Heavy Metals Speciation in Dust Samples from Various Parts of Ebonyi State, Nigeria

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Abstract

Dust on our roads constitutes a major source of environmental hazard. Little attention is paid to the enormous challenges resulting from its polluting effect and health implications. In this investigation, twenty five dust samples were collected from 5 locations within Ebonyi North, South and Central Senatorial Zones between March and April 2008. Dust samples were collected using $1m^2$ HDPE containers, oven dried at $70^{O}C$ and sieved through 100µm nylon sieve. 1g of each sample was digested using $HCl/HNO_3/H_2O_2$ acid mixture and the concentration levels of 8 selected metals were measured using ICP-MS. Average concentrations of heavy metals in dust samples were 518.6ppb, 13.7ppb, 128.48ppb, 6540.20ppb, 6.19ppb, 10.84ppb, 1.06ppb and 6.69ppb for Al, Ca, Mn, Fe, Ni, Zn, Cd and Pb respectively while the relative abundance of metals in samples were: Fe > Al > Mn > Ca > Zn > Pb > Cd. Descriptive statistics, Pearson correlation and one way analysis of variance (ANOVA) were used to analyze the data. Positive and negative correlations exist between the heavy metals indicating that they come from both point and non-point sources into the atmosphere. One way repeat measures ANOVA at $P<0.05$ (95% confidence level) show that F_{cal} (1.99) $<F_{tab}$ (18.50) implying that no significant difference exist between the trace metal levels in dust samples from 5 different locations investigated.

Soil, anthropogenic influences and quarrying were likely sources of these metals.

Key words: Dust, metals, pollution, environment

Introduction

Recently, more attention has been shifted to heavy metal pollution in urban areas as a result of the deleterious effects of some trace metals on human health and the environment. Small amounts of trace metals like Cu and Zn are harmless but some other metals like Hg, Pb, As and Cd are toxic even at very low concentrations (Dockery and Pope, 1996; Willers et al., 2005). For instance, exposure to lead in small doses may be harmful to the central nervous system, blood circulation and enzyme systems whereas exposure to lead in high doses can affect human intelligence and blood Pb level. Cases of long term exposure to Pb can inhibit the mental development of children (Ahmed and Ishiga, 2006; Poon and Liu, 2001; Sezgin et al., 2003).

Dust is composed of complex chemical compounds which originate from interaction of gaseous, liquid and solid substances produced from different sources and activities (Akhter and Madany, 1993; Hjortenkrans et al., 2006; Singh et al., 2005). It contributes significantly to pollution in the urban environment and several sources of entrained dust in the environment include sinking particles in air, vehicle exhaust, house dust, soil dust and aerosols carried by air and water (Fergusson and Kim, 1991; Naqerotte and Day, 1998; Sezgin et al., 2006).

Dust is pervasive and can affect human health and well-being. Populations exposed to these elements are faced with serious health problems including nervous and neurophysical effects (Ling-Chu, 2006; Solomon, 2001).The presence of metals in potentially toxic forms and in potentially toxic concentrations in the air and soils can lead to the contamination of water supplies (Hodson, 2001; Nguyen, 2005) and also have phytotoxic effects and result in trace element contamination of edible crops (Liao, 1997). Urban dust which serves as a sink for heavy metals and organic pollutants are useful indicators of the degree of distribution of contaminants in the environment (Al-Khashman, 2007; Lu et al., 2009; Shinggu et al., 2010). Interest in the levels of contaminants associated with urban dust has risen in the last decades, particularly the concentration and distribution of substances (metals) like lead, copper, cadmium and zinc and their source identification (Yongming, 2006).

Heavy metals borne in dust tend to accumulate in topsoil due to atmospheric deposition via interception, impaction and sedimentation (Li et al., 2001; Lu et al., 2009; Sezgin et al., 2006). Mutual interactions between air and soil pollutions lead to transfer of heavy metals into soils via precipitation and contribution to atmospheric contamination by soil dust (Chen et al., 1997; Patel et al., 2001; 21; Ritter and Rhinefierd, 1983).

Vast majority of studies carried out on the concentration and speciation of heavy metals in dust samples collected from developed countries in Europe, North America and even rising economies in Asia and South America (Jaradat and Momani, 1999). However, in developing countries in Sub-Saharan Africa, there seems to be a scarcity of published data on the concentration and speciation of heavy metals in urban dusts, hence the importance of this research cannot be overemphasized.

