https://chemclassjournal.com/
ChemClass Journal Vol. 9 Issue 4 (2025); 295 - 311
e-ISSN:3092-8214 p-ISSN:3092-8206
doi.org/10.33003/chemclass-2025-0904/22

Air Pollution Assessment and Metals Bioaccumulation Studies in the vicinity of Umuoghara and Amoffia-Ngbo Quarry Sites

Orinya Onyebuchi Frederick [1,2,3(*)], Odo Joseph Uche [1,2], Agu Kizito Akachukwu [1], Aja Patrick Maduabuchi[4], and Ikwuazom Okwunna Onyekachi[1]

[1]Department of Medical Biochemistry, David Umahi Federal University of Health Sciences, Uburu
[2]Department of Medical Biochemistry, Ebonyi State University, Abakaliki
[3]International Institute of Toxicology, Environmental and Occupational Health Research, DUFUHS
[4]Department of Biochemistry, Ebonyi State University, Abakaliki.

***Corresponding author:** Email: orinyafreedman@gmail.com, orinyaof@dufuhs.edu.ng, Phone: 08039508303

Abstract

This study focused on the assessment of particulate matter emission, dust composition, and heavy-metal accumulation in guinea pigs exposed to quarry environments of Umuoghara (UMR) and Ammofia-Ngbo (UMR), Ebonyi State, Nigeria. Measurements of TSPM, PM_{10}, and $PM_{2.5}$ conducted quarterly at three distances (0 m, 5 m, and 10 m away from the perimeter) revealed significantly higher ($p<0.05$) concentrations in both quarry sites relative to the control site, with emissions consistently highest in Ammofia-Ngbo and also followed a seasonal trend January > April > July > October. The chemical analysis showed that all dust samples contained elevated levels of heavy metals (Fe, Pb, Cd, Cu, Zn, Mn, Ni, Cr, As, and Hg) and physicochemical parameters compared to the control, with some metals totally absent in the control samples. The PAH concentration was significantly higher in 'UMR' when compared to site 'AMN'. These could be due to the intensive use of diesel-powered generators for quarry operations in site 'UMR'. Sixty male guinea pigs exposed for 3–12 months exhibited significant ($p<0.05$) time-dependent increases in blood concentrations of Pb, Cd, Cu, Zn, Fe, Mn, As, Cr, and Ni, thus confirming systemic accumulation associated with quarry dust exposure. The presence of toxic metals and PAHs above the recommended air-quality standards indicated considerable risk to the environment and human health, which may lead to respiratory, hepatic, neurological, and carcinogenic effects. The findings highlight the urgent need for governmental enforcement of dust-emission standards and improved occupational and community health protection measures in quarrying areas of Ebonyi State.

Key words: Dust emission, heavy metals, metal accumulation, particulate matter, physicochemical properties, polyaromatic hydrocarbons.

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Introduction

Industrial activities are major sources of environmental pollution, especially where clustered [1]. Quarry industries introduce minerals into the environment in the form of dust. The elements or compounds present in the dust may be toxic to humans, animals and plants [2]. In Ebonyi state, exploitation of limestone, and rocks used in construction works constitute one of the greatest pollution sources of public health and safety concerns. Quarrying can generate particulate matter with diameter ranging from 1 - 75 µm. This can be graded into total suspended particulate matter (TSPM), PM_{10} (inhalable particulate matter), and $PM_{2.5}$ (respirable particulate matter). TSPM has diameter less than 50 µm, PM_{10} has diameters less than 10 µm, while $PM_{2.5}$ has diameters less than 2.5 µm [3]. PM_{10} and$PM_{2.5}$ can be dispersed over long distances and can penetrate the respiratory system of human and animals [4].

The number of stone crushing industries in Ebonyi State, South-East Nigeria has been on the rise recently. Quarrying in Ebonyi state is mostly a labor intensive activity, with crushers clustered as seen in Umuoghara quarry industrial cluster. The industry employs a lot of rural people and since these workers also reside close to these areas, environmental and occupational exposures coexist and increase vulnerability of all members of the community to the health impacts of quarry dust. Although quarry contributes positively to the economy of the state and provides job for the teaming poor and unskilled population, there is need to consider the adverse effects on the workers, neighboring communities and the entire vicinity. Reports have shown that the health impacts of dust on workers in stone crushing industries, varies widely depending on the composition of the dust, its pH and the concentration inhaled [5].

