Assessment of Ambient Air Quality around Ihetutu Minefield, Ishiagu, Nigeria

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ABSTRACT

This study assessed the levels of physicochemical characteristics and heavy metals in ambient air around Ihetutu community in Ishiagu, Nigeria, to evaluate the impact of prolonged Pb-Zn mining and several other related activities on air quality in the area. Particulates, heavy metals, microclimatic and gaseous parameters in ambient air were analyzed for the assessment. Sampling and quality measurements were done during rainy, late rainy, dry and late dry seasons between 2018 and 2019, from study and control areas. Samples were analyzed for particulates and heavy metals in the laboratory while microclimatic and gaseous parameters were measured in-situ using standard field equipment and procedures. Mean and seasonal concentrations of parameters were determined to evaluate the ambient air quality at various locations in the study area. Results showed high mean values of some parameters including; ambient temperature (35.19°C), Relative Humidity (65.78%), SO₂ (0.33ppm), NO₂ (0.30ppm), PM₁₀ (89.73µg/m³), Cu (0.03mg/L), Zn (0.06mg/L), Fe (0.39mg/L), Mn (2.28mg/L), Ni (0.04mg/L) and Pb (0.05mg/L). Highest Noise level in the study area was 60.40 dB(A). SO₂ and NO₂ were below detection limits during the dry seasons, but with mean levels above daily average limits of DPR, NESREA, and WHO, due to their high levels during the rainy seasons, except at Amaonye Square. CO mean levels were above FMEnv daily average limit but within DPR limit. PM₁₀ mean values were within NESREA recommended daily average limit while dry season values were above. Zn and Fe pollution along the stations were in the order of SAS3>SAS4>SAS5, while Pb pollution was SAS3>SAS4=SAS5. Generally, trend of heavy metal pollution was Mn>Fe>Pb>Zn>Cd=Cu=Ni. Highest positive correlation within the heavy metals was between Zn and Fe ($r = 1.000$). There were also no statistically significant differences in means of the parameters among sampling stations ($p > 0.05$). The results revealed pollution of ambient air in the area by heavy metals and gaseous substances, especially around the mining sites and high traffic areas. Proper monitoring of the operations of mining companies and other artisan activities is recommended, to ensure that ambient air status in the area is excellent and within standard guidelines.

Keywords: Ambient air, concentrations, particulates, outdoor, workplace.

1.0 INTRODUCTION

Atmospheric impacts of mining activities are mainly from generation of dust, and this can be analyzed temporally and spatially in workplace and ambient air qualities around mining communities [1]. Mining activities contribute to the problem of air pollution that adversely affect human health, plants, animals, and valuable objects in and around mining areas either directly or indirectly. The most important emissions or air pollutants during mining are particulate matters, sulfur dioxide, nitrogen dioxide and heavy metals, which deteriorate the air qualities in the mining areas. Activities leading to air pollution in mining areas include drilling, blasting, loading and

unloading of overburden, ore, haul roads, transport roads, stock yards, exposed overburden dumps, ore handling plants, exposed pit faces, presence of fire, exhausts from heavy earth moving machinery, crushing of metal ores [2]

Heavy metals such as zinc, cadmium, lead, iron and mercury are common air pollutants emitted mainly from various industrial activities. Although the atmospheric levels are low, they contribute to the deposition and build-up in soils. Heavy metals are persistent in the environment and are subject to bioaccumulation in food-chains [3].

Particulate levels in ambient air are raised by exhaust emissions from mobile sources such as

cars, trucks, heavy equipment. There are also gas emissions usually from the combustion of fuels in stationary and mobile sources, explosions, and mineral processing. Large-scale mining has the potential to contribute significantly to air pollution, especially in the operation phase [4]. According to the National Environmental Standards and Regulations Enforcement Agency (NESREA) [5], in the National Environmental (Air Quality Control) Regulations, no emissions released from the premises of business operational areas or personal facilities into ambient air should exceed 60% of the prescribed ambient air quality standards, while also considering contributions from other facilities.