The toxicity of trace elements depends largely on the particular form in which the element is present in the human system. For e.g. Cr (VI) ions tend to be more toxic than Cr (III). On the other hand, although both methyl mercury and inorganic mercury are toxic, they tend to show different patterns of toxicity (Katz and Salem, 1994). Thus, these different chemical forms of an element or its compounds are referred to as species. Speciation refers to the analytical activity of identifying different chemical forms of a particular element or its compounds and their distribution. Speciation is also used to indicate the distribution of species in a particular sample or matrix (IUPAC, 2000).

Some metals exist in isotopic forms whereas others do not e.g. lead has four stable, naturally occurring isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb; and of all these, ^{206}Pb, ^{207}Pb and ^{208}Pb are all radiogenic while ^{204}Pb, is a non-radiogenic stable isotope. Atmospheric Pb tends to become concentrated in the uppermost, organic-rich soil horizons, while Pb in ground water should be dominated by that derived from rock weathering (Veron et al., 1994). Potential complications to the use of Pb isotopes, such as anthropogenic contamination, immobility of Pb in ground water, and the possibility for highly radiogenic Pb to exist in accessory minerals, can also be used to an advantage e.g. dating. Anthropogenic Pb (Veron et al., 1994) and accessory-phase Pb in minerals have distinct compositions, and the immobility of Pb produces concentration covariance (Nimz, 1998).

Cadmium isotopes are radioactive and pose potential hazards as they concentrate in the liver and kidneys, cadmium can also deposit in other organs and tissues depending on its chemical form. The main concern is cancer induction from the beta particles associated with its radioactive decay. Cadmium also exhibits chemical toxicity. Inhaled cadmium can damage the respiratory system, causing bronchial and pulmonary irritation. Chronic exposure may result in emphysema and chronic bronchitis. Repeated low exposures may also cause permanent kidney damage, leading to kidney stones and other health problems. Cadmium is classified by the Environmental Protection Agency (EPA) as a probable human carcinogen.

Workers who breathe large amounts of aluminum dusts can have lung problems, such as coughing or changes that show up in chest X-rays. Some workers who breathe aluminum-containing dusts or aluminum fumes have decreased performance in some tests that measure functions of the pulmonary system (Nwibo et al., 2012). An uptake of very large quantities of nickel can lead to the development of lung cancer, nose cancer, larynx cancer and prostate cancer, sickness and dizziness after exposure to nickel gas, lung embolism, respiratory failure and birth defects, asthma and chronic bronchitis etc. Exposure to nickel and its compounds may also result in the development of dermatitis and itching. Other metals such as Fe, Ca, Zn etc in large concentrations can affect human health and well-being.

Quarry workers suffer from 'silicosis', through inhalation of minute dust particles (0.1 to 150 µm) high in silica. Other respiratory and skin problems have also been reported among manual stone crushers e.g. in Abia State (Ugboguet al., 2009) and pulmonary cases among stone crushers at Umuoghara crushing site in Ezza North Council Area of Ebonyi State (Nwibo et al., 2012). Various elements are introduced into the environment from a variety of emission sources ranging from natural sources including erosion, volcanoes and biogenic emissions to anthropogenic emission such as industrial emission, fuel, combustion, transportation, construction activities etc. The impact of construction activities which generates huge volumes of dust can be significant especially in the dry season.

The Wind is a major agent of distribution and transport of dust. Metal pollution by dust constitutes significant areas of study in the developed countries. Metallic pollutants like Pb, Cu, Zn, Hg, Cr, Mn, As etc has been reported (Yongming, 2006). Unfortunately, very little attention is paid to this area in developing countries and therefore, very little information is available. Previous investigations in Abakaliki revealed significant concentrations of some of these contaminants in dust (Omaka, 2010).

Ebonyi State is well known for rice and yam cultivation. Although pockets of mining have been going on within the area, recently quarrying activities has assumed prominence to compliment the State Government's drive for more revenue. This has some negative consequences such as the enrichment of the air with metallic and non-metallic contaminants, which ultimately can lead to the pollution of the environment (Ebonyi State Ministry of Commerce and Industry, 1999).