Dust from stone quarries contains heavy metals such as As, Hg, Mn, Cu, Zn and Pb and Fe [6]. The presence of particulate-bound PAHs was reported in PM2.5 in a highly industrialized area of Mexico [1]. In the atmosphere, low molecular weight PAHs (2- and 3-ring PAHs) are mainly distributed in the gaseous phase, while heavier PAHs tend to be associated with particulate matter [7,8]. These and other compounds when inhaled may have harmful effects on humans and animals within the vicinity. Most of the constituent heavy metals are toxic to organisms even at low concentrations. While, others such as Manganese (Mn), Magnesium (Mg), iron (Fe), Copper (Cu), and Zinc (Zn) are also essential for life processes at low concentrations [9].

Concentrations of essential elements in healthy organisms are tightly regulated. Adverse effects manifest when the control mechanisms break down as a result of either very low level or excess concentration of the metals [10]. Heavy metals accumulate in organisms via direct absorption across the body wall, inhalation from the

surrounding air, and through contaminated food. The most toxic form of a metal is its free ion and the concentration of this ionic form often serve as the best indicator of toxicity, except mercury which is more toxic in its organic form, methylmercury [11].

Quarrying industry in Ebonyi State employs thousands of workers, including men and women, young and old who work without protective measures. The disregard or lack of awareness of dust emission limits by quarry industry owners and the general poor status of people working in these areas have posed a public health challenge. There is lack of environmental monitoring and very low implementation of dust control measures in these areas resulting in degradation of the environment surrounding the locations where stone crushing industries are established and contribute to health problems among quarry workers, people and animals living around these areas. It has been reported that metals in respirable dust-suspended particulate leads to pulmonary problems [12], and cause hematological and hepatic disorders which increases with duration of exposure [13], while high molecular weight PAHs have potential for carcinogenic and genotoxic effects [14, 15].

The health effects of dust in the air are better appreciated if we consider the fact that an active person typically inhales 10,000 to 20,000 litres of air daily [16]. Industrial emissions of gases, particulate matter (PM), and toxic compounds are being reduced via pollution control measures [17], but most developing countries including Nigeria, are yet to aggressively pursue reduction of dust emission in most industrial areas. More worrisome is that majority of the workers do not know that exposure to the quarry dust for a duration can lead to accumulation of the toxic constituents which in turn will lead to severe health effects. Determining metal concentrations in body fluids is usually employed as a biomarker for the exposure of humans to heavy metals [18]. The aim of this research was to determine the average quantity of particulate matter emitted in two different quarry sites; their composition and the possible accumulation of heavy metals in exposed guinea pigs.

Materials and Methods

Study Area

The two quarry sites are located at Umuoghara (umr) community in Ezza North Local Government Area, and Ammofia Ngbo (amn) community in Ohaukwu Local Government Area, while the control (ctr) is at CAS Campus of Ebonyi State University about 10 km and 20 km from the two quarry sites respectively. The first is small scale crushers built in clusters 174 crushers, while the later an industrial scale crusher. The geographical coordinates are ($6^{o}18'$N and $8^{o}2'$E), ($6^{o}22'$N and $8^{o}9'$E) and ($6^{o}19'$N and $8^{o}4'$E) respectively.

Measurement of particulate emission

Particulate matter emission was measured in the months of January, April, July, and October, using Met One Instrument, Aerocet Model 531 series in the three sites. The instrument was suspended on a wooden pole at the height of 1.5 meters. The Sampling was carried out at three different points AQ1, AQ2, and AQ3 corresponding to 0m (area within the quarry site), 5 m, and 10meters away from the edge of the quarry site respectively. All measurements were taken on a dry non rainy weather and replicated three (3) times.

Collection of Dust Sample

Quarry dust was collected from Umuoghara stone crushing site (umr), Amoffia Ngbo stone crushing site (amn), and CAS Campus; with Whatman filter paper. Quarry dust was allowed to settle on Whatman filter papers attached (face up) to a wooden attached to a wooden pole held with Teflon tape for 8 hours at three different air quality (AQ) monitoring points (AQ1, AQ2, and AQ3) from each quarry site and pooled for analysis.

2.4 Chemical analysis of dust

Determination of heavy metals in dust sample

15ml of triacid mixture (70% HNO_3, 70% H_2SO_4, and 65% $HClO_4$ in the ratio of 5:1:1) was added to each beaker, containing 1 g of the dust sample. The mixture was then digested at 80°C till the solution became transparent. The digested samples were then allowed to cool, filtered through whatman filter paper no. 42 and into a 50ml volumetric flask and diluted to the mark volume with deionised water and the concentration of the metals Fe, Cu, Pb, Zn, Cd, Si, Cr, Ni, Mn, As, Hg was measured with Varian AA240 Atomic Absorption Spectrophotometer [19].

