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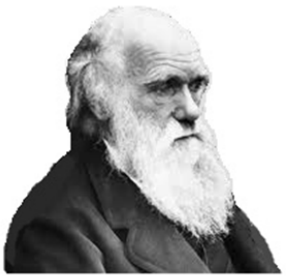

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A holistic review of heavy metals in water and soil in Ebonyi SE, Nigeria; with emphasis on its effects on human, plants and aquatic organisms

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ABSTRACT

A comprehensive review of literature was carried out to evaluate the presence of heavy metals (HMs), with a view to study its effect on man, plants and aquatic organisms in Ebonyi State, southeastern Nigeria. From reviewed literature it was observed that the major source of HM in soil and water can be attributed to anthropogenic activities such as mining and quarrying. Geogenic activities were also implicated by some scholars. Detail analysis showed that 62 % of HMs in water and soil is attributed to mining, while 23 % is attributed to indiscriminate waste disposal, and 15 % is due of other human and geogenic activities. The accumulation of HMs in plants, soil and water poses a serious risk to human, plants and aquatic organisms within the study area. The occurrence of HMs in soil and water if not properly monitored may tend to increase in years to come and this may have negative impact on plants and aquatic organisms. Severe health effects of humans are inevitable. Therefore, constant re-evaluating of HM in water and soil in the area is highly required.

***Keywords*:** Heavy Metal, Water, Soil, Human, Uptake, Nigeria

Abbreviations

AAS	Atomic Absorption Spectroscopy
HM	Heavy Metal
MEI	Metal Enrichment Index
PLI	Pollution Load Index
HI	Hazard index

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THQ Target Hazard Quotient
EDI Estimated Daily Intake
ICP-MS Inductively Coupled Plasma, Mass- Spectrometer

1. INTRODUCTION

Heavy metal (HM) is found in the earth crust naturally, but found its way into soil and water resources due to human and geogenic activities. According to [1]; [2]; [3] water bodies and soil being ecologically and economically significant are most vulnerable to both natural and anthropogenic source of pollution. HMs is one of the 21stcentury environmental problems that affects plants, animals, aquatic organism and humans, and one of the major environmental challenges that is currently facing the study area due to the high level of unabated illegal mining going on in the area. HM is considered to be highly soluble in the aquatic environments and therefore they can be absorbed easily by living organisms. [4] Further suggested that soil, sediments and aquatic environments play an important role in all biogeochemical cycles and need to be contaminant free for proper functioning of the ecosystem. Human exposure to HM via occupation, environment or diet can cause both the acute and severe adverse health effects.

According to [5] exposure of HMs in human beings over a long period of time may lead to muscular, physical and neurological degenerative processes that mimic Alzheimer's disease, muscular dystrophy, and multiple sclerosis.

HM is found in soil, water, sediment, air, plants and may spread to environment components which may be caused by nature of interactions occurring in this natural system. The interaction of HM chemically or physically may trigger change in the environment, this may result to pollution of water bodies and soil. HM toxicity has proven to be major sources of concern as it pose several health risks to humans. HM have biological role to play in the human body, but on the contrary their toxicity may lead to malfunctioning of humans [6]. [3]; [7] were of the opinion that the two major source of HM in soil is usually the natural and anthropogenic sources. They further reported that the natural source of HM in soil is associated in geochemical processes coupled with soil parental material, while the anthropogenic sources is attributed to combustion of fossil fuels agricultural and mining activities. It is observed that anthropogenic activities are reported to be the major sources of HM in soil when compared to geogenic process.

There has been series of report that mining activities within the several mines across Ebonyi state are major source of HM in soil and water around most of active and abandoned mine site within the study area [8]. [9]; [10] reported that low concentration HM in soil such as Cu, Ni, and Co, Zn, in soil are needed for certain biochemical and physiological processes in living organisms. When these HMs exceed the stated threshold concentrations they may be considered toxic. [11] Pointed out that Cd is one of the major HM that is considered to cause harmful effects on physiological processes of animals, humans, plants and aquatic organism.

