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DISTRIBUTION PATTERN OF SOME HEAVY METALS IN THE DUST PARTICULATES OF FUNTUA TEXTILE LIMITED, KATSINA, NIGERIA

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ABSTRACT

The sequential extraction of Cd, Cr, Cu, Ni, and Pb in industrial dust particulates collected in ten different sections/Departments of Funtua textile limited and the control site from Dikke village was carried out in order to ascertain the percentage of bioavailable fractions. Analyses of metals in the extracts were done using Flame Atomic Absorption Spectrometry (FAAS). The sequential extractions showed that significant amount of Cu25.87(O₁) to 92.73% (E₁) was associated with non-residual and0.09 (E₁) to 56.94% (O₂) organic bound fractions; similarly, Cd was also associated with the nonresidual fractions across the sites with values $42.22(W_2)$ to 97.78% (E₂). Cr and Ni exhibited the highest percentage of $73.46(W_1)$ to 100.00 % (W₂) and 23.64 (E₂) to 77.26 % (S₁), respectively. Pb in the particulate dust samples was significantly associated with the non-residual fraction and carbonate bound fraction with range of $21.71(D)-61.68(S_2) \%$ across the sites. This study revealed contamination of the particulates dust especially with Cu, Cr and Pb; this implies health risks to human, living or carrying out daily activities along the corridors of this industry. Keywords: Flame Atomic Absorption Spectrometry, Funtua textile, Heavy metals, Particulates dust,

Sequential extraction

INTRODUCTION

Soils are the reservoir for many materials; beneficial and harmful (Odoh et al., 2011). These include biological, chemical as well as heavy metals. Total metal content of soils is useful for most geochemical works but often the speciation (bioavailability) of these metals are more important to the environmentalist (Tack and Verloo, 1995). Speciation is defined according to Tack and Verloo (1995) as "the identification and quantification of differently defined species, forms, or phases in which an element occurs". It is widely accepted that to assess the environmental input of soil pollution, the determination of metals speciation will give more information about the potential for release of contaminants and subsequent toxicity. Therefore, in environmental studies of risk assessment, chemical partitioning among the various phases is more useful than the measurement of total heavy metal contents (Albores et al., 2000;Osakwe, 2010;Uba et al., 2008; Odoh et al., 2011). Among the procedures for sequential extraction is that of Tessier et al. (1979). Unlike organic pollutants, heavy metals do not decay and thus pose a different kind of challenge for remediation.

There is no information on speciation of metals in the particulate dust of Funtua textile limited, Katsina State, Nigeria. Despite being one of the leading functional textile industries in northern Nigeria. This work was therefore undertaken to assess the heavy metal load of particulate dust using modified sequential extraction method of Tessier *et al.*(1979).The metals investigated

include Cd, Cr, Cu, Ni, and Pb. These metals were selected because of their toxicity (Cd, Cr, Ni, and Pb) and also as an indicator of environmental pollution, Wood (1974) indicated that these metals have known pollutant properties, are toxic and readily available to the environment. Therefore, monitoring of particulate matter especially with heavy metals is imperative.

Based on the above facts, the present study assessed the distribution pattern of some heavy metals (Cd, Cr, Cu, Ni, and Pb) in industrial particulates dust in Funtua textile limited using modified sequential extraction method by Finzgar *et al.* (2007).

MATERIALS AND METHODS

Study Area

Funtua is located at latitude $11^{\circ}32$ N and longitude $7^{\circ}19'$ E (Figure 1), it is a Local Government area of Katsina State. It has an area of 448 km² and a population of 420,110 (National Population census,2012). The mean annual rainfall in the area is 1024 mm. Annual temperature varies between 21.9 -29.2°C (Africa Atlas, 2002). The selected area for this investigation was Funtua Textile Industry. It was established to make effective use of the cotton which is grown in large quantity at Funtua town and environs. The industry is active 24 hours a day, six days a week. The sampling points were selected from each department and two random points within the vicinity: Ginning Department (G), Spinning Department: Blowing & Carding (S₁), Combing, Spinning & roving (S₂).

Weaving Department: Doubling & Bleaching (W_1), Weaving knitting (W_2), Dyeing Department: Dyeing & finishing (D), Engineering Department: Maintenance (E_1), Power House (E_2), Ginning surrounding (Outside O_1), Dyeing surrounding (Outside O_2), with a Control area (C) at Dikke Village about 2 km away from the study area.