Evaluation of Physicochemical properties

The quarry dust pH, Electrical Conductivity (EC), Cation Exchange capacity (CEC), nitrate, sulphate and phosphate were determined using standard methods [20].

Determination of Polyaromatic hydrocarbons (PAHs)

The analysis was conducted using isotope dilution mass spectrometry coupled with high-resolution gas chromatography. Known internal standards were added to samples, followed by matrix-specific solvent extraction, fractionation, and chromatographic analysis. Specifically, 20 g of sample mixed with anhydrous sodium sulfate was Soxhlet-extracted with hexane for 6 hours. The extract was concentrated, saponified with methanolic potassium hydroxide under reflux, cooled, diluted with water, and re-extracted with hexane. The combined extracts were dried, concentrated, and subjected to silica gel column clean-up. Sequential elution with hexane and hexane–dichloromethane provided PAH-

enriched fractions. These were concentrated, re-dissolved in acetonitrile, and analyzed by gas chromatography using a capillary column and flame ionization detector (FID). Final concentrations of PAHs were determined by comparing sample chromatographic peaks to those of the internal standards [21].

Experimental animal grouping

Sixty (60) male guinea pigs were divided into 3 groups of twenty (20) guinea pigs each and labeled 'umr' for Umuoghara, 'amn' for ammofia Ngbo and 'ctr' for control. Each group was further subdivided into 4 subgroups of 5 guinea pigs each and kept in 4 separate cages. The subgroups were labeled umr_1 to umr_4, amn_1 to amn_4 and ctr_1 to ctr_4. Subgroups 'umr' were exposed to Umuoghara, 'amn' to Amoffia Ngbo quarry site, while 'ctr' (control) was kept at CAS Campus of Ebonyi State University. The exposed were brought out in the morning and taken into a nearby house at the end of work each day. Subgroups with subscripts 1, 2, 3 and 4 from each group were exposed for a period of three, six, nine and twelve months respectively and investigated accordingly at the end of each exposure.

Blood metal analysis

Blood sample was collected by ocular puncture using capillary tube. Concentrated HNO_3 was added to $5cm^3$ of the blood sample in a round bottom flask and digested using a heating mantle. To the mixture, $5cm^3$ of HCl was added under continuous heat at 80°C. The samples were digested until clear solutions were obtained and evaporated to near dryness. Another 5ml of concentrated HNO_3 was added to the blood sample and stored at 4 °C. These were then diluted to 25.0 cm^3 each with de-ionized water [22]. The metals: Pb, Cu, Mn, Fe, Cd, Zn, As, Ni, Hg, Cr, were measured with AAS [19].

Statistical analysis

Results were statistically analyzed using two-way ANOVA and turkey multi-comparison test done with graphpad prism software version 60. Values at $P<0.05$ were considered to be significant**.**

Results

Quantity of Particulate Matter Emitted at the Experimental Sites

The results of the quantity of dust (particulate matter) emitted in umuoghara (umr) and ammofia Ngbo (amn) quarry sites in relation to the control (ctr) site are presented in figures 1 to 3. The emission was significantly higher ($p<0.05$) than control in both quarry sites for TSPM, PM_{10} and $PM_{2.5}$. The particulate matter (TSPM, PM_{10}, $PM_{2.5}$) emitted at site 'amn' were significantly higher ($p<0.05$) than those of site 'umr' with the exception of the result of PM_{10} recorded in October. The particulate matter emission followed the order Jan > Apr > Jul > Oct. The level of all the particulate matter measured were found to follow the trend AQ1 > AQ2 > AQ3 in both quarry sites.

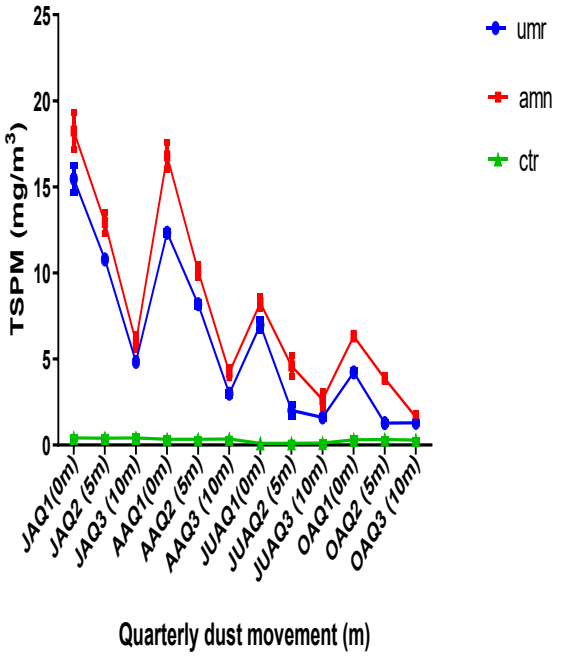


Figure 1: Total Suspended Particulate Matter (TSPM) in both quarry and control sites.