The Ihetutu Hill is located in Ishiagu, Ebonyi State of Nigeria, and is within the Lower Benue trough. Lead-zinc and hard rock (aggregate) mining have been ongoing in the

area for several decades. The Ishiagu area covers an expanse of land of about 450 km² and supports an estimated population of over two hundred and fifty thousand people [6,7]. The study area falls within latitudes 5° 51' N and 5° 59' N and longitudes 7° 24' E and 7° 40' E (Figure 1). The area is accessible through the Enugu-Port Harcourt Railway line, the Enugu-Port Harcourt oil pipeline, and the Enugu-Port Harcourt Express Road [8].

Availability of clean air is of utmost importance to all humans, hence the significance of this research to ascertain the quality of air the local dwellers and workers at the various mine sites in Ihetutu are exposed to. The objective of the study therefore is to assess the level of pollution of outdoor air by toxic substances released from the mines and other natural and anthropogenic sources in the study area.

Figure 1: Map Showing Sampling Stations in Study and Control Areas

2.0 MATERIALS AND METHODS

2.1 Sampling and Air Quality Measurement

Ambient air sampling was carried out at four designated sampling stations including control station in the four seasons (Table 1). Station coordinates and wind directions were determined using a GPS meter. A gas analyzer (Madur GA.21 Plus, Aeroqual series 200) was used to determine gaseous parameters directly on site. Ambient temperature, wind speed and

relative humidity were determined using an anemometer. Noise levels were measured with the aid of a noise meter. A handheld particulate counter was used to sample for particulate matters. The counter was allowed to run for about 1 hr at a flow rate of 100 L/min, and then the filter membrane removed, rapped in an aluminum foil, and stored in a polyethylene bag for analysis. The filter membranes were dried in the laboratory for about one hour at 105°C and cooled in a dessicator to room temperature.

Particulate levels (PM_{10} and $PM_{2.5}$) were determined using Equation 1;

$$\text{Conc } (\mu\text{g}/\text{m}^3) = \frac{(M_s - M_o)}{V} \times 10^{-3} \quad (1)$$

Where M_s = Mass of filter paper after sampling, M_o = Mass of filter paper before sampling, and V = Volume of sample (mL).

Table 1: Summary of sampling field data.

Sampling Stations	Sampling Dates	Sampling Seasons	Station locations	Latitude	Longitude
CAS1 (control)	11/05/2018; 29/09/2018; 30/11/2018; 12/04/2019	RNS; LRS; DRS; LDS	Near Aku Stream, Uturu	N 5°51'34"	E 7°31'13"
SAS3	11/05/2018; 29/09/2018; 30/11/2018; 12/04/2019	RNS; LRS; DRS; LDS	Pb-Zn mine Site, Ihetutu	N 5°51'35"	E 7°31'13"
SAS4	11/05/2018; 29/09/2018; 30/11/2018; 12/04/2019	RNS; LRS; DRS; LDS	Amanchala Junction, Ihetutu.	N 5°55'41"	E 7°29'5"
SAS5	11/05/2018; 29/09/2018; 30/11/2018; 12/04/2019	RNS; LRS; DRS; LDS	Amaonye Square	N 5°56'59"	E 7°33'28"

RNS = Rainy Season; LRS = Late Rainy Season; DRS = Dry Season; LDS = Late Dry Season

2.2 Digestion and Analysis of Heavy Metals

0.5 g of grinded and homogenized filter membrane was weighed into a 125 mL beaker. 100 mL of distilled water, 0.5 mL HNO_3 , and 5 mL of HCL were added to the beaker in a fume hood. The samples were heated on a hot plate at 90°C in the fume hood until the volume was reduced to 20 mL. Mixture was cooled and filtered into a 100 mL volumetric flask with the aid of glass funnels and filter papers, to remove solids particles from the content. The volume was made up to the 100 mL mark with distilled water from a wash bottle and then taken for analysis. Standard procedure, ASTM D1971/D4691 [9] was employed for the analysis of heavy metals in the samples, using flame atomic absorption spectrophotometer (FAAS).

