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Chemical Speciation and Health Risk Assessment of Fine Particulate Bound Trace Metals Emitted from Ota Industrial Estate, Nigeria

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Abstract. In this study carcinogenic and non-carcinogenic health risk due to exposure to $PM_{2.5}$-bound trace metals from an industrial area in Southwestern Nigeria was estimated. A four-step chemical sequential extraction procedure was employed for the chemical extraction of arsenic (As), cadmium (Cd), chromium (Cr) copper (Cu), manganese (Mn), nickel (Ni), and zinc (Zn). Samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS). Results reveal Cr and Cu as the most dominant exchangeable fraction metals, indicating possibility of their being readily soluble once $PM_{2.5}$ is inhaled. Cd and Cr record the highest bioavailability index of 0.7. The cumulative lifetime cancer risks due to inhalation exposure for adults (4.25×10^{-2}), children 1-6 years old (4.87×10^{-3}), and children 6-18 years old (1.46×10^{-2}) were found above Environmental Protection Agency's acceptable range of 1×10^{-6} to 1×10^{-4}. The hazard index values for all studied trace metals suggest significant potential for non-carcinogenic health risks to adults and children. The choice of chemical speciation as an essential tool in facilitating a better predictive insight on metal bioavailability and toxicity for immediate remediation action has been highlighted.

1. Introduction

In Nigeria, significant amount of atmospheric particulates have been produced in recent years due to industrialization, unregulated waste management, emissions from vehicles, biomass burning, and rapid urbanization [1], [2]. Enhanced levels of PM in industrialized communities have heightened pollution problems in such areas and have been reported [1]-[4]. This has led to continuous deterioration in local and regional air quality with considerable mortalities and economic loss in these communities. Ota industrial estate (latitude 6 ° 32'N, longitude 2 ° 57'E) was established in 1983 as one of largest industrial hub in Ota, Nigeria. Over the past years, about thirty industries have been established and are domiciled within this industrial estate. The industrial processes include melting of aluminum and recycling of metal scraps and used batteries, manufacturing of plastics, steel and galvanized pipes, chemicals, pharmaceuticals, cosmetics, cooking utensils, and roofing sheets. Residential estates are also found within the Ota industrial estate [5], [6].

Fine particulate matter (PM), i.e. particles with diameter less than 2.5 μm ($PM_{2.5}$), is a complex mixture of chemicals including loosely bound toxic metals that have been associated with several adverse health and environmental problems [1], [2]. Health risks resulting from exposure to trace metals include reproductive toxicity, cancer, genetic damage, and neurotoxicity [7], [8]. Several literatures have established that metals from anthropogenic sources are commonly found in the fine particles. Industrial processes, coal combustion, construction and demolition, refuse incinerations, vehicle exhausts and non-exhaust sources such as wear from brakes and tyres are the major sources of Cd, Cr, Ni, Cu, Zn, Mn, Pb, V, Fe, Ba, K, and Al [9], [10]. Chemical speciation is an important analytical tool that offers a way for the elucidation of the chemical form(s) and the quantitative estimation of a specific element in toxicological and biochemical investigations to assess the bioavailability and mobility of metals in environmental and bio-physicochemical systems [10]-[15]. In order to evaluate the risk posed by metal toxicity, it is important to focus more on the determination of bio-available metals rather than total metals since they are readily available once inhaled [8], [10].

However, information on the pollution status of the present study area is sparse with nonexistent research data ever documented on the characterization and risk evaluation of atmospheric fine particulate bound metals. In addition, there are limited studies on the chemical forms of trace metals bound to atmospheric particulates in other cities in Nigeria. Therefore, the key objectives of this study are: (i) to determine and investigate the concentrations and partitioning of fine particulate matter bound trace metals (Cr, Cd, As, Ni, Zn, Cu and Mn); (ii) to evaluate the carcinogenic health risks and non-carcinogenic health risk posed to residents due to inhalation of particulate-bound metals in the study area.