The data are presented as mean ± SD (n=6) and significant
difference at p<0.05.
*umr = Umuoghara quarry site
amn = Amoffia Ngbo quarry site
ctr = Control Site

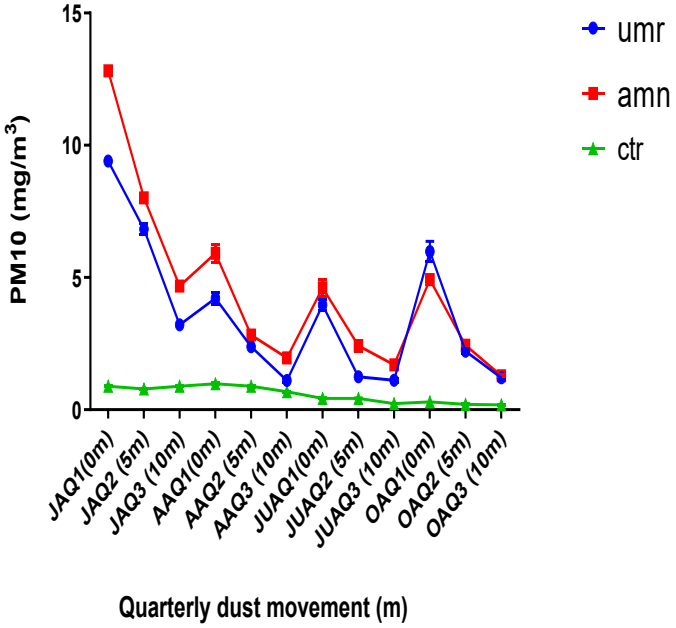


Figure 2: Particulate Matter with diameter ≤ 10 mm (PM10)) in both quarry and control sites.

The data are presented as mean ± SD (n=6) and significant difference at p<0.05.
*umr = Umuoghara quarry site
amn = Amoffia Ngbo quarry site
ctr = Control Site

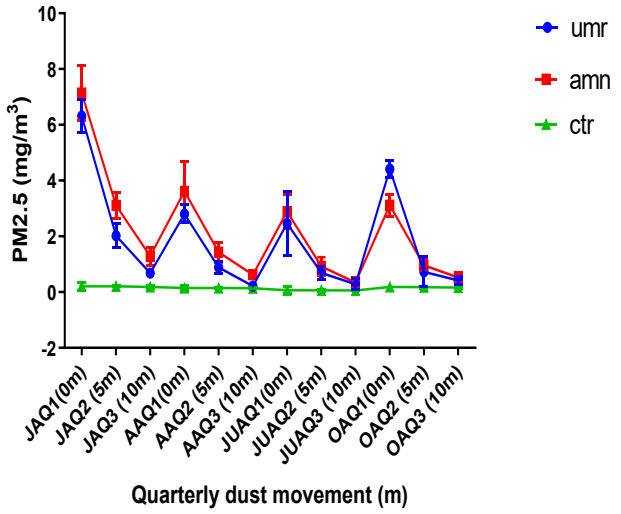


Figure 3: Particulate Matter with diameter ≤ 2.5 mm (PM2.5) in both quarry and control sites.

The data are presented as mean ± SD (n=6) and
significant difference at p<0.05.
*umr = Umuoghara quarry site
amn = Amoffia Ngbo quarry site
ctr = Control Site
JAQ = January air quality monitoring position
AAQ = April air quality monitoring position
JUAQ = July air quality monitoring position
OAQ = October air quality monitoring position

Constituents of the Dust Samples from Umuoghara (umr) and Amoffia Ngbo (amn) quarry sites

The results of some chemical and physicochemical properties of dust from the two quarry sites and that of the control are shown in Tables 1-3. The metals and physicochemical properties were significantly higher ($p<0.05$) in both sites than the control site. Site 'amn' also showed a significantly higher concentration of Cr, Si, Ca, Ni, Fe, Zn and Mn than 'umr'. Polyaromatic hydrocarbons (PAHs) were significantly higher ($p<0.05$) in 'umr' than 'amn' with few exceptions. The concentrations of the anions recorded were significantly ($p<0.05$) higher in 'amn' than 'umr'.