3.0 RESULTS AND DISCUSSION

3.1 Microclimate of the Study Area

3.1.1 Temperature

The mean ambient air temperature at the sampling stations ranged from 34.49 – 35.19 °C, with the maximum recorded at the mine site (SAS3) and the minimum recorded at Amanchala Junction (SAS4) (Table 3). The trend for ambient air temperature showed that SAS3>SAS5>SAS4. Mean temperature at the control station near Aku stream (CAS1) was 33.75 °C and was lower than the values the mean values from the study area. Ambient temperature was highest during the late dry season (LDS) at SAS5 while it was highest during the dry season (DRS) at the mine site, Amanchala Junction (SAS3), and the control site (CAS1) (Table 2). Temperature inversion which limits the vertical circulation of air and results in air stagnation and trapping of gaseous pollutant could lead to the high values of pollutants in dry seasons [10]. Also, according to some literatures, temperature has a positive correlation to the concentration of particulate matters but a negative correlation to relative humidity [11].

Table 2: Seasonal Values of Physico-chemical Parameters and Heavy Metals in Ambient Air

Parameters	CAS1				SAS3				SAS4				SAS5			
	RNS	LRS	DRS	LDS	RNS	LRS	DRS	LDS	RNS	LRS	DRS	LDS	RNS	LRS	DRS	LDS
Wind speed (m/s)	1.80	1.60	1.20	1.30	2.20	2.00	1.60	1.20	0.80	0.50	0.30	2.00	1.00	1.20	1.80	1.50
Noise dB(A)	50.20	52.60	60.90	54.50	51.80	55.10	69.30	65.60	54.20	50.40	59.60	58.70	57.20	56.20	60.80	59.80
Amb. Temp. (°C)	35.70	30.00	35.20	34.10	34.00	35.20	36.00	35.55	35.70	30.36	36.80	35.09	34.40	33.20	34.80	36.31
Rel. Hum. (%)	59.70	60.10	63.80	62.40	60.40	60.60	66.90	75.20	60.20	62.40	71.20	62.80	64.60	62.40	52.50	60.70
SO ₂ (ppm)	0.06	0.09	<0.1	<0.1	0.09	0.12	<0.1	<0.1	0.26	0.07	<0.1	<0.1	0.05	0.04	<0.1	<0.1
NO ₂ (ppm)	0.04	0.07	<0.1	<0.1	0.20	0.10	<0.1	<0.1	0.18	0.10	<0.1	<0.1	0.01	0.03	<0.1	<0.1
CO (ppm)	2.60	0.17	<0.1	<0.1	3.41	2.87	4.92	2.68	<0.1	<0.1	3.00	0.04	<0.1	<0.1	2.00	1.89
PM ₁₀ (µg/m ³)	4.00	3.00	189.00	36.00	5.00	24.90	239.00	90.00	3.00	4.00	227.00	44.80	2.00	2.00	173.00	46.00
PM _{2.5} (µg/m ³)	1.00	1.00	35.40	19.20	2.00	18.00	50.00	21.80	1.00	1.00	60.00	13.60	2.00	2.00	26.00	10.00
SPM (µg/m ³)	26.20	27.00	46.40	35.80	36.40	46.80	68.00	38.90	60.60	35.10	59.80	20.50	57.10	37.80	50.60	31.50
Copper (mg/L)	<0.01	<0.01	<0.01	<0.01	0.02	0.03	0.03	0.05	0.02	0.02	0.02	0.04	0.01	0.00	0.01	0.02
Zinc (mg/L)	<0.005	<0.005	<0.005	<0.005	0.02	0.06	0.06	0.09	0.01	<0.005	0.03	0.04	<0.005	<0.005	0.01	0.02
Iron (mg/L)	0.01	0.01	0.23	0.21	0.04	0.07	0.68	0.76	0.03	0.02	0.32	0.44	0.02	0.02	0.21	0.33
Manganese (mg/L)	1.10	1.09	1.12	1.15	2.40	2.39	1.59	2.75	2.31	2.32	1.27	2.66	1.16	1.16	1.11	1.78
Nickel (mg/L)	<0.001	<0.001	<0.001	<0.001	0.03	0.04	0.03	0.05	0.01	<0.001	0.02	0.03	<0.001	<0.001	0.01	0.02
Lead (mg/L)	<0.009	<0.009	<0.009	<0.009	0.04	0.04	0.06	0.08	0.02	0.04	0.03	0.05	<0.009	<0.009	0.01	0.04
Cadmium (mg/L)	<0.002	<0.002	<0.002	<0.002	0.02	0.02	0.04	0.04	0.02	0.02	0.03	0.03	<0.002	<0.002	0.01	0.02