According to [12] high concentrations of HMs reduce plant growth, lower biomass production, reduces protein content and synthesis of chlorophyll pigments, which could lead to severe reduction in crop yields. [13]; [14] suggested that the uptake of HM by plants via absorption and subsequent accumulation is a potential threat to animal and human's health. HM toxicity on plants, human and environment cannot be under estimated as it has led to several health challenges and even death of animal and man across various states in Nigeria.

Several studies carried out within the study area also suggested that mining activities around active and abandoned mine site is the major source of HMs in water and water. Although some authors attributed presences of HMs in water to solid waste disposal (see Table 1). Literature of the mining areas of Ebonyi State, SE Nigeria reveals no holistic review of HM in soil and water in the area. There is therefore, an urgent need to review the occurrence of HMs in soil and water within the study area. The objective of this study is to evaluate the effect of HMs in water and soil, with emphasis on its effect on man, plants and aquatic organisms. It is expected this research will help to advert future menace associated with in soil and water.

Table 1. Brief information on HM in Ebonyi State.

Type of Analysis	Location	Method/ Determination	Result	References
Soil and water	Ishiagu and Akpoha	ANOVA and Post hoc test and physic-chemical analysis	Quarry activities is responsible for presences of HM in water and soil	[35]
Water	Abakaliki and its Environs	AAS analysis	There is presence of iron, lead, arsenic and cadmium in groundwater	[36]
Soil	Enyigba, Ameri and Ameri	AAS analysis	Reported that presence of HM in soil. The high values may indicate both geologic and anthropogenic origin.	[37]
Soil and plants	Ikwo	ANOVA and AAS Analysis	Their findings suggested the presence of HM in soil and plants is attributed to mining activities.	[38]
Water	Ebonyi	AAS analysis	HMs were below FAO/WHO Set standard	[39]
Water	Oshiri and Ishiagu Mine	AAS analysis	Attributed the presence of HM in Water to mining activities.	[33]
Soil	Abakaliki	AAS analysis	They attributed HM in soil in Abakaliki to solid waste disposal within the study area.	[40]
Soil	Mkpuma Akpatakpa, Achara Ohankwu and Ishiagu mine	AAS analysis	Findings showed lead mining is the major source of HM in the Environment.	[41]
Soil and Water	Ezza	AAS analysis	HM in soil and water is caused as result of mining activities at Ameki.	[42]

Water	Enyigba	AAS analysis	The study revealed that HMs concentration in water were above the permissible limit. Hence water is unsuitable for drinking.	[43]
Water	Enyigba	AAS analysis	Findings revealed that water is slight polluted with HMs	[44]
Water	Ameka and Enyigba	AAS analysis	Their findings showed that surface water is polluted with HMs and this pollution is attributed to mining activities within Ameka and Enyigba.	[45]
Water	Enyigba, Mkpuma Akpatakpa, Ameka, Amorie, Aman-chara and Alibaruhu	AAS analysis	Water resources is polluted with HMs especially around active Mine site	[46]
Water	Enyigba	AAS and Statistical analysis	They suggested water is highly contaminated with cadmium, arsenic and lead within Enyigba mining district.	[47]
Water	Enyigba, Ameri and Ameki	AAS and Statistical analysis	The presence of HM is attributed mining activities within the area	[48]
Soil	Enyigba	ICP-MS	Their findings suggested that there Was slight decrease in the concentration of HM in soil away from mining Enyigba Pb-Zn site	[49]
Soil	Abakaliki		They attributed the presence of HM to automobile waste from mechanic village.	[50]
Soil	Mkpuma Ekwoku	AAS analysis	They concluded that zinc, lead, cadmium in soil is as a result of local geology and past mining activities.	[51]
Soil	Enyigba	AAS analysis	Findings revealed that the Presence of HM is as a result of Pb-Zn mining in Enyigba area.	[52]
Soil	Enyigba	AAS and Statistical analysis	From there study it was Observed that Pb-Zn in soil are due to mine waste from mining activities.	[53]
Water	Enyigba	ICP-MS	Water is contaminated with HM which make the water unsafe for domestic use	[55]