Table 4 showed significantly ($p<0.05$) higher concentration of metals in the exposed animals than the control group. Pb, Cd, Cu, Zn, Fe, and As increased significantly (($p<0.05$)) with the duration of exposure in a time dependent manner. Ni, Cr, and As were totally absent in the control groups. Significantly ($p<0.05$) higher concentrations of metals were observed in guinea pigs exposed at site 'amn, compared to those exposed at 'umr'.

Table 1: Concentration of Metals in mg/kg of Dust Samples from Umuoghara (Umr) and Amoffia Ngbo (Amn) quarry sites

Parameter (mg/kg)	Umr	Amn	Ctr
Chromium	2.11 ± 0.40^{a}	10.05 ± 0.82^{b}	ND
Silicon	4.10 ± 1.50^{ac}	$6.33 \pm 1.20d^{c}$	5.20 ± 0.40^{c}
Arsenic	5.01 ± 1.60^{g}	3.26 ± 0.68^{f}	0.02 ± 0.00^{e}
Nickel	2.26 ± 0.24^{a}	6.89 ± 0.20^{c}	ND
Iron	51.88 ± 2.80^{j}	83.37 ± 2.60^{k}	10.14 ± 1.30^{g}
Mercury	0.10 ± 0.12^{l}	0.34 ± 0.08^{l}	ND
Cadmium	0.13 ± 0.04^{lm}	0.11 ± 0.01^{m}	ND
Manganese	8.34 ± 1.00^{c}	13.16 ± 1.50^{bh}	2.2 ± 0.02^{n}
Zinc	13.997 ± 1.30^{h}	15.72 ± 2.00^{ih}	2.68 ± 0.20^{a}
Copper	0.53 ± 0.10^{m}	1.26 ± 0.70^{f}	0.42 ± 0.01^{m}
Lead	0.99 ± 0.04^{am}	0.88 ± 0.20^{flm}	0.03 ± 0.01^{e}

Results are mean ± standard deviation of three values. Values with the same letter are not significantly different. ND = not detected, 'umr' = Umuoghara, 'amn' = Amoffia Ngbo quarry sites, ctr = control.

Table 2: physicochemical properties of dust samples from Umuoghara (Umr) and Amoffia Ngbo (Amn) quarry sites

Physicochemical properties	Umr	Amn	Ctr
CEC cmol/kg	0.12 ± 0.00^{a}	0.13 ± 0.00^{a}	0.07 ± 0.00^{b}
Conductivity µ/cm	8.5 ± 0.08^{b}	13.2 ± 0.04^{a}	4.75 ± 0.02^{c}
PH	5.23 ± 0.00^{b}	6.45 ± 0.00^{a}	6.70 ± 0.00^{a}
SO_4^{2-} (mg/l)	34.20 ± 1.60^{b}	38.42 ± 2.40^{a}	10.22 ± 2.20^{c}
PO_4^{3-}(mg/l)	1.32 ± 0.50^{b}	1.03 ± 0.20^{c}	2.4 ± 0.20^{a}
NO_3^{-} (mg/l)	25.29 ± 0.48^{b}	29.83 ± 1.20^{a}	8.16 ± 1.00^{c}

Results are mean ± standard deviation of three values. Values with the same letter along rows are not significantly different. umr = Umuoghara, amn = Amoffia Ngbo quarry sites, ctr = control.

Table 3: Concentration of Poly Aromatic Hydrocarbons (PAH) in µg/kg of Dust Samples from Umuoghara (Umr) and Amoffia Ngbo (Amn) quarry sites

Component(µg/kg)	Umr	Amn	Ctr
Naphthalene	0.115 ± 0.01^{b}	0.436 ± 0.02^{c}	0.026 ± 0.01^{a}
Pyrene	0.224 ± 0.03^{b}	0.301 ± 0.02^{b}	0.019 ± 0.01^{a}
Fluoranthene	0.013 ± 0.00^{a}	ND	ND
Benzo (k) fluoranthene	0.413 ± 0.01^{c}	0.283 ± 0.01^{b}	ND
Benzo (a) pyrene	0.163 ± 0.02^{b}	0.087 ± 0.00^{a}	0.032 ± 0.01^{a}
Benzo (1-2-3-cd) pyrene	$0.205 \pm 0.01^{b,}$	0.103 ± 0.01^{b}	ND
Benzo (g-h-i) pyrene	0.630 ± 0.01^{d}	0.406 ± 0.01^{c}	ND
Dibenzyl (a-h) anthracene	0.188 ± 0.03^{f}	0.154 ± 0.02^{e}	0.123 ± 0.02^{b}

Results are mean ± standard deviation of three values. Values with the same letter are not significantly different. umr = Umuoghara, amn = Amoffia Ngbo quarry sites, ctr = control.