3.1.2 Relative humidity

Relative humidity is the ratio of the amount of water vapour present in the air to the highest possible amount of water vapour at the same temperature. The highest mean value of Relative humidity (RH) was 65.78% recorded at the mine site (SAS3) while the lowest value was 60.05% at Amaonye Square (SAS5) (Table 3). The mean value at Amanchala Junction (SAS4) was 64.15% while that of the control site (CAS) was 61.50%. Relative humidity mean values in study area were in the order of SAS3>SAS4>SAS5 (Table 2). Average ratios of particulates (PM_{2.5} and PM₁₀) increase significantly with relative humidity, and higher relative humidity aggravates particulate matter pollution of air in the winter (dry season) [12]. The high levels of particulates recorded in the study area could also be due to the increased relative humidity. Increase in relative humidity in the atmosphere also reduces amount of solar radiation reaching

the earth's surface, as the air absorbs the heat from the solar radiation [13]. This makes the air layer closer to the earth surface to be colder than the upper layers. Pollutant concentration in the air thus increases because of the reduction in the up-going air currents, which also leads to the trapping of pollutants in the air.

3.1.3 Wind speed

Average wind speed was 1.75 m/s (maximum level) at the mine site (SAS3) and 0.90 m/s (minimum level) at Amanchala Junction (SAS4) while at Amaonye Square (SAS5) it was 1.38 m/s (Table 3). Average wind speed at control station near Aku stream (CAS1) was 1.48 m/s. The highest wind speed recorded at the mine site (SAS3) could be due to the topography of the location and absence of surrounding trees, which resulted to the exposure of the entire mine site to intense wind blowing across the area.

3.1.4 Noise

Mean noise levels recorded for the three sampling stations in the study area were 60.45, 55.73, and 58.50 dB(A) at SAS3, SAS4 and SAS5 respectively while that of control station (CAS1) was 54.55 dB(A) (Table 3). The high noise level at Amaonye (SAS5) and the control station near Aku stream (CAS1) could be due to the closeness of the two stations to major roads where there were high vehicular movements and other human engagements while that at the mine site (SAS3) were due to noise from haulage and other operational trucks, excavation machines/equipment, and several other human activities at the site. Noise levels in both study and control areas were within FMEnv [14] recommended level of 90 dB(A). Noise levels were higher in the dry seasons. This was due to increased operations at the mine site which also led to increase in sound generation. Also, noise level increased with increase in ambient temperature, as speed of sound increases with increasing temperature [15].

3.2 Assessment of gaseous substances (SO₂, NO₂ and CO)

Seasonal concentrations of SO₂ and NO₂ in ambient air were below detection limit during the dry seasons, at all stations including the control (Table 2). However, all sites recorded some values for the two gases in both rainy (RNS) and late rainy (LRS) seasons. Mean concentrations of SO₂ and NO₂ at the mine site (SAS3) and Amanchala Junction (SAS4) (Table 3), were above the daily average limits recommended by NESREA [5], DPR [6], and WHO [15], while at Amaonye Square (SAS5) their concentrations were within recommended limits (Table 4). Mean values of SO₂ amongst the stations were in the order; SAS4>SAS3>SAS5 while NO₂ values were in the order SAS3>SAS4>SAS5.