Soil and vegetable	Enyigba	ICP-MS	Their findings showed that HM was found in soil and vegetable as result of Pb-Zn mining	[16]
Water	Abakaliki	AAS analysis	The study showed the Presence of arsenic in water. The presence of As could be attributed to application of fertilizer during farming.	[55]
Soil	Abakaliki	AAS and Statistical analysis	Their findings suggested that the Concentration of HM is higher in Mechanic	[56]
Soil and rice plant	Two active Mine Site from three senatorial zoneb in Ebonyi state	Physicochemical properties of soil Was determined using Gallenkamp model FH 500 flame photometer and statistical analysis	Results revealed water is considered unfit for domestic	[58]
Water	Ohaozara	AAS analysis	They reported the presence of Pb, As and Fe in groundwater	[59]
Water	Enyigba	AAS analysis	He reported that HM such as cadmium, lead, arsenic and nickel was found to be high in groundwater within the area.	[60]
Soil	Enyigba	AAS analysis	Reported that HM were above set Standard and attributed the high concentration of HM to geology and human activities	[61]
Water	Ebonyi	AAS analysis and Statistical analysis	Presence of HM in drinking in study area	[62]
Water	Enyigba	AAS analysis	Findings showed that HM were Below the WHO, (1993) permissible limit	[63]

1. 1. Sources of Heavy Metals

Presently, the study area is endowed with abundant mineral resources that cut across various part of the state. The illegal exploitation of these minerals has led to the presence of HMs in soil and water resources. Other sources of HMs are land application of fertilizers, animal manures, sewage sludge, pesticides, mine tailings, mechanic wastes and disposal of high metal wastes.

1. 2. Location, Climate, Vegetation and Hydrology

Ebonyi state is accessible through various networks of roads see Fig. 1. The two major seasons that exist within the study area are the dry and the wet seasons. The wet season spans

from March to ending of October, while the dry season spans from October to ending of February, with temperature ranging from 25 °C to 29 °C between the dry season, and 16 °C and 28 °C during the rainy season.