A variety of instrumental techniques such as Atomic Absorption Spectrometry, Optical emission spectroscopy, X-ray fluorescence, inductively coupled plasma-mass spectrometry and Neutron activation analysis has been used for the acquisition of data on the elemental concentrations in the environment (Patanaik, 2010). Atomic absorption spectrometry is one of the most frequently employed techniques for investigating the behaviour of metals in the environment. However, it is limited to mono-element character and poor detection limits. Methods that permit multi-element analysis are necessary because the sample may not be large enough for separate determinations (Patanaik, 2010). Sensitive techniques such as spark source mass spectrometry, isotope dilution mass spectrometry and neutron activation analysis can also be used but due to high costs of their purchase and maintenance, they are not found in many routine environmental laboratories (Patanaik, 2010).

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a technique that can solve a wide variety of inorganic analytical issues, hence it is the preferred analytical technique used in this study. It can be applied to elemental as well as isotopic analysis. In elemental analysis, it can be used in two different ways to provide semi-quantitative (semi-quant) and quantitative (quant) analysis. It is also applied in environmental studies due to its low detection, good precision and accuracy, low interference effects and capability of simultaneous determination (multi element) determination (Patanaik, 2010).

Objective of this work was to investigate the level of 8 selected metals (Zn, Pb, Cd, Ni, Mn, Fe, Cr and Cu) in urban dust samples from 5 selected locations within Ebonyi state using acid digestion followed by inductively coupled plasma mass spectrometry as extraction protocol. The data generated was then compared with the time weighted average (TWA) limit for metals in the atmosphere as stipulated by the Occupational Safety and Health Association (OSHA).

Methodology

Description of Study Area

Ebonyi State has a land mass of about 5,935 km^2 and lies between longitude 5050^1 and 6045^1 E and latitude 7030^1. Large deposits of solid minerals abound in the State, with its rich vegetation. Seasonal variations of hot, mild and cold weather characterize the area with a mean temperature of $30^{o}C$ in the hottest period (February to April) and $21^{o}C$ for the coldest period (December to January). The climate is of tropical humid type characterized by occasional heavy rainfall with accompanying winds (Awoke and Okorji, 2004).

Five sampling locations were investigated and they covered the 3 senatorial zones of the state (Ebonyi North, South and Central). Location 1 was at Amasiri town in Afikpo North LGA; location 2 was at Idembia town in Ezza South LGA. Location 3 was at Sharon town in Izzi LGA while location 4 was at the Pure and Applied Sciences Campus of Ebonyi State University, located along Abakaliki-Enugu Expressway. Location 5 was at Mgbo town in Ohaukwu LGA. Location 1 served as a control site while other locations were polluted sites found near quarrying and road construction sites.

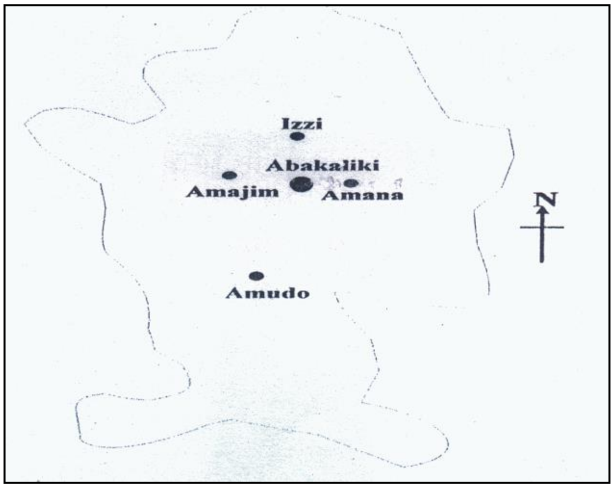

Fig. 1: Map of Ebonyi State showing sampling sites

Soils and Mineralogy

The study areas comprises of high leached red soils of tropical forest region. One of the study areas (Abakaliki) is well known for lead-zinc deposits in Africa where soil and streams have developed from naturally enriched parent materials, including black shales, hydrothermally mineralized rocks and mine dumps (Omaka et al., 2011).

Sampling and sample collection

Samples were collected from various parts of Ebonyi State. Sampling areas covered the 3 senatorial zones in the state and sampling period was from March 2008 to April 2008. Figure 1 shows a map of Ebonyi state indicating the sampling sites. Samples were collected using clean $1m^2$ High Density Polyethylene (HDPE) cellophane container. Each HDPE container was first rinsed with de-ionized water and soaked in detergent overnight after which it was rinsed 5 times with de-ionized water and later soaked in 10% HNO_3 overnight. This step eliminates adsorption onto the surfaces of the containers. The containers were later washed with de-ionized water and stored in airtight cellophane bags (Omaka, 2010). All collected samples were stored in airtight HDPE bottles, labeled and then transported to the laboratory. In the laboratory, all samples were dried in an oven at $70^{O}C$ and then sieved through 1mm mesh nylon sieve in order to remove debris and small stones (Sugimae, 1989).