CO mean concentrations in ambient air at Amanchala junction (SAS4) and Amaonye square (SAS5) were 1.52ppm and 1.95ppm respectively, while at SAS3 (mine site) and CAS1 (control station near Aku stream), CO levels were 1.39 ppm and 3.47ppm respectively (Table 3). CO mean levels at all stations, including control, were above the daily average limit of FMEnv [14], though within the limits of DPR [16] (Table 4). Mean values of CO amongst the stations were in the order; SAS3>SAS5>SAS4. High CO

concentrations could result from incomplete combustion of petroleum products from vehicles and other mechanical sources. Due to its high affinity to haemoglobin in the red blood cells, CO is extremely poisonous, as it prevents the transportation of oxygen by haemoglobin to essential parts of the body cells [17]. Also, according to reports [18], CO, NO_x and SO_x could come from trapped substances and other subsidiary activities taking place within the immediate surroundings of an operational area. The gases are acidic oxides that when dissolved in water will form acids.

3.3 Assessment of Particulates

3.3.1 Suspended particulate matter (SPM)

The mean concentrations of SPM in ambient air in the study area were 47.53µg/m³, 44.00µg/m³, and 44.25µg/m³ at SAS3, SAS4, and SAS5 respectively. SPM mean values at all three study area stations were in the order SAS3>SAS5>SAS4, and higher than its mean value at the control site near Aku stream (CAS1) (Table 3). Mean SPM values at all sites including the control (CAS1) were within the daily average limits of FMEnv [4], and WHO [15], DPR [16] (Table 4). Suspended particulate matter (SPM) in ambient air results from a wide range of finely divided solids that are dispersed into air from combustion processes, industrial activities or natural sources [19]. It constitutes the sum of all suspended solid and liquid particles in the air, with sizes ranging from about 0.1 – 30 µm in diameter. This complex mixture contains particles such as dust, pollen, soot, smoke, and liquid droplets that could be hazardous [15].

3.3.2 PM₁₀ and PM_{2.5}

Mean values of PM₁₀ in the study area were 89.73µg/m³, 69.70µg/m³, and 55.75µg/m³ at SAS3, SAS4 and SAS5 respectively. PM_{2.5} mean concentrations were 14.15µg/m³, 22.95µg/m³, and 18.90µg/m³ at SAS3, SAS4, and SAS5 respectively. Control (CAS1) PM₁₀ and PM_{2.5} mean values were higher than that of SAS5, in both cases (Table 3). PM₁₀ mean levels were within NESREA [5] daily average limit of 150µg/m³. However, dry season (DRS) concentrations at all three stations in the study area were above the NESREA [5] daily average limit (Tables 2 and 4). Mean values of PM₁₀ in the study area were in the order of

SAS3>SAS4>SAS5 while $PM_{2.5}$ values were in the order of SAS3>SAS4>SAS5 (Tables 2). Generally, particulate matters values obtained from both study and control areas showed significant seasonal variation between rainy and dry seasons, as higher concentrations were recorded in the dry seasons for samples analyzed. The higher values obtained in the dry season (DRS) when maximum values were recorded, could be due to much dust generation and dispersion in the air and less rainfall during the dry season. This could also be the reason highest values were recorded at the mine site (SAS3) where much dust were generated due to constant excavation, haulage, crushing, rock blasting, dumping of wastes, and other operational activities, especially in the dry seasons.

Also, particulate matters concentrations decreased with increasing distance from the mining locations, and increase in relative humidity. This was corroborated by the reports of some earlier researchers [12, 18, 20].