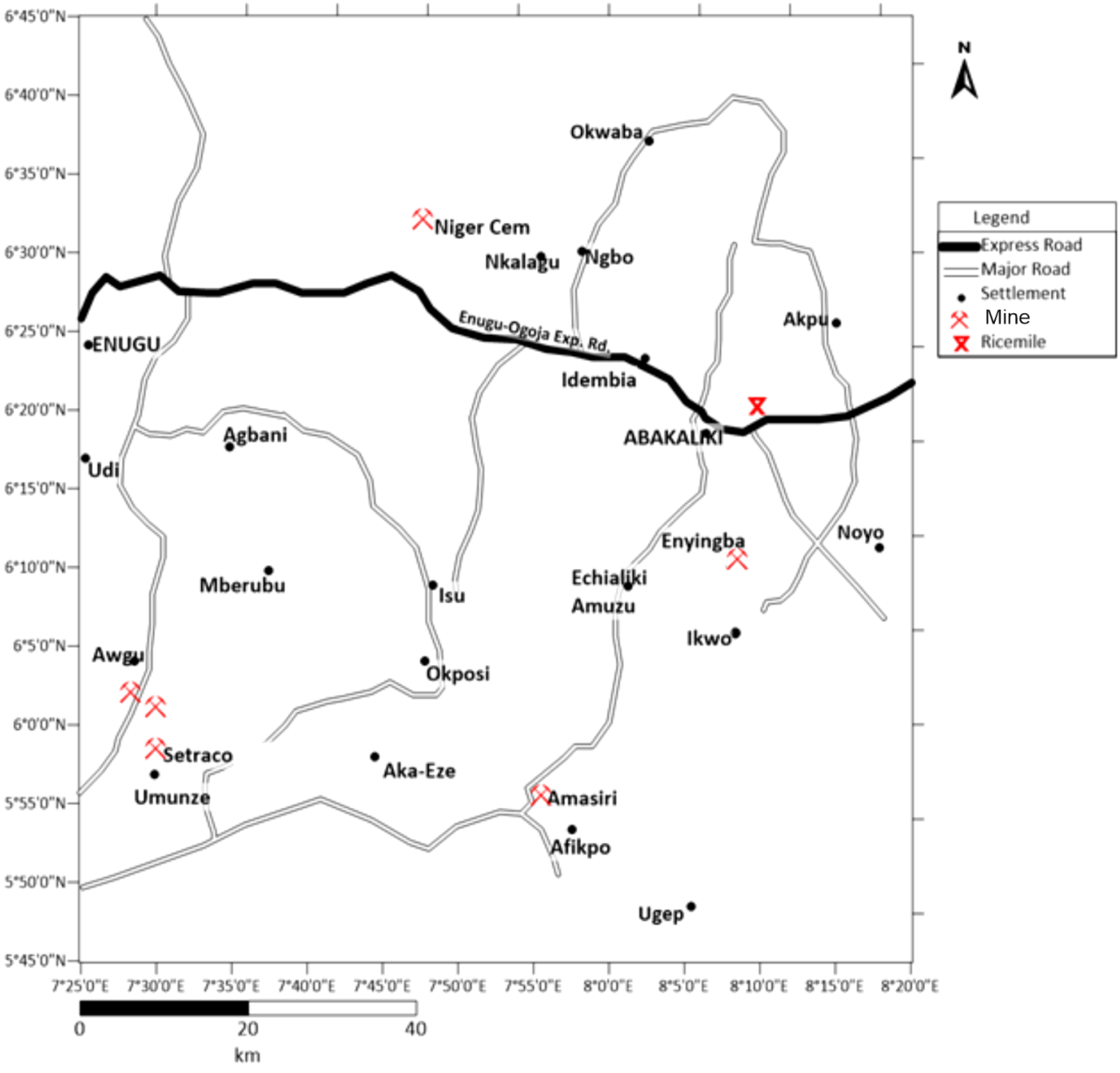

Figure 1. Location Map of the study area (Source: [18]).

The study area lies within the rainforest region of southeastern Nigeria, with humid climate and evergreen vegetation. The average monthly and annual rainfall ranges from 3.1 mm in January to 270 mm in July and 1750 to 2250 mm respectively. The study area comprises of vegetation with dense trees and underground creepers, the trees are mostly tall in some locations, with buttress roots around river bodies, while the vegetation is influenced by various

factors including drainage, geology, topography and rainfall. [15] Further pointed out that the area is of low land rainforest region. The drainage system of the study area is dendritic with the Ebonyi River as the major river that drains the area. [16] Acknowledged that most of the mines within Ebonyi State are located in sporadic in small hilly areas that drain into these streams, which are located in the lowlands. Other tributaries such as the Iyiodu and Ngada rivers control the drainage with the underlying lithology ([17]; [18]). According to [18] the climate of the study area tends to favour the dispersion of the resultant pollution from the mining and quarry activities. High amount of rainfall also results in surface runoff that transport HM and assist its infiltration into groundwater.

2. GEOLOGY OF THE STUDY AREA

Table 2. Stratigraphic column of the study area (After, 34)

Period	Age	Group	Formation	Member
Cretaceous	Turonian	Eze-Aku	Nkalagu Eze Aku shales	
	Albian	Asu River	Abakaliki Volcanics	Pyroclastics Dolerites/diorites
			Asu River shales	Shales and Sandstones
Precambrian Basement Complex				

The study area lies within the Southern Benue Trough with a sedimentary succession of pre-Santonian periods that span from Albian and Turonian age (see Table 2). The Asu River Group of the Albian age is represented by [19] with two formations Abakaliki and Ebonyi Formations that underlie it [20]. [21] Stated that the lithofacies of Asu River Group consists of alternating shales and siltstones with occurrences of fine grained micaceous and feldspathic sandstones, mudstones, and limestones. [22] Were of the view that there have reports of intrusions of magmatic rocks ranging from basic/intermediate igneous rock within the Ishiagu area. [23] Further reported the presences of pyroclastic intrusions within the Abakaliki area. The Eze Aku Group is Turonian age, it unconformably overlies the Asu River Group.