Acid Digestion

After drying and sieving, 1.0g of each ample was acid digested with a mixture of HCl, HNO_3 and H_2O_2as prescribed by the US EPA 305A Method (US EPA 1992). Heavy metal (Zn, Pb, Cd, Ni, Mn, Fe, Cr and Cu) contents in digested samples were then determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Results and Discussion

Descriptive statistics for the trace metal contents of dust samples from different locations within Ebonyi state are given in Table 1 while the stipulated guideline limits for metals (in time weighted averages, TWA) in urban dust set by the Occupational Safety and Health Association (OSHA) are given in Table 2.

Iron had the highest concentration followed by aluminum, manganese, calcium, zinc, lead and cadmium in that order i.e. Fe>Al>Mn>Ca>Zn>Pb>Cd. The high Fe, Al and Zn content of dust in the study areas may be attributed to the mining and quarrying activities going on in these areas which lead to the excavation of mineralized rocks containing these metals. The average concentration of Al in the dust samples was 518.60 ppb which was less than 905ppb (TWA) stipulated by OSHA as permissible limit for Al in air (OSHA, 2007). The mean Ca concentration recorded in this study (13.7 ppb) was higher than the 6.113ppb (TWA) limit stipulated by OSHA for Ca in air/dust (OSHA, 2007).

For Mn, the 128.48ppb mean concentration was higher than the 89ppb (TWA) set as permissible limit for Mn in air (OSHA, 2007). Although Mn is an essential element, very high concentration of it in respirable dust can be dangerous to human health. Smelting from incineration and coal fires may be a major contributor to anthropogenic Mn present in dust samples from areas investigated (Mafuyai *et al*., 2014). The mean Fe concentration of 6540.20ppb observed was considerably higher than the 2183ppb (TWA) stipulated by OSHA for Fe in air/dust (OSHA, 2007). Previous reports showed high levels of Fe from dust in samples from the College of Agricultural Sciences (CAS), Ishieke and Enugu – Abakaliki Express road areas of Abakaliki (Omaka, 2010).

Table 1: Descriptive Statistics of metal levels in dust samples from selected areas within Ebonyi State

Element	Range	Mean (ppb)	Median	SD	Variance	Sum	Skewness
Al-27	308-866	518.60	459.00	233.66	54597.30	2593	0.877
Ca-44	5623-19940	13.7	1.51	5.79	3.36	68333	-0.548
Mn-55	44.20-229.00	128.48	75.70	90.70	8226.71	642.40	0.532
Fe-57	1675-12690	6540	4291	4.84	2.34	32701	0.533
Ni-60	2.96-9.60	6.19	6.14	2.61	6.83	30.96	0.113
Zn-64	3.25-33.40	10.95	7.27	12.72	161.73	54.76	2.10
Zn-66	2.74-34.60	10.73	6.50	13.49	182.08	53.65	2.11
Cd-111	0.12-1.35	0.74	0.91	0.50	0.25	3.72	-0.200
Cd-114	0.06-1.86	1.37	1.70	0.74	0.60	6.84	-2.029
Pb-206	1.46-21.30	6.14	2.75	8.50	72.18	30.72	2.206
Pb-207	1.72-24.70	7.09	3.00	9.86	97.32	35.45	2.213
Pb-208	1.69-23.40	6.83	3.06	9.29	86.32	34.14	2.204

The main source of Ni in dust is due to the corrosion of vehicular parts (Lu et al., 2009). The high rate of old vehicles plying our Nigerian roads may have contributed significantly to the Ni content of the dust samples. Mean Ni concentration in the dust samples was 6.19ppb which was lower than the stipulated 21 ppb limit for Ni in air (OSHA, 2007). However, mean Zn concentration of 10.84 ppb observed was significantly lower than the 752 ppb stipulated by OSHA for Zn in air/dust (OSHA, 2007). Also, the mean Cd concentration of 1.06ppb was slightly lower than the 2ppb stipulated by OSHA for Cd in dust/air (OSHA, 2007).