Sample Collection and Pre-treatment

Twenty-two (22) samples of particulates dust were collected across the sampling points using a plastic brush and tray (Loredo *et al.*, 2003; Yeung *et al.*, 2003) and stored in clean polythene bags (Al-Kashman, 2004), thereafter, labelled accordingly. The homogenized particulate dust samples were air dried and sieved through a 75 μ m stainless steel sieve to remove extraneous matter such as pieces of brick, paving stone and other debris. Care was taken to reduce the disturbance of the fine particles, which could be readily

lost by re-suspension (Manta *et al.*, 2002).Range of temperature across the sites was $28.39^{\circ}C(W_2)$ – $32.07^{\circ}C(C)$ and $29.50^{\circ}C$ (W_2)– $32.43^{\circ}C(O_1)$ for morning and evening periods respectively.

Quality Assurance

All reagents used were of analytical grade, distilled deionized water was used. All the glass wares and polythene sample bottles were washed with liquid soap, rinsed with distilled water, soaked in 10% HNO₃ for 24 hours and rinsed thoroughly with distilled de-ionized water and thereafter dried (Todorovi *et al.*, 2001). Validation of the technique was conducted on the digested dust sample. This was done by spiking the predigested sample with multi-element standard solution (5 mg/dm³ of Cd, Cu, Ni, Pb and 0.5 mg/dm³ Cr) as reported by Awofolu, (2005).

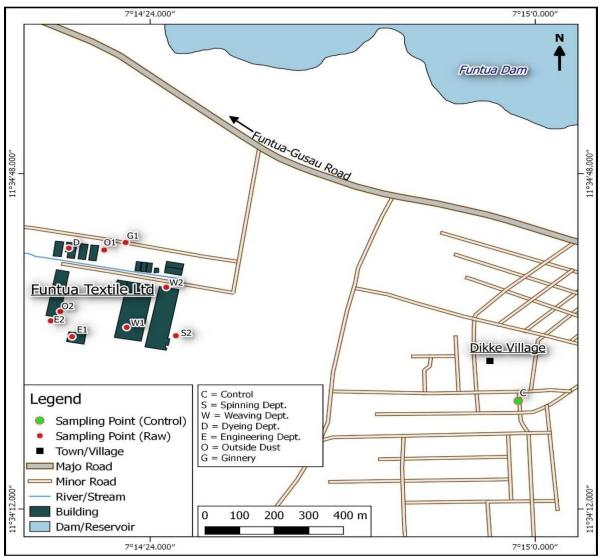


Figure 1: Map of Funtua Textile Ltd. Showing Sampling Point Source: Modified from the Administrative Map of Funtua L.G.A.



Plate I: Particulates dust sampling at Ginning Department (G)

Metal Extraction of Industrial Particulates Dust

Sequential extraction was done using Finžgar *et al.* (2007) method. The method was modified by Tessier *et al.* (1979). This modified method fractionates heavy metals into six geochemical fractions. The extraction was carried out with initial mass of 1.0 g air-dried dust samples in polypropylene centrifuge tubes of 50 cm³ capacity. However, Mg(NO₃)₂ was used instead of MgCl₂ to avoid an increase in the solubility of heavy metals within the particulates dust in the solution matrix (Shuman, 1985). The extractions of the dust samples were carried out on three sub-samples as follows:

Fraction I (Water soluble phase):One gram (1 g) of the air-dried dust sample (sieved) was mixed with 10 cm³ of de-ionized water with continuous agitation for 1 hour. The mixture was centrifuged and the supernatant decanted and made up to 50 cm³ with de-ionized water prior to analysis.

Fraction II (Exchangeable phase): The residue from step 1 was shaken at room temperature with 16 cm³ of 1 M Mg(NO₃)₂ at pH 7.0 for 1 hour. The mixture was then centrifuged and supernatant filtered and made up to 50 cm³ with distilled de-ionized water.

Fraction III (Oxidisible phase bound to Organic matter): Residue from 2 + 10 cm³ H₂O₂ 8.8 M + 6 cm³ HNO₃ 0.02 M was shaken for 5 hours + 1 hour at 98 $^{\circ}$ C. 10 cm³ of 3.5M CH₃COONH₄ was added as an extracting agent, then the mixture was centrifuged and

supernatant filtered and made up to 50 cm³ with distilled water prior to analysis.