These includes all the lithostratigraphic units deposited in the late Cenomanian to Turonian age in the SBT [24] which includes the Eze-Aku shales, the Nkalagu limestone, and Amasiri sandstone. [25]; [26] were of the view that integration of magmatism, tectonism and diagenesis trigged major alteration of chemical constituents of rocks within the area, thereby baking them and leading to their common use as construction materials [27]; [28]. [29] reported that Pb–Zn minerals occur in veins as open space–fillers within en echelon, tensional, and steeply dipping fracture systems and that in the dark-gray to black shales of the Asu River Group also encouraged their rampant excavation.

The rocks are extensively fractured, folded and faulted. The lead-zinc Ore is found in the Albian carbonaceous shale of the Asu River Group. The mineralization is structurally controlled and localized in fissures, fault zones and gently dipping veins. The veins are steeply dipping and have been proven to over 150m depth. They vary in width from less than a meter to 20m and in length from 30m to 120m. The dominant Ores in the area are observed from the fissures which contain lodes of sphalerite (ZnS), and /or galena (PbS) in association with smaller quantities of copper. The deposits have been mined on and off for several decades. In the Enyigba, Ameri and Ameka areas near Abakaliki, there is incontrovertible evidence of post mineralization deformation that the lodes were developed at the end of Santonian folding ([30]; [31]). Pb – Zn Ore mine areas of Abakaliki district have been implicated in various disease conditions [32].This post Albian mineralization and igneous activities in SBT has led to the deposition and subsequent illegal mining activities within the study area, which in turn has play a major role in the introduction of HM into soil and water within the study area [32].

3. DISCUSSION

3. 1. Occurrence of HM within mine locations in study area

According to [16] and [8] mining of Pb-Zn in Enyigba and its environs has been ongoing for over 32 years, with small scale mining presently going on within the area. The presence of mining activities, indiscriminate waste disposal, has led to occurrence of HM in soil and water. Report according to [64] revealed that HM in soil around Ameri, Enyigba and Ishiagu mine site showed the presence of HMs such as Mn, Pb, Zn, Ni and Ag in soils, which has led to soil contamination in that area. They were of the opinion that HM in soil is as a result of both geology and anthropogenic activities. [16] Assessed HM in soil around the Enyigba mining district using 49 soil samples, from their findings it was observed that HM such as Pb, Zn, Cd, Cu and Cr was found in soil with their concentrations above statutory limits. In the same way, [63] evaluated the presence HMs in water at Enyigba and its environs, from their study it was observed that HM such as Ni, Pb, As and Cd were below [65] permissible limit. Based on their findings, they concluded that water is considered fit for domestic.

A similar study was conducted by [61] on evaluating HM contamination in soil within the vicinity of Enyigba Pb-Zn mine using MEI and PLI. Findings showed a trend of As > Cd > Co >Mn> Cu > Ni >Pb> Zn in soils. He concluded that the presence of the HM is linked to human and geological activities. [47] Assessed HM in drinking at Enyigba community, Abakaliki, using 12 water sampled. Findings from their study suggested that HMs such as arsenic, cadmium and lead were above [65]. They attributed high concentrations of the aforementioned HMs within the study area to indiscriminate waste disposal, geogenic and anthropogenic process. [60] Assessed HMs concentration in groundwater within Enyigba mining area of Ebonyi state, SE Nigeria.

Four groundwater samples were used to evaluate the concentration of HMs within the study area. Findings from his study revealed that groundwater showed high concentrations of cadmium, lead, nickel and arsenic. He concluded that groundwater is contaminated and considered not fit for domestic. Studies carried out by [60] on contamination of HM in water resource (surface and groundwater) around the mining district of Enyigba Pb-Zn mine revealed water resources showed the presences of HMs in order Cd >>> As >> Pb > Ni > Zn > Cu.