Table 4: Concentration of metals in mg/kg blood samples of guinea pigs exposed to Umuoghara (Umr) and Amoffia Ngbo (Amn) quarry sites

Parameters(mg/kg)		3 Months	6 Months	9 Months	12 Months
Pb	Umr	47.63 ± 0.49	44.20 ± 2.0	64.72 ± 1.26	80.0 ±1.20
	Amn	61.32 ± 1.12	73.80 ± 1.0	82.40 ± 1.31	86.80 ± 1.30
	Ctr	38.70 ± 0.70	40.50 ± 0.50	40.80 ± 0.53	35.60 ± 0.36
Cu	Umr	17.88 ±1.50	29.50 ± 0.10	34.40 ± 0.20	40.10 ± 1.70
	Amn	32.10 ± 2.0	36.02 ± 2.0	38.08 ± 1.02	42.10 ± 2.10
	Ctr	9.07 ±1.51	6.06 ± 0.70	8.20 ± 2.18	9.60 ± 2.50
Mn	Umr	122.70 ± 0.10	143.76 ± 0.20	150.14 ±2.20	160.10 ±1.00
	Amn	142.48 ± 2.12	148.30 ±1.10	153.65 ±1.12	169.40 ±0.90
	Ctr	80.14 ± 0.19	73.56 ± 2.30	72.82 ± 0.30	72.26 ± 1.45
Fe	Umr	172.80 ± 0.11	240.60 ±1.60	260.00 ±1.90	276.70 ±1.10
	Amn	194.55 ± 0.80	258.29 ±1.31	272.80 ±0.38	286.04 ±2.30
	Ctr	66.73 ± 1.11	61.42 ± 2.0	82.82 ± 1.80	96.74 ± 1.0
Cd	Umr	60.44 ± 0.10	115.70 ±0.11	126.73 ±0.50	128.30 ±0.20
	Amn	83.08 ± 2.10	121.52 ± 1.70	130.20 ± 1.50	139.00 ± 1.30
	Ctr	33.80 ± 1.0	30.15 ± 2.10	28.60 ± 1.40	32.40 ± 1.90
	Amn	1.06 ± 0.07	3.12 ± 0.20	4.42 ± 0.40	4.02 ± 0.53
	Ctr	0.13 ± 0.05	0.18 ± 0.12	0.09 ± 0.01	0.92 ± 0.10
Zn	Umr	6.93 ± 0.50	12.11 ± 0.80	17.20 ± 1.50	20.11 ± 1.0
	Amn	11.59 ± 0.20	18.84 ± 0.90	19.0 ± 0.62	22.86 ± 1.40

	Ctr	4.71 ± 0.20	6.20 ± 1.20	7.84 ± 2.15	8.62 ± 0.50
	Umr	12.60 ± 0.40	14.76 ± 1.00	18.80 ± 039	24.20 ± 0.57
As	Amn	13.80 ± 1.30	20.52 ± 0.18	29.80 ± 0.08	30.12 ± 0.32
	Ctr	0.00	0.00	0.00	0.00
	Umr	0.65 ± 0.02	0.80 ± 0.08	1.83 ± 0.06	2.20 ± 0.05
Ni	Amn	0.93 ± 0.05	1.25 ± 0.16	2.00 ± 0.12	2.44 ± 0.16
	Ctr	0.00	0.00	0.00	0.00
	Umr	1.09 ± 0.28	1.12 ± 0.25	1.98 ± 0.20	3.30 ± 0.20
Cr	Amn	2.08 ± 0.18	2.64 ± 0.19	2.88 ± 0.04	4.15 ± 0.14
	Ctr	0.00	0.00	0.00	0.00

Results are mean ± standard deviation of three values. Values with the same letter are not significantly different. umr = Umuoghara, amn = Amoffia Ngbo quarry sites, ctr = control.

Discussion

The extraction of minerals from surface mines and quarries produces significant dust emissions which can cause serious environmental and health hazards on both site personnel and the wider community [23]. The risk of exposure to quarry dust is high in developing countries due to poor awareness of the health implications, lack of environmental governance and poor implementation of dust control measures.