The higher concentrations of particulate pollutants recorded during the dry seasons could also result from the longer residence time of particulates in the atmosphere in the dry seasons because of low winds and low mixing height [21]. Particulate matters in ambient air are responsible for harmful effects on human health, even in the absence of other air pollutants [15]. They may also cause damage by the discoloration and destruction of painted surfaces, corrosion of metals and building surfaces, soil textiles and clothing; and could as well lead to climate change [11].

Table 3: Mean Values of Physico-chemical parameters in Ambient Air

Parameter	SAS3	SAS4	SAS5	CAS1 (Control)
Wind speed (m/s)	1.48	1.75	0.90	1.38
Noise dB(A)	54.55	60.40	55.73	58.50
Amb. Temp. (°C)	33.75	35.19	34.49	34.68
Rel. Hum. (%)	61.50	65.78	64.15	60.05
SO ₂ (ppm)	0.08	0.21	0.33	0.09
NO ₂ (ppm)	0.06	0.30	0.28	0.04
CO (ppm)	1.39	3.47	1.52	1.95
PM ₁₀ (µg/m ³)	58.00	89.73	69.70	55.75
PM _{2.5} (µg/m ³)	14.15	22.99	18.90	10.00
SPM (µg/m ³)	33.85	47.53	44.00	44.25

Table 4: Ambient Air Quality Standard Guidelines and Values

Pollutant	FMEEnv (long-term Limits, 24 hrs)	DPR	NESREA	WHO
SO ₂ (ppm)	0.05 mg/m ³	0.1–0.15 ^a mg/m ³	0.12 ^a mg/m ³	0.1–0.15 ^a mg/m ³
NO ₂ (ppm)	0.085 mg/m ³	0.15 ^a mg/m ³	0.12 ^a mg/m ³	0.08–0.11 mg/m ³
CO (ppm)	1.0 mg/m ³	10 ^a mg/m ³	5 ^b mg/m ³	0.001 ^b mg/m ³
PM ₁₀ (µg/m ³)			150 ^a µg/m ³	
SPM (µg/m ³)	0.15 mg/m ³	60–90 ^a µg/m ³		150–230 ^a µg/m ³
Lead	0.005 mg/m ³	0.0005–0.001 ^d mg/m ³	0.0014 ^a mg/m ³	
Nickel			20.0 ^c mg/m ³	
Cadmium	0.003 mg/m ³		5.0 ^c mg/m ³	
Chromium	0.001 mg/m ³			
Manganese	0.01 mg/m ³			
Mercury	0.0003 mg/m ³			

Note: a = daily average; b = 8-hr average; c = annual average; d = 1-hr average mean; NESREA[5]; FMEEnv[14]; WHO[15], DPR[16]

3.3.3 Heavy metals in ambient air

Copper

Mean concentrations of copper in ambient air was at maximum at the mine site (SAS3) with 0.04 mg/L while the minimum value (0.01 mg/L) was obtained at Amaonye Square (SAS5); and at Amanchala Junction (SAS4), the mean concentration of copper was 0.02 mg/L. Concentration at control station (CAS1) was below detection limit (<0.01 ppm) (Table 2). Seasonal concentrations were highest in the late dry season (LDS) at all sampling stations in the study area (Figure 2).

Manganese

Manganese has a maximum mean value of 2.28 mg/L at the mine site (SAS3) while its minimum mean value of 1.30 mg/L was recorded at Amaonye Square (SAS5). Mean concentration at Amanchala Junction (SAS4) was 2.14 mg/L while at the control site (CAS1), it was 1.12 mg/L (value lower than the mean values of the study area sampling stations). Also, the highest seasonal concentration of manganese in ambient air (2.75 mg/L) was recorded in the late dry season (LDS) at the mine site (SAS3) (Table 2) (Figure 2). Manganese concentrations at the various sampling stations in both study and control areas were higher than the recommended 24-hour average limit of 0.01