He concluded HMs such as lead, arsenic and cadmium showed high concentration when compared to other HMs. This was linked to the presence of HMs in water sources as far as illegal mining activity is currently ongoing.[48] evaluated the occurrence of HM in surface and groundwater in the vicinity of Pb-Zn mining area at Ameri, Ameka, Enyigba Ebonyi state SE Nigeria. Findings from their study revealed that surface water showed higher concentration of HMs when compared to groundwater. They reported that the risk of HMs leaching and groundwater contamination from the mine wastes is very high with considerable likelihood of HM transport by water percolating through the wastes/soils. On the other hand [44] studied surface water within mining district of Enyigba of Ebonyi, results from the study revealed that surface water is contaminated with HMs such as arsenic, cadmium, lead and zinc and that high concentrations of these HM was found in open mine pond. [46] Studied the presences of HMs in water within Ameka mining area, using PLI. This was carried out using the Varian AAS 240 Atomic Absorption Spectrophotometer. Findings revealed that water within the study area is said to be acidic. The acidity was attributed to the chemical activities of Pb-Zn mining activities in the area.

They concluded that HMs found in water were above the threshold limit. [59] Studied HMs in water resources in Ohaozara, Ebonyi State using AAS analytical method. They reported that the presence of lead, arsenic, copper and iron in sampled water. This is in line with several reports of lead across the study area ([33]; [68]). [62] Studied drinking water across various local government area of Ebonyi between wet and dry season. He reported high concentration of HMs in drinking water across the study area and concluded the presence of these HMs has led to water contamination which in turn has led to different kind of illness. [58] Studied surface water (Ebonyi River) with the sole aim of determining physicochemical properties of the water. Results revealed high concentration of lead and zinc as compared to other HMs. That implies that surface water resources of Ebonyi River are considered unsafe for drinking. [68] Assessed groundwater from shallow hand-dug well and borehole within Abakaliki metropolis. Results from their study revealed the presence of Cd, Pb, Cu and Zn in water.

They attributed the presence of these HMs in groundwater to anthropogenic activities such indiscriminate waste disposal and geogenic activities. According to findings from [69] to a large extent the occurrence of Pb in water is particular to a geographical location, it occur mostly in Pb-Zn mining area. The occurrence of Pb in water has been reported in various communities in Jos, Ebonyi others state in Nigeria were mining is currently ongoing. They further advised that groundwater should be treated before it should be used for various use. Although further report by [69] suggested that presence of Cu in water is associated with certain states (Lagos, Ogun, Kano, Kebbi, Bayelsa, Oyo, Edo and Akwa Ibom) in Nigeria. They concluded that the concentration Cu in water occur in the order South-west > South–south > Northern region > south-east and Cu occur mostly in groundwater and less found in surface water.

3. 2. HM in Soil as result of other activities

According to [66] and [67] waste is generated universally and is a direct consequence of human activities. Study conducted by [56] around abandoned mechanic and non-mechanic in Abakaliki analyzed the presence of mercury, lead, iron and cadmium using AAS analysis and statistical method. Findings revealed that the area around mechanic village showed high concentration of HMs when compared non-mechanic site. That implies that the occurrence of HMs around mechanic area could be attributed to anthropogenic activities.