The data on particulate emission showed that there was significantly ($P<0.05$) higher TSPM, PM_{10} and $PM_{2.5}$ at both quarry sites than the control site at all three air quality sampling positions. This is an indication that stone quarrying activities can lead to air pollution of the surrounding environment. The results exceeded the 24h and annual mean pollution limit of 15µg and 5µg recommended by WHO for $PM_{2.5,}$ 45 µg/m^3 24-hour mean and 15 µg/m^3 annual mean for PM_{10} in ambient air respectively [24]. The significantly higher concentration of particulate matter recorded at site 'Amn' than site 'UMR' may be attributed to the fact that rock crushing at 'Amn' is of industrial scale and uses a motorized conveyor belt which may be additional point source of dust emission, although employs lower number of workers thereby minimizing direct exposure. However, it results to higher dust emission and causes indirect health burden to nearby residents. The highest value recorded in January and the lowest in July for all the sites suggested that weather conditions such as humidity affect the emission and dispersion of particulate matter. The decrease in the quantity of dust with increase in distance also indicated that the quarry dust is the chief source of particulate matter in these areas. Wind can carry dust particles well beyond the site boundaries. Residents living in proximity (downwind) to quarries can potentially be affected by dust up to 0.5 km from the source, although continual or severe concerns about dust are most likely to be

experienced within about 100m of the dust source [25].

A similar study [26] recorded PM_{10} of 125.0 µg/m^3 as the highest level and 69.4 µg/m^3 as the lowest, then 116.2 µg/m^3 as the highest and 67.5 µg/m^3 as the lowest in two distinct communities around a quarry industry. They also observed that health records obtained from the health centers showed a noticeable increase in dust related diseases in the study area. Generation of $PM_{2.5}$-sized particles may impose serious respiratory health effects over the workers engaged in mining, crushing, and transportation of sandstone [27]. Our result also agreed with the report of [28] on the quantity of particulate matter emitted around crushing areas of Pulau Chondong, Kelantan". They found that chronic exposure to granite dust is a major risk factor for respiratory symptoms such as phlegm (46%), dyspnea (36%), cough (32%), and chest tightness (22%) among quarry workers [28]. For its large surface area and strong adsorption capacity, PM can adsorb, combine and transport polycyclic aromatic hydrocarbon (PAHs), polychlorinated biphenyls (PCB), heavy metals, bacteria, viruses and other toxic substances and potential carcinogens [1].

The result showed that the concentration of metals was higher in dust samples from both quarry sites than that of the control. It was also observed that metals such as Cr, Ni, Hg, and Cd were present in the dust samples from the two quarry sites amongst other metals but were not detected in the control samples. This indicates that the quarry dust may be the sole source of these metals within the vicinity. Similar research by [29] at Umuoghara quarry cluster recorded the concentration of metals which is concordant with our data except for Ni and Fe. The highest concentration recorded for Fe (83.37 ± 2.60) at 'amn' and (51.88 ± 2.80) at 'UMR' compared to the lowest (10.14 ± 1.30) recorded at the control is suggestive of the presence of heavy metals in the quarry dust. There was significant heavy metal concentration (Cd, Pb, Cu, Ni) in soils and plants near quarry sites, highlighting environmental and potential health risks similar to those reported by this study [30]. The research emphasizes heavy metal accumulation, toxicity, and implications for food safety and ecosystem health. A high contribution of toxic metals in the ambient particulate matter around a slag based cement plant was also reported by Animashaun, et al [31]. These are in agreement with our observations.

The concentration of the polyaromatic hydrocarbons recorded in the dust from the two quarry sites are both significantly higher than that of the control. PAHs concentration is higher in 'UMR' than 'amn'. This could be due to multiple use of diesel engines for power generation as 'UMR' is a cluster of over 160 crushers each with its own diesel engine for power generation as a result of poor electricity supply in these industrial

areas. Other researchers have also linked PAHs in ambient particulate matter to the use of diesel and other petrochemicals [32, 33,].

The pH of the dust from both quarry sites studied was lower than that of the control. Quarry dust from 'UMR' recorded a pH of 5.23 while that of Amn was 6.45. This was comparable to the average pH of 6.3 - 9.1 reported in literature [34]. Dust pH influences their chemical reactivity, solubility and bioaccessibility thus, affects the ability to cause irritation of the skin, eyes and respiratory tract, and also its ability to cause cellular damage [35]. The higher concentrations of sulphate and nitrate in the dust from both quarry sites suggest that the quarry stones are rich salts of these anions. High concentration of NO_3^- and SO_4^{2-} in dust samples was also reported [34].