mg/m³ by FMEEnv [14] (Table 4), though lower than OSHA legal limit of 5.0 mg/m³ for manganese in air (averaged over an 8-hour work day) [22]. Also, air contains low levels of manganese, and breathing air so infested with the metal may expose one to it. Manganese is released into the air from mining activities, automobile exhaust, and industries using manufacturing products containing manganese. Workers exposed to high levels of manganese in workplace air including the Pb-Zn mine site SAS3), may suffer nervous systems defects, and other health effects with combination of symptoms which when sufficiently severe is referred to as *manganism*. This comes with some behavioral changes and other nervous systems effects, which include movements that may become slow and clumsy; schizophrenia, dullness, weak muscles, headaches and insomnia. There is also the probability of men in the area suffering serious health effects such as loss of sex drive and sperm damage if they are constantly exposed to manganese for too long [22].

Nickel

The mean concentration of Nickel in ambient air was also at maximum at the mine site (SAS3) while the minimum value was obtained at Amaonye Square (SAS5), 0.05 and 0.01 mg/L respectively. Mean value at Amanchala

Junction (SAS4) was 0.02 mg/L while at the control site (CAS1), Ni concentrations were below detection limit (<0.001 ppm) (Table 2), and thus with a zero mean value. Highest seasonal concentration of Ni in ambient air (0.05 mg/L) was recorded in late dry season (LDS) at the mine site (SAS3) (Figure 2), where Ni particulates were also expected to make up the gaseous pollutants found in the dust generated from the various operational activities at the site. However, Ni concentrations at all sampling stations were within the recommended annual average limit of 20.0 mg/m^3 by NESREA [5] (Table 4).

Zinc

Highest mean concentration of zinc (0.06 mg/m^3) was at the mine site (SAS3) while its lowest mean concentration (0.02 mg/m^3) was at Amaonye Square (SAS5). Mean concentration at Amanchala Junction (SAS4) was 0.03 mg/L while at the control station (CAS1) it was zero, as seasonal concentrations were below detection limit (Tables 2). Also, highest seasonal concentrations were recorded during the late dry season (LDS) (Figure 2) when there were increased activities at the Pb-Zn mines site. These activities led to injection of gaseous pollutants in the ambient air at the workplace through the dust they generated.

Iron

Maximum mean concentration of iron in ambient air (0.39 mg/m^3) was recorded also at the mine site (SAS3), where lots of excavations, rock-blasting, crushing; haulage, transportation; shifting and dumping of wastes especially during the dry seasons were carried out. These activities generated lots of dusts thereby polluting the ambient air in the workplace with several gaseous pollutants in the dust [18]. The minimum mean concentration of iron (0.15 mg/m^3) was recorded at Amaonye Square (SAS5) which was about 1.1 km away from mine sites. Mean concentration at control station (CAS1) was lower compared to values recorded in the study area. Iron concentrations were lower in the rainy seasons (Figure 2). This followed the report [10] that, concentrations of atmospheric pollutants are usually low in the rainy seasons due to the impact of heavy rainfalls scavenging them even as they are emitted from both

natural and anthropogenic sources. This could be the reason for the low concentrations of iron recorded during the rainy seasons.

Lead

Lead concentration in ambient air was also highest at the workplace of the mine site (SAS3), with a mean value of 0.05 mg/m^3 while its lowest value was recorded at Amaonye Square (SAS5) as 0.02 mg/m^3 . Also, mean concentration of lead at Amanchala Junction was 0.03 mg/L while its mean value at the control station near Aku stream (CAS1) was zero, with seasonal concentration below detection limit (Table 2). Lead concentrations at all sampling stations in the study area were higher in the dry seasons (Figure 2), and above standard guideline values of NESREA [5], FMEnv [14], and DPR [16] (Table 4). High lead concentrations in ambient air especially at the mine site (SAS3) were expected, considering the huge lead deposits and the various mining activities constantly carried out at the site including; excavation, blasting, crushing and transportation of ores, shifting and dumping of wastes that generate lots of dusts especially during the dry seasons [18].