2. Experimental

2.1. Sample collection

$PM_{2.5}$ samples were collected from the study sites on 47 mm diameter PTFE filters using Environtech Gravimetric Sampler (Model SLE-FPS105) between July 2014 and January 2015, exception of August. The filters were equilibrated in a desiccator for 48 hours and weighed thrice before and after sampling for accuracy, using four digits microbalance (Mettler Toledo Me 204). Filters were handled only with tweezers coated with Teflon tape to reduce the possibility of contamination. Laboratory and field blank filters were collected to reduce the gravimetric bias due to filter handling before, during and after sampling. A total of 20 samples were collected. After weighing, samples were preserved in the refrigerator at 4 °C prior to analysis.

2.2. Determination of chemical speciation

The modified Tessier derived procedure developed by [16], using a combination of mechanical shaker and micro wave oven was followed to fractionate the $PM_{2.5}$-bound trace metals into four fractions, namely, soluble and exchangeable metals (F1), acid soluble carbonates, Mn, Fe oxides and reducible metals (F2), metals bound to organic matter, oxidisable and sulphidic metals (F3) and residual metals (F4). Table 1 outlines the multistep procedure adopted for this work. Extracts from each fraction were carefully filtered and aliquot of 10 mL of the supernatant was drawn with a micropipette and placed in a preconditioned 15 mL polyethylene tube. The same four-step chemical extraction procedure was performed on blank filters. All the extracts were preserved at 4 °C in the refrigerator before analysis with ICP-MS. Sequential extraction instrument used were, pH meter (mettler Toledo), mechanical shaker (ZWY-11OX 30, Zhicheng), high speed centrifuge (HC-3514, Zonkia), and closed vessel microwave reaction system (CEM MARS 6, One Touch Technology). All reagents used in this research were of analytical grade.

Table 1. Chemical speciation reagents and extraction conditions.

Metallic fraction	Reagent	Experimental conditions
F1: Soluble and exchangeable metals	15 mL H_2O (PH= 7.4)	Shaker agitation, 3 H at RT[a] 3 min centrifugation at 5000 rmp
F2: Carbonates, oxides & reducible metals	10 mL $NH_2OH.HCl$ (0.25M) at pH=2.0	Shaker, 2H at RT 3 min centrifugation at 5000 rmp
F3: Bound organic matter, oxidizable	a) 7.5 mL H_2O_2, 30% b) + 7.5 mL H_2O_2, 30%	Shaker at $\Delta T(95^oC)^b$ Shaker at $\Delta T(95^oC)^b$

and sulphidic metals	c)+15mL NH_4AcO [2.5M] at pH=3.0	Shaker,90 min at RT 3 min centrifugation at 5000 rmp
F4: Residual metals	10 mL (HNO_3: HCl: HF) (ratio = 2: 6:2) + boric acid	20 min at MW oven

[a]RT= room temperature; [b]ΔT= applied heat; MW= microwave [16]

2.3. Determination of bioavailability index (BI)

The first two fractions (F1 and F2) are labile fractions and completely bioavailable. The bioavailability index (BI) was calculated as shown in equation 1:

$$BI = F1 + F2 \Big/ \sum_{i=1}^{4} F_i \tag{1}$$

2.4. Analysis of trace metals using inductively coupled plasma mass spectrometry

All solution samples were analyzed for 7 trace metals, Cr, Cd, As, Ni, Zn, Cu and Mn, using ICP-MS (Agilent 7500ce Series), equipped with an octopole collision cell following the instrument operating conditions. Calibration of the ICP-MS instrument was performed with multi-element calibration standards from 10 to 1000 mg/L. During the measurement, ^{6}Li, ^{45}Sc, ^{72}Ge, ^{103}Rh, ^{115}In, ^{159}Tb, ^{71}Lu and ^{209}Bi at 100 mg/L were used as the internal standards to monitor possible instrumental drifting and to compensate the matrix effect. The calibration of the ICP-MS instrument performed with multi-element calibration standards showed that the correlation coefficients (r^2) for all trace metals ranged from 0.994 to 1.000. Recovery test results done to evaluate the efficiency of the extraction procedure for the samples was in the range of 85% – 95%, method detection limits (MDLs) values for trace metals ranged from 4.29×10^{-5} to 2.56×10^{-3} µg/m^3, while the method precision, expressed as relative percent difference (RPD) was in the range of 5 to 12%. All quality control procedures were strictly adhered to from sampling to data analyses and report [17], [18].