All the metals analyzed recorded significantly ($p<0.05$) higher concentration in the exposed guinea pigs than the control. The concentration also increased with increase in duration of exposure. This is an indication that metal from quarry dust when inhaled can accumulate in the blood and organs. The longer the duration of exposure the higher the accumulation until a threshold that can cause health problems is reached. Although some of these metals have crucial biological functions, sometimes their chemical coordination and oxidation-reduction properties make them escape control mechanisms such as homeostasis, transport, compartmentalization and binding to required cell constituents. These metals displace other metals from their natural binding sites causing malfunctioning of cells and hence toxicity. Previous research has found that oxidative deterioration of biological macromolecules is primarily due to binding of heavy metals to the DNA and nuclear proteins [11].

The concentrations of the metals recorded were higher in guinea pigs exposed to site amn when compared to those of site UMR. This may be attributed to the higher emission of dust/PM in the former as recorded in our results. Metals, such as As, Cr and Ni were present in the blood samples of guinea pigs exposed to the two quarry sites but were not detected in the control animals. This may indicate that there was no other nearby source of these elements at the time of this research except the quarry industry. The observed higher concentrations of Pb, Zn, Cu, Co, Fe in the blood samples of exposed animals correlate very well to the concentrations of these metals recorded in our dust samples.

A significant increase in the concentration of heavy metals in the blood of rats following frequent respiratory exposure to $PM_{2.5}$ was reported [36], which is in agreement with our observation that exposure of guinea pigs to quarry dust lead to accumulation of metal in the blood samples which increased in concentration with the duration of exposure.

Although some heavy metals are essential elements and a small amount of them show some

health benefits such as chromium and manganese, yet their excessive intake can cause damage. Some heavy metals such as lead and arsenic are well known to be toxic to human body. Lead as a heavy metal element can pass the blood-brain barrier (BBB), accumulate in brain and eventually cause damage to the central nervous system [11]

Our study showed increase in concentration of lead with length of exposure which could lead to selective accumulation in some organs. The liver is the main detoxification organ and accordingly it may have high content of the accumulated lead. Brain may be another important target organ for lead accumulation due to slow excretion [36].

Manganese is a co-factor of oxidative phosphorylation and can be accumulated by mitochondria rich cells in liver, brain, and hair [37]. High levels of manganese can induce toxic effect on multiple organs so it adversely affects the functions of the liver, cardiovascular, reproductive, immune system and central nervous system [36]. Our result showed a significantly ($P<0.05$) higher concentration of manganese in the blood samples of guinea pigs exposed at both quarry sites than those of the control. Copper is an essential trace element but excessive intake can lead to toxicity. Cu is mainly concentrated in the liver and when the concentration exceeds the ability of liver detoxification, it would be released into the blood *[38]*. Chronic copper poisoning can cause hepatomegaly and abnormal liver function, lung fibrosis and nervous system disorders including poor memory and attention, instability, multiple neuritis [38]. Higher concentration of copper in the blood of exposed animals, which also increased with length of exposure, was observed in this study and long term exposure to the quarry dust would probably lead to liver damage [13].

Cadmium may induce acute liver and kidney damage as well as chronic damage of other organs and systems [39]. Ni can cause skin allergies, lung fibrosis, kidney injury and cardiovascular system deterioration [40]. Long term accumulation of chromium has been linked to lung cancer and hepatocellular carcinoma, Arsenic can cause lipid peroxidation and DNA damage, binds thiol or sulfhydryl groups in tissue proteins of the liver, lung, kidney, spleen, gastrointestinal mucosa, and keratin-rich tissues (skin, hair, and nails) and can also lead to [41, 11].

Our result showed higher concentration of these metals in the exposed guinea pigs than in the control groups, while some were totally not detected in the control animals. Their presence can lead to increase in the risk of cancer and hematopoietic dysfunction [13, 36]. Manifestation of toxicity of individual heavy metal differs depending on dose and duration of exposure, species, gender, and environmental and nutritional factors.

Conclusion

The quarterly particulate matter emission was significantly ($p<0.05$) higher in the quarry sites compared to the control area, within all sampling

positions. The average emission of all particulates (TSPM, PM_{10}, and $PM_{2.5}$) were higher in site amn than UMR. There were presence of significant ($p<0.05$) quantities of toxic metals and poly aromatic hydrocarbons in mg/kg of dust samples from both quarry sites compared to the control. Exposure to the quarry dust without protection has resulted to accumulation of toxic metals in the blood of the exposed guinea pigs. This will result to different adverse systemic health effects. This report should evoke action from the ministry of health and environment of Ebonyi State Government towards enforcement of environmental regulations to ensure compliance to dust emission standards by independent quarry owners and protect the health of teaming poor population used as laborers in the quarry industries.

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