Fraction IV (Acid soluble fraction bound to carbonate): A volume of 25 cm³, 0.05 M Na₂EDTA was added to the residue from 3, shaken for 6 hours and the mixture was centrifuged and the supernatant filtered and made up to 50 cm³ with distilled water prior to analysis.

Fraction V (Reducible phase bound to Fe-Mn oxides): Residue from 4 + 17.5 cm³ of 0.1 M NH₂OH.HCl + 17.5 cm³ of 3.5 M CH₃COONH₄ was shaken for 1 hour, the mixture was then centrifuged. The supernatant was filtered and made up to 50 cm³ with distilled water prior to analysis.

Fraction VI (Residual phase bound to silicates and detrital materials): Residue from 5 was digested by using HCI-HNO₃/HF (0.35:12 $^{W}/_{V}$ soil solution ratios) in acid digestion in a Teflon cup. It was then ash-dried for 2 hours and evaporated to dryness. The residue was diluted to 50 cm³ with distilled de-ionized water prior to analyses.

After each successive extraction, the sample was centrifuged at 3000 rpm for 15 minutes. The supernatant was removed with pipette and filtered with Whatman No. 42 filter paper. The residue in each case washed with distilled de-ionized water followed by vigorous hand shaking and then 15 minutes centrifugation before the next extraction (Shuman, 1985).

Sample Digestion

A mass 2.0 g of the dried sample was accurately weighed into a conical flask and10 cm³ of nitric acid was added and the mixture was heated on a hot plate until the sample was almost dry and then cooled. The procedure was repeated with another 10 cm³ of concentrated nitric acid followed by the addition of 10 cm³ of 2 M Hydrochloric acid. The digested dust was warmed with 20 cm³ of 2 M HCl and filtered into a 50 cm³ volumetric flask through Whatman filters (No. 1), thereafter, diluted to the mark with double distilled water (Divrikli *et al.*, 2003). The metals in the final solutions were determined by Atomic Absorption Spectrophotometer (Varian AA650FS).

RESULTS AND DISCUSSION

Among the six geochemical fractions, the highest concentrations of Cd were recorded in the non-residual fractions of E_2 , as presented in Figures: 2 – 12 which shows that they would be released into the environment easily. Also, the percentages of the bioavailable fractions of Cd were significantly high across the sites with the exception of particulate dust of sites C, W1 and W_{2} , respectively. This indicates that the Cd studied would be readily bioavailable to the environment for contamination in all but sites C, W₁ and W₂ respectively. Thus, Cd could be easily transferred into the food chain through the uptake by plants growing in the soils, or through inhalation of the particulate dust. These characteristics, in addition to health hazards of Cd to human health, suggest that frequent examination of the levels of this element in soil samples could determine potential health hazards to residents and workers living near and within the factory. Overall, the total extractable fractions of Cd across the sites were above the USEPA, (1998) limit of 3.0 mgkg⁻¹ for Cd in soil. The presence of the appreciable percentages of Cd in the mobile phase suggests that Cd in these dust particulates was potentially highly bioavailable for plant uptake (Uba et al., 2008; Xian, 1989). The results obtained in this study were in agreement with those reported by Harrison, (1981); Kuo et al. (1983); Miller and Mcfee, (1983) anUba et al.(2008).

Furthermore, the highest concentrations of Cr across the sites were recorded in the residual fractions, with site W_2 (100%) having the highest value and site W_1 (73.46%) having the lowest value. According to Venkateswaran et al. (2007). The leaching of Cr to the environment may not easily occur. Cr (VI) is a highly toxic metal that has been linked to cancer in human following prolonged inhalation (USEPA, 1998). Similarly, the percentage bioavailable and non-residual fractions of Cr were significantly low across the sites which suggests that Cr is not easily released into the environment and hence to plants. Most of the values of Cr obtained in the residual and non-residual fractions were above the critical level of 0.03 mgkg,⁻¹ for soils recommended by FEPA, (1991). Furthermore, the Cr content of the soil fractions was strongly associated with the residual fractions which are in agreement with those reported in similar studies by Uba *et al.* (2008). The concentrations of Cu in the extractable fractions as determined by sequential extractions across the sites shows the highest concentrations of Cu were recorded in the non-residual fractions, although appreciable percentages were also recorded in the residual fractions.