Cadmium

Mean concentrations of cadmium in ambient air were 0.03 mg/L both at the mine site (SAS3) and Amanchala Junction (SAS4); and 0.02 mg/L at Amaonye Square (SAS5) while at the control station near Aku stream (CAS1), its mean concentration was zero, as its seasonal concentrations were all below detection limit (<0.002 ppm). The highest seasonal concentration of cadmium in ambient air (0.04 mg/L) was recorded in both dry (DRS) and late dry (LDS) seasons at the mine site (SAS3) (Table 2) (Figure 2). Cadmium levels were also higher than the recommended 24-hour average limit of 0.003 mg/m^3 by FMEnv [14] but within annual average limit of 5.0 mg/m^3 of NESREA [5] (Table 4). High cadmium concentrations especially at Amanchala Junction (SAS4) during dry seasons could also be due to temperature inversion which limits the vertical circulation of air, and thus results in the stagnation of air and trapping of pollutant in the area [10].

Figure 2: Seasonal Concentrations of Heavy Metals in Ambient Air

3.3.4 Correlation

Correlations among heavy metals in the study area were all strongly positive, with the highest coefficient between Zn and Fe ($r = 1.000$), and the lowest between Ni and Mn ($r = 0.759$)

(Table 5). The positive correlations pointed to similar sources of heavy metal pollution [23,24], which could be the mining operations and other dust generating activities including road construction in the area.

Table 5: Correlations of Heavy Metals in Ambient Air

	<i>Cu</i>	<i>Zn</i>	<i>Fe</i>	<i>Mn</i>	<i>Ni</i>	<i>Pb</i>	<i>Cd</i>
<i>Cu</i>	1						
<i>Zn</i>	0.948	1					
<i>Fe</i>	0.953	1.000	1				
<i>Mn</i>	0.928	0.762	0.773	1			
<i>Ni</i>	0.947	0.999	0.998	0.759	1		
<i>Pb</i>	0.990	0.984	0.987	0.866	0.983	1	
<i>Cd</i>	0.990	0.894	0.901	0.971	0.892	0.960	1

3.3.5 Analysis of variance (ANOVA)

ANOVA was performed at a significance level, $\alpha = 0.05$. The results showed no statistically significant differences in means of the parameters among the sampling stations, as p -value (0.999) was higher than the significance level.

4.0 CONCLUSION

The study has confirmed the deterioration of ambient air quality in and around Ihetutu Pb-Zn mining areas of Ishiagu. Levels of physicochemical parameters and heavy metals analyzed were higher than most pre-mining/background values obtained from the control station near Aku stream in Uturu (about 12 km away from the study area), and referenced standard guidelines. There was an indication of pollution of ambient air, resulting from the regular mining of Pb-Zn and other artisan activities in the area, as most parameters were above referenced standard guidelines. Trend of heavy metal pollution, in study area, from the investigation, was $Mn > Fe > Pb > Zn > Cd = Cu = Ni$, while seasonal variations were mostly in the order of $LDS > DRS > LRS > RNS$. Also, deterioration of

ambient air qualities along sampling stations was in the order of $SAS3 > SAS4 > SAS5$. The study also revealed that workplace air at the mining sites was the most deteriorated, considering the high level of toxic substances released to the atmosphere directly from the mining operations. Mining activities in the area have become major sources of high levels of toxic substances released to the atmosphere, with significant adverse health implications on the lives of the people living and working in the area; and other animals, plants and valuable objects in the environment. It is thus, recommended that the government through its regulatory agencies including National Environmental Standards and Regulations Enforcement Agency (NESREA) and the Federal Ministry of Environment, properly monitor and regulate the activities of these mining companies and other related activities. This would ensure that ambient air status in the area is excellent, and not adversely affected by these activities, and is also within standards guidelines. Further study should also be carried out on the health risk of the heavy metal pollution of the workplace/outdoor air on the people in the area.

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