2.5. Health risks assessment

The health risk estimate for a receptor exposed to the target trace metal species via the inhalation pathway was characterized into two forms namely non-carcinogenic and carcinogenic health risk. It was assessed using the inhalation dosimetry methodology outlined in EPA's Risk Assessment Guidance for Superfund (RAGS). The non-carcinogenic health risk, was computed by using the hazard quotient (HQ) formulae as follows:

$$Inhalation\ HQ = EC \big/ \left(RfC \times CF \right) \tag{2}$$

Where HQ is the hazard quotient, EC is the exposure concentration (µg/m^3), RfC is the inhalation reference concentration (mg/m^3) and CF is the conversion factor, 1000 (µg/mg) [19,20]. The concentration of the target metal in air (µg/m^3) was used as the exposure metric [20]. The exposure air concentration (µg/m^3), (EC), was calculated for each individual contaminant according to equation 3:

$$EC = \frac{CA \times ET \times EF \times ED}{AT} \tag{3}$$

Where CA is the concentration of the metal in the air to which the person is exposed (µg/m^3), ET is the exposure time (hours/day), EF is the exposure frequency (days/year), ED is the duration exposure (years), and AT is the averaging time (hours).

On the other hand, the cumulative lifetime cancer risk was calculated as shown:

$$Risk_{inhalation} = \sum_{i=1}^{n} IUR_i \times EC_i \tag{4}$$

Where, IUR is the inhalation unit risk (µg/m^3)$^{-1}$ and EC is the exposure air concentration (µg/m^3). IUR and R*f*C values were obtained from databases provided by the EPA's Integration Risk Information System (IRIS) and Provisional Peer Reviewed Toxicity Values (PPRTVs) [19], [21].

3. Results and discussion

3.1. Chemical speciation of $PM_{2.5}$-bound trace metals

The import of easily released trace metals can only be known from determination of bio-available concentrations which is very useful in risk assessment of metal toxicity [7], [9]. In Ota industrial estate, speciation results were obtained for Cr, Cd, As, Ni, Zn, Cu and Mn, (figure 1). Increased percentage distribution of soluble and exchangeable fraction (F1) obtained in OTE were Cr (46%) and Cu (32%) while Cd (67%) was dominant in the reducible fraction (F2). Metals present in the soluble and exchangeable fraction amongst all other fractions pose the greatest risk to human health because they are easily adsorbed on particle surfaces and released into aqueous solutions [13], [16]. This implies that Cr and Cu would be readily bioavailable once inhaled into the respiratory system. However, even though Cd and Ni is present, it is only dominant in the carbonates, oxides and reducible fractions. Therefore, Cd and Ni can only be a threat to human health under acidic aquatic conditions. The chemical speciation trend in the $PM_{2.5}$-bound trace metal levels was F4 > F2 > F3 > F1. Trace metals present in the residual fraction are said to be stable due to their stronger association with the crystalline structures of the minerals and as such are of no threat to the human health.

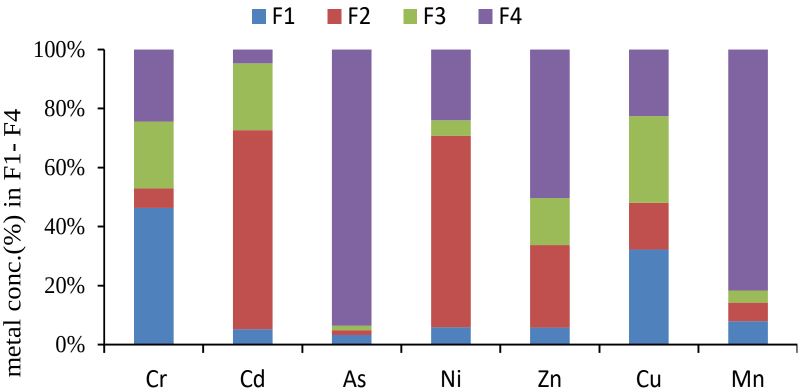

Figure 1. Average fractionation percentage of $PM_{2.5}$-bound trace metals.