The high amount of Cu being associated with the nonresidual fraction across sites show that Cu may be easily transferred into the food chain through water reservoir, uptake by plants growing on the factory soil which could have potential negative impact on the environment and consequently on human health. The total extractable concentrations of Cu in all the dust particulates samples (Table: 1) were below the toxic limit of 140 mgkg⁻¹ set by EC, (2005) and also below 100 mgkg⁻¹ toxic limits set by USEPA, 1998. On comparing the concentrations of Cu in the residual and non-residual fraction, the higher percentage of the non-residual fraction was generally found in dusts of site E1. The bioavailability of Cu across the sites was generally high; this clearly shows that the metal would be released into the environment easily as it is known to be associated with organic humus so it need not be subjected to harsh conditions. The relatively high value of Cu in the residual fraction () indicates that it's largely embedded in the crystal lattice of the soil fraction and should not be available for environmental pollution except under harsh conditions.

The concentrations of Cu obtained in this study were similar to those reported by Uba et al., (2008). Moreso, the highest value of the extractable fractions of Ni was found in the residual fraction. Also, relatively high values of Ni were found in the non-residual fractions which suggest possible contamination of plant around the vicinity of the factory by Ni.On the other hand the high value of Ni in the residual fraction shows that they would be released into the environment under very harsh conditions by sequential extraction procedure. The values of Ni in the dust particulates were above the FEPA, 1991 (maximum permissible limits of 3.0 mgkg⁻¹). The non-residual fraction has the highest potential of contamination of food chain, surface water and ground water (Leita et al., 1991). The relatively high percentage bioavailability of Ni suggest that it could be readily available to the environment for contamination causing environmental toxicity during mobility especially at site E₂ which is engineering unit with a lot of wastes like spent engine oil, used generator batteries and oil mist. The extractable fractions of Pb in the studied areas among the extractable fraction of Pb, the highest concentration of Pb were recorded in the non-residual fraction (Figures: 2 – 12). On comparing the levels of Pb recorded in the residual and non-residual fraction, the former constitutes also relatively high percentage of the total extractable fraction as compared with the latter, which suggests that Pb at these sites would need to be subjected to harsh conditions before they can be bioavailable to the plants. Also, the levels of Pb recorded among the fractions were below the USEPA, (1998) toxic limits of 100 mgkg⁻¹ in soil.

The findings in this study were in agreement with what was reported by Kabata-Pendias and Pendias (1992) who stated that there was a strong association of Pb with organic matter. In general, the oxide (organic bound) fractions scavenge Pb in natural and polluted soils (Kuo *et al.*, 1983; Xian, 1989) indicating the tendency of Pb to be released into the environment. The percentage bioavailable Pb was quite low compared to other metals and fractions. Pb is notorious for its lack of soil mobility, primarily due to its precipitation as insoluble phosphate, carbonate, and hydroxide which have low solubility in water (Rieuwerts *et al.*, 2006). Low levels of bioavailable Pb or low mobility found in soils (dust) has been attributed to one or combination of low native Pb, very slow solubilisation of Pb from soil minerals, strong adsorption of Pb on soils surface or co-leaching of Pb with dissolved organic matter (Rieuwerts *et al.*, 2006).The values obtained in this study were similar to those reported by Uba *et al.*(2008). Heavy metal speciation studies are important since slight changes in metal availability and in environmental conditions can lead to serious health problems such as respiratory, cardiovascular and other diseases.

