 86 µg/m³ and 10 µg/m³ for PM_{10} and $PM_{2.5}$ respectively were observed at the Quality Control Lab while the highest concentrations of 8255 µg/m³ and 462 µg/m³ for PM_{10} and $PM_{2.5}$ respectively were observed at the EAF-2. The mass concentration distribution is better observed from Figure 1(a-e). 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 (Fig.1a, b). This might be as a result of particle sizes emitted when the furnaces are in the charging stage. 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 raining season in Nigeria, was not as a result of seasonal change but due to the nature, quantity of scrap and the additives used during the process of production (Fig.1a, b). Also, we observed that the measurements in EAF-1 & 2 especially for $PM_{2.5}$ exceeded the US EPA 24-h average standard of 65 µg/m³ with average measured annual mass concentrations exceeding annual standard of 15 µg/m³ in all the sites. The suspended particulate matter (SPM) at every sampling site was also higher than the ambient air quality standard of 250 µg/m³ 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 with 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} Pb at various sites. These particles are inhalable, and are therefore likely to get into the respiratory system and get absorbed into the blood. In the scrap iron and steel smelting industry, Pb concentrations were higher than the USEPA national ambient air quality standard of 1.5 µg/m³ at all sites except the air conditioned quality control laboratory. The implication of this is that workers were being exposed to high level of this toxic pollutant. Toxicity potential calculated for these sites were much higher than 1, except for the quality control laboratory (Table 3).

4. Conclusion

This study has shown the extent of pollution in the ambient air in workplaces in a scrap iron and steel smelting industry due to emission of trace elements. It was observed that there were high mass concentrations in some of the production sections especially in the electric arc-furnaces. 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 because of the wind direction in the industry (North-East) at 030°, emitted pollutants from the furnaces are blown in the direction of continuous casting which makes the measured elemental concentrations at that section very high.

Table 2: Average elemental concentrations ($\mu g/m^3$) of PM_{10} and $PM_{2.5}$ particulates.

Element	DL (ng/cm^2)	EAF-1		EAF-2		Cont. Cast		Rolling Mill		Qual. Contr	
		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
Si	4	10.0	9.4	22.2	6.4	16.1	12.9	1.9	9.0	0.0	0.0
P	0.6	2.5	0.4	5.1	0.9	4.4	1.1	0.8	0.3	0.4	0.2
S	0.4	7.4	3.4	17.2	1.4	14.5	8.4	7.7	1.95	2.2	0.5
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

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

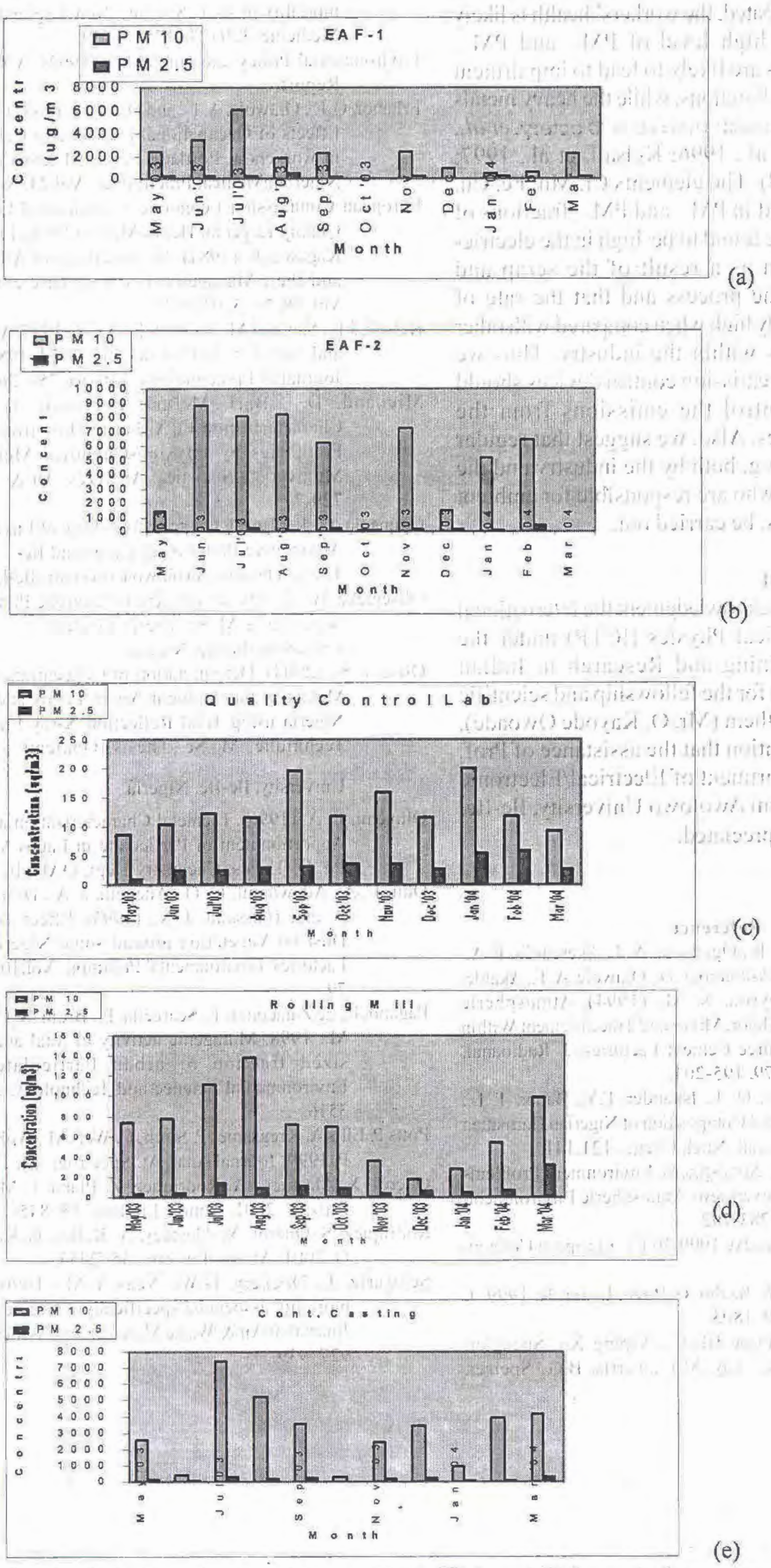

Fig 1(a-e): Each section mass concentration of PM_{10} and $PM_{2.5}$ particulate matter.

We want to emphasize that if the emission of the pollutants is left unabated, the workers' health is likely to be at risk. The high level of PM_{10} and $PM_{2.5}$ particulate fractions are likely to lead to impairment of the workers' lung functions, while the heavy metals are likely to cause health problems (Dockery, *et al.*, 1993; Schwartz, et al., 1996; Kelsall, et al., 1997; Pagano, *et al.*; 1998). 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 that the rate of emission are relatively high when compared with other production sections within the industry. Thus we recommend that the emission control devices should be repaired to control the emissions from the production processes. Also, we suggest that regular air quality monitoring, both by the industry and the government agents who are responsible for ambient air quality standards, be carried out.

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