3.2. Bioavailability index (BI)

Bioavailability index of metals shows the amount of soluble fraction present in the cell membrane through inhalation pathway [7]. The calculated trace metal bioavailability index results presented in table 2 indicated that Cd and Ni had the highest BI value of 0.7, followed by Cr and Cu (0.5). Amongst these metals Cd, Cr and Ni are the most toxic and their higher bioavailability index values indicate the possibility of their being fully available to physiological activities once inhaled into the respiratory system [14], [15].

Table 2. Bioavailability index of $PM_{2.5}$-bound trace metals.

Trace metals (μg/m^3)	Cr	Cd	As	Ni	Zn	Cu	Mn
Soluble fraction	4.78	0.449	0.232	0.111	32.8	0.173	0.054
Insoluble fraction	4.25	0.169	11.5	0.041	64.5	0.187	0.326
Bioavailability index	0.5	0.7	0.02	0.7	0.3	0.5	0.1

3.3. Carcinogenic health risk of inhaled $PM_{2.5}$-bound trace metals

Table 3 shows the incremental lifetime cancer risk (ILCR) at the study sites for four (4) carcinogenic trace metals, As, Cd, Cr and Ni capable of producing tumors of the respiratory tract, nasal passage, trachea, bronchus, and lung. It is usually assumed that even a minute exposure to these trace metals is a potential risk [8], [22]. The USEPA considers cancer risks between 1×10^{-6} (i.e., 1 in 1,000,000) and 1×10^{-4} (i.e., 1 in 10,000) to be generally acceptable [20]. Bioavailable form rather than total content of trace metal in airborne $PM_{2.5}$ was used in order to give a better and more accurate health risk estimate [7], [14], [15]. Two approaches were considered: cumulative risks to adult and children aged 0-6 and 6-18 years at the site due to inhalation of trace metals in air. From results presented in Table 3, the sum of the cumulative lifetime cancer risks across all investigated carcinogens due to inhalation exposures ranged as follows: adults (4.25×10^{-2}); children 1-6 years old (4.87×10^{-3}) and children 6-18 years old (1.46×10^{-2}). It is evident that the results obtained were above USEPA's acceptable risk range of 1×10^{-6} to 1×10^{-4}. Individual carcinogen showed that the range of the incremental lifetime cancer risks of Cd and Ni due to inhalation exposures for adults and children 1-6 and 6-18 were within the acceptable risk range of 6×10^{-4} to 6×10^{-2} μg/m³ and 4×10^{-3} to $4.0\times10^{-}$ μg/m³, respectively. On the contrary, Cr recorded elevated levels for adults (4.11×10^{-2} μg/m³) and children within ages 6–18 (1.42×10^{-2} μg/m³) above the USEPA's stipulated risk of 8.0×10^{-5} - 8.0×10^{-3} μg/m³. This would result in greater than a one-in-ten-thousand increased risk of developing cancer during one's lifetime. Also from Table 3, As exceeded EPA's acceptable risk range of 2.0×10^{-4} - 2.0×10^{-2} μg/m³. These results indicate that one (1) person out of a million people could get cancer after exposure to arsenic trace metals in ambient air inhaled from the investigated study area. Similar findings were observed by [15]. Thus, air particle pollution may pose serious health risks to the residents within the affected age categories in the study area.

3.4. Non-carcinogenic health risk of inhaled $PM_{2.5}$-bound trace metals

When an HQ and HI value exceeds one (HQ>1; HI>1), there is a possibility that some non-cancer effects may occur, the reverse happens with (HQ>1; HI>1) [19], [23]. The hazard quotients (HQs) of Cr, Cd, As, Ni and Mn were computed to determine the non-carcinogenic health risks for adults, children aged 0-6 and 6-18 years at the study site. Evaluation of the overall potential risk, by summing HQ values for the five trace metals gave the hazard index (HI). Results in Table 4, showed that the HQ for adults, children aged 0-6 and 6-18 years ranged between 2-80, 1-46 and 3-137, respectively. Implying a significant potential for non-cancer adverse health effects from all the five inhaled trace metals since the HQ is greater than 1 (HQ>1).