SITES	FRACTIONS (%)	Cd (%)	Cr (%)	Cu (%)	Ni (%)	Pb (%)
G	Bioavailable	56.45	0.00	41.01	32.34	30.39
	Non-residual	59.68	10.17	42.76	32.34	48.21
	Residual	40.32	89.83	57.24	67.66	51.79
S1	Bioavailable	67.39	0.00	35.85	22.74	38.80
	Non-residual	77.17	1.02	37.71	22.74	75.42
	Residual	22.83	98.98	62.29	77.26	24.58
S ₂	Bioavailable	66.67	0.00	24.41	27.62	22.09
	Non-residual	85.19	0.44	32.19	27.62	38.32
	Residual	14.81	99.56	67.81	72.38	61.68
W1	Bioavailable	30.36	3.00	34.98	30.94	33.57
	Non-residual	44.64	26.54	64.68	32.79	57.35
	Residual	55.36	73.46	35.32	67.21	42.65
	Bioavailable	34.44	0.00	22.16	28.91	25.15
	Non-residual	42.22	0.00	28.96	28.91	42.29
	Residual	57.78	100.00	71.04	71.09	57.71
D	Bioavailable	74.29	8.47	51.63	66.46	41.56
	Non-residual	91.43	11.48	74.48	66.46	78.29
	Residual	8.57	88.52	25.52	33.54	21.71
E ₁	Bioavailable	83.64	0.00	0.09	38.43	23.44
	Non-residual	92.73	6.27	92.73	60.33	74.07
	Residual	7.27	93.73	7.27	39.67	25.94
E ₂	Bioavailable	64.44	21.19	53.40	69.56	38.94
	Non-residual	97.78	23.88	67.02	76.36	75.34
	Residual	2.22	76.12	32.98	23.64	24.66
O ₁	Bioavailable	49.15	0.00	25.87	35.31	24.06
	Non-residual	66.10	10.24	25.87	35.31	47.62
	Residual	33.90	89.76	74.13	64.69	52.38
O ₂	Bioavailable	39.68	2.04	56.93	36.04	24.42
	Non-residual	57.14	2.04	60.15	36.04	46.44
	Residual	42.86	97.96	39.85	63.96	53.56
C	Bioavailable	21.15	4.17	27.98	24.66	27.26
	Non-residual	44.23	4.17	27.98	24.66	50.36
	Residual	55.77	95.83	72.02	75.34	49.64

The %Bioavailable, % Non-residual and %Residual forCd, Cr, Cu, Ni, and Pb across the sampling points were summarized in Table: 1.The Cd, Cr, Cu, Ni and Pb across the sampling points were summarised in Figures: 2 – 12.

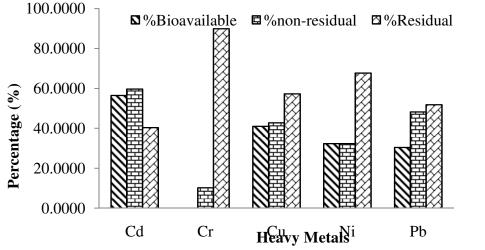
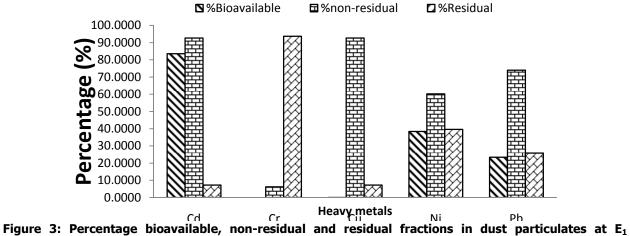


Figure 2: Percentage bioavailable, non-residual and residual fractions in dust particulates at G (Ginnery section) of Funtua Textile LTD



(engineering section) of Funtua Textile LTD

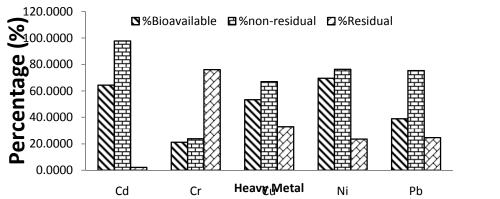


Figure 4: Percentage bioavailable, non-residual and residual fractions in dust particulates at E_2 (power house section) of Funtua Textile LTD

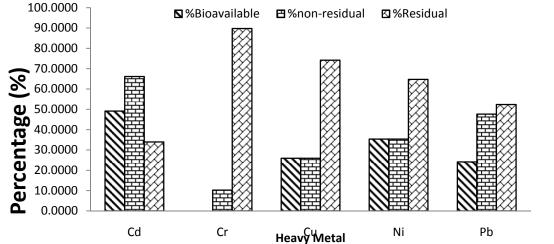


Figure 5: Percentage bioavailable, non-residual and residual fractions in dust particulates at O₁ (ginning surrounding section) of Funtua Textile LTD

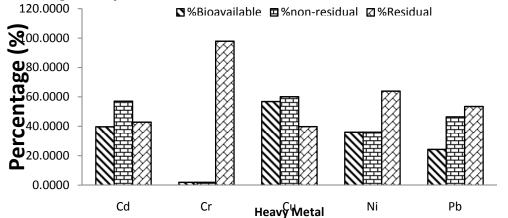


Figure 6: Percentage bioavailable, non-residual and residual fractions in dust particulates at O₂ (dyeing surrounding section) of Funtua Textile LTD