Table 2: Comparison of results of present study against stipulated OSHA (TWA) guideline limits

Element	Present study Ppb	OSHA/TWA(2007) ppb	OSHA/TWA (2007) ppm	OSHA /TWA (2007) mg/m^3
Al	518.60	905.00	0.905	1.00
Ca	13.70	6.113	0.006	10.0
Mn	128.48	89.00	0.089	0.20
Fe	6540.20	2183	2.183	5.00
Ni	6.19	21.00	0.021	0.05
Zn	10.84	752.00	0.752	2.00
Cd	1.06	2.00	0.002	0.01
Pb	6.69	6.00	0.006	0.05

OSHA: Occupational Health and Safety Association
TWA: Time Weighted Average

Pb is a potential toxin and the mean Pb concentration of 6.69ppb was slightly above the 6ppb stipulated by OSHA for Pb in air/dust (OSHA, 2007).The metals with the lowest concentrations in the dust samples analyzed are Pb and Cd. The use of unleaded gasoline tends to minimize the vehicular emission of Pb whereas the presence of Cd in automobile fuel and soil tends to increase the risk of its intoxication with resultant health effects such as kidney failure (Saud and Mustafa, 2012).

Table 3: Pearson Correlation Analysis of different trace elements found in dust samples from selected areas in Ebonyi State

	Al-27	Ca-44	Mn-55	Fe-57	Ni-60	Zn-64	Zn-66	Cd-111	Cd-114	Pb-206	Pb-207	Pb-208
Al-27	1	-0.355	-0.011	-0.034	-0.202	0.857	0.846	0.264	0.558	0.804	0.811	0.803
Ca-44		1	0.869	0.910′	0.981″	-0.780	-0.793	-0.375	-0.27	-0.810	-0.804	-0.812
Mn-55			1	0.989″	0.916′	-0.510	-0.524	-0.168	0.453	-0.575	-0.565	-0.576
Fe-57				1	0.960″	-0.541	-0.557	-0.146	0.380	-0.612	-0.602	-0.613
Ni-60					1	-0.674	-0.690	-0.244	0.121	-0.729	-0.721	-0.730
Zn-64						1	1.000″	0.329	0.316	0.989″	0.990″	0.989″
Zn-66							1	0.322	0.307	0.991″	0.992″	0.992″
Cd-111								1	0.552	0.211	0.213	0.215
Cd-114									1	0.209	0.219	0.212
Pb-206										1	1.000″	1.000″
Pb-207											1	1.000″
Pb-208												1

′: Correlation is significant at the 0.05 level (2-tailed)

″: Correlation is significant at the 0.01 level (2-tailed)

Correlation analysis of the data obtained was done using Microsoft EXCEL 2007 Statistical Tool Package. Results showed that negative correlations existed between the following pairs of metals : (Ca-Mn), (Ca-Fe), (Ca-Ni), (Ca-Zn), (Ca-Cd), (Ca-Pb), (Mn-Zn), (Mn-Cd), (Mn-Pb), (Fe-Zn), (Fe-Cd), (Fe-Pb), (Ni-Zn), (Ni-Cd) and (Ni-Pb) (see Table 3). The negative correlation infers a non-point source of contaminants. In other words, the trace metals involved comes from different sources into the environment.

However, positive correlations exist among these following pairs of metals: (Al-Zn), (Al-Cd), (Al-Pb), (Ca-Mn), (Ca-Fe), (Ca-Ni), (Mn-Fe), (Mn-Ni), (Mn-Cd), (Fe-Ni), (Fe-Cd), (Ni-Cd), (Zn-Cd), (Zn-Pb) and (Cd-Pb) (see Table 3). Positive correlation relationship indicates that the trace metals have a common anthropogenic origin. In other words, they come from point sources of pollution into the environment. One way repeat measures

ANOVA at P<0.05 (95% confidence level) show that F_{tab} (18.50) > F_{crit} (1.99) implying that a significant difference exists between the trace metal levels in dust samples from the 5 different locations investigated. This further implies that the trace metals come from different natural and anthropogenic sources into the environment thus, negating the hypothesis that they come from similar sources into the environment (Miller and Miller, 2000).

Conclusion and Recommendations

The deleterious effects of metals present in dust can pose significant health problems on long term and short term basis. Results from this investigation shows that elements such as Ca, Mn, Fe and Pb exceeded the stipulated OSHA/TWA limits for these metals in urban dusts. On the other hand, Al, Ni and Zn levels in the dust samples were relatively lower than the OSHA/TWA stipulated limits for the corresponding metals. On the basis of these findings, more attention needs to be paid to elements that recorded relatively high concentrations (especially Pb) in order to reduce their potential toxic health effects.

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