Table 3. Carcinogenic health risks assessment of $PM_{2.5}$-bound trace metals via inhalation.

Categories	Elements	CA	EC	IUR	$Risk_{inhalation}$	$\sum Risk_{inhalation}$
Adults	Cr	4.78	3.43	1.2×10^{-2}	4.11×10^{-2}	4.25×10^{-2}
	Cd	4.49×10^{-1}	3.22×10^{-1}	1.8×10^{-3}	6.00×10^{-3}	
	As	2.32×10^{-1}	1.67×10^{-1}	4.3×10^{-3}	7.00×10^{-4}	
	Ni	1.11×10^{-1}	8.00×10^{-2}	2.4×10^{-4}	1.91×10^{-5}	
Children 1-6 years	Cr	4.78	3.93	1.2×10^{-2}	4.72×10^{-3}	4.87×10^{-3}
	Cd	4.49×10^{-1}	3.69×10^{-2}	1.8×10^{-3}	6.64×10^{-5}	
	As	2.32×10^{-1}	1.91×10^{-2}	4.3×10^{-3}	8.21×10^{-5}	
	Ni	1.11×10^{-1}	9.12×10^{-3}	2.4×10^{-4}	2.19×10^{-6}	
Children 6-18 years	Cr	4.78	1.18	1.2×10^{-2}	1.42×10^{-2}	1.46×10^{-2}
	Cd	4.49×10^{-1}	1.12×10^{-1}	1.8×10^{-3}	2.02×10^{-4}	
	As	2.32×10^{-1}	5.73×10^{-2}	4.3×10^{-3}	2.46×10^{-4}	
	Ni	1.11×10^{-1}	2.74×10^{-2}	2.4×10^{-4}	6.58×10^{-6}	

Table 4. Non-carcinogenic health risks assessment of $PM_{2.5}$-bound trace metals via inhalation.

Categories	Elements	CA	EC	R*f*C	HQ	HI=∑ HQ
Adults	Cr	4.78	8.00	1.0×10^{-4}	80	194
	Cd	4.49×10^{-1}	7.52×10^{-1}	1.0×10^{-5}	75	
	As	2.32×10^{-1}	3.89×10^{-1}	1.5×10^{-5}	26	
	Ni	1.11×10^{-1}	1.86×10^{-1}	1.4×10^{-5}	13	
	Mn	5.37×10^{-2}	9.00×10^{-2}	5.0×10^{-5}	2	

Children 1-6 years	Cr	4.78	4.58	1.0×10^{-4}	46	111
	Cd	4.49×10^{-1}	4.30×10^{-1}	1.0×10^{-5}	43	
	As	2.32×10^{-1}	2.23×10^{-1}	1.5×10^{-5}	15	
	Ni	1.11×10^{-1}	1.06×10^{-1}	1.4×10^{-5}	8	
	Mn	5.37×10^{-2}	5.15×10^{-2}	5.0×10^{-5}	1	
	Cr	4.78	13.7	1.0×10^{-4}	137	334
Children 6-18 years	Cd	4.49×10^{-1}	1.29	1.0×10^{-5}	129	
	As	2.32×10^{-1}	6.68×10^{-1}	1.5×10^{-5}	44	
	Ni	1.11×10^{-1}	3.19×10^{-1}	1.4×10^{-5}	23	
	Mn	5.37×10^{-2}	1.54×10^{-1}	5.0×10^{-5}	3	

4. Conclusions

The highest concentrations for carcinogenic metals Cr and Cd were found in the soluble and exchangeable (F1) and reducible metals (F2) fractions of fine particles, respectively. The sum of the cumulative lifetime cancer risks due to inhalation exposures across all investigated carcinogens for adults, children 1-6 years old and children 6-18 years old were found above EPA's acceptable risk range while the cancer risks for each individual carcinogen indicated exceedance in only As and Cr trace metals. HQ and HI for all categories computed were found greater than one (HQ>1;HI>1) which is an indication of significant health risks most especially to residents and persons who by reason of their occupation spend most of their time within the study area. There is an urgent need for enforcement for pollution control and abatement policy and frequent industrial emission monitoring.

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