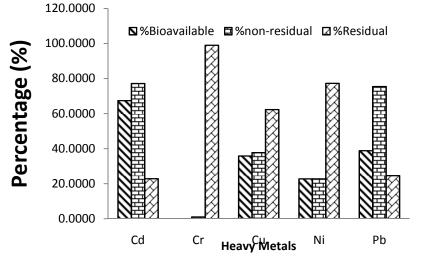


Figure 7: Percentage bioavailable, non-residual and residual fractions in dust particulates at S_1 (blowing and carding section) of Funtua Textile

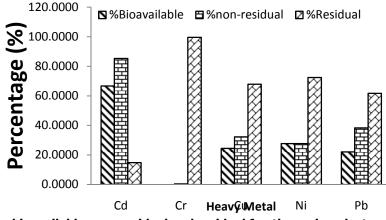


Figure 8: Percentage bioavailable, non-residual and residual fractions in dust particulates at S_2 (spinning and roving section) of Funtua Textile LTD

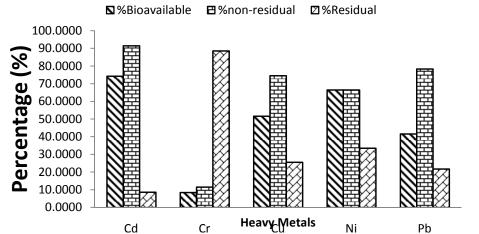


Figure 9: Percentage bioavailable, non-residual and residual fractions in dust particulates at D (dyeing section) of Funtua Textile LTD

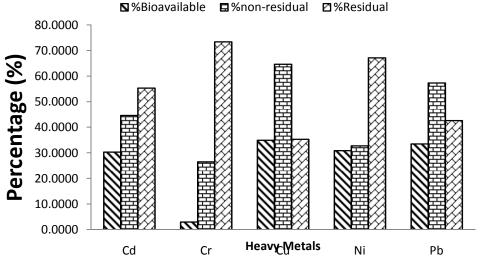


Figure 10: Percentage bioavailable, non-residual and residual fractions in dust particulates at W₁ (doubling and bleaching section) of Funtua Textile LTD

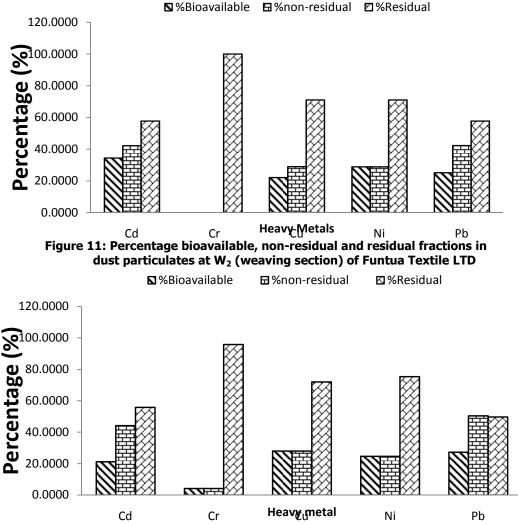


Figure 12: Percentage bioavailable, non-residual and residual fractions in dust particulates of C (control section) at Dikke village

CONCLUSION

The industrial dust collected from Funtua textile limited shows high concentrations of heavy metals (Cd and Cu)which could lead to serious environmental hazards. The sequential extractions procedure showed significant amount of Cu were associated with non-residual and organic bound fractions. Similarly, Cd is also associated with the non-residual fractions across the sampling sites. For Cr and Ni, their occlusion in crystal lattice (residual fraction) of the soil fractions exhibited the highest percentage. Lead (Pb) in the particulate dust samples was found to be significantly associated with the non-residual fraction and carbonate bound fraction with a range of $21.71(D)-61.68(S_2)$ % across the sites. This study indicated that industrial particulate dust pollution due to metals such as Cu, Cr and Pb may pose serious health risks to the residents in this rapidly developing industry.

Recommendation

It is therefore recommended that for a safer environment, proper textile management programmes, proper legislative frame work to regulate pollution and finally proper implementation of these measures be encouraged

Conflict Of Interest

Authors have declared that no conflicting interest exist **Acknowledgments**

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Contribution of authors:

Author S. Uba read and corrected the manuscript performed the statistical analysis. Author S. Abdulkadir designed the study, managed the literature searches and wrote the first draft of the manuscript and Author Y.A Dalltu approved the design and supervised the experiment

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