3. 3. Impact of HM on aquatic organism

Several models have been developed [70] to estimate the risks of HMs in human and animal health. Examples are; HI, THQ and EDI among others. HM pollution in water is less pronounced and direct than other form of marine pollution, but the adverse effect on aquatic, ecosystems and humans is highly extensive. According to [71] HM contamination is not only limited to soil and water but also affect aquatic organisms. HM in water resources also have negative effect on aquatic organisms and man. Studies has shown that aquatic organisms showed inter and intra specific variation in the accumulation of HM. Several scholars have reported that HMs such as Zn, Cr, Fe, Mn and Cu may not be hazardous except in situation where they exceed threshold value. Other HMs such as Cd, As, Hg and Pb are non essential and are harmful to biota in small concentrations ([72]; [73]; [74]). [75] Are of the opinion that the presence of HMs differs in aquatic organisms species based on certain factors such as age of aquatic organism, developmental phase and other physiological factors. It is a known fact that aquatic organisms store little concentration of Hg in their tissues and thus represent a major dietary sources of this HM for human. [75] Reported that the most pronounced source of Hg and as intake in man is through aquatic organism (fish). In the same vein, [76] reported high concentration of HM in aquatic organisms. [77] Reported that fish is considered as fundamental biomarkers that is used to monitor HM contamination in aquatic ecosystem. Fishes are the highest trophic occupants of aquatic ecosystem, toxicity of HMs negatively affect the physiological and physical behavior of aquatic organism (fish), and fish is considered to be one of major constituents of human diet globally.

3. 4. Impact of HM in human

The accumulation of HM in human can result to several kind of disease such as kidney damage, liver disease, nervous disorder, hypertension and many others for this see more in Table. 3. Several scholars were of the opinion that HM such as Pb can be seen in computer monitor glass, printed wiring boards, disposals of cathode ray tubes ([68]; [55]). [78] Reported that short term exposure of Pb can result in diarrhea, vomiting, coma and convulsions. Pb in infants can affect their nervous systems, some other symptoms associated with intake of Pb in human are abdominal pains, constipation, appetite loss, irritability, fatigue, sleeplessness, and headache for more on this see Table 3.

Table 3. Effect of HM on human, plants and aquatic organisms

Heavy metal	Sources	Effect on Human being	Plant	Aquatic Organism (fish)
Cadmium	It is usually found in protective coatings (electroplating) for metals like iron; preparation of Cd-Ni batteries. Presence in	Retardation, diarrhea, bone deformation, kidney damage, anemia, central nervous system disorder, hypertension and liver	Result in chlorosis, weak plant growth	Absorb HM through uptake via water

	phosphate fertilizers, sewage sludge to farm land	damage [79].		
Lead (Pb)	plumbing, ammunition, storage batteries and cable coverings,	Nervous system and hematopoietic system [80].	Result in chlorosis, weak plant growth	Uptake of HM by plants through absorption process
Chromium (Cr)	Industrial, mining waste and landfill leaching	Exposure to human to Cr may eventually lead to cancer	Result in low yield, and they may even be accompanied by reduced nutrient uptake	Uptake of HM, by plants through absorption process
Arsenic (As)	Mining, smelting of gold, Lead, Copper and Nickel, Pesticides Production of iron and steel (ATSDR, 2015)	Presence of As in human can lead to cardiovascular system and hepatic damage ([81]; [82]). It can lead to nervous disorder and high blood pressure	Result in low yield, and they may even be accompanied by reduced nutrient uptake	Uptake of HM by plants through absorption process
Manganese (Mn)	Industrial, mining waste and landfill leaching	In can result to nervous disorder in man		
Nickel (Ni)	effluent water generated from mining activities	Ni may lead to Respiratory irritants, lung cancer, prostate cancer, dizziness, larynx cancer and may cause pneumonitis	Result in disorders in plant metabolism and a reduced ability to fix molecular nitrogen in leguminous plant	Uptake of HM by plants through absorption process
Mercury (Hg)	Industrial and mining waste	Affect kidney, neurological deficits and memory loss	Result in disorders in plant metabolism and a reduced ability to fix molecular nitrogen in leguminous plant	Uptake of HM by plants through absorption process

3. 5. Impact of HMs on plants

Plants source of nutrient is from the sun and soil, in most situation plants are selective in the uptake of nutrients from soil, but in some situations they absorb non-essential or toxic elements. [33] Reported that HM intake in plant is a highly complex process and involves metal transfer from soil sap to the cells of roots. Several scholars have showed the process of contaminant uptake by plants and its mechanism. HM such as Co, Cd, As, Ag and transition elements such as Al have greatly affected the growth of plants, when they are above the threshold value. Study by [83] revealed that the uptake process of soil cadmium by plants is enhanced at low pH for more of this see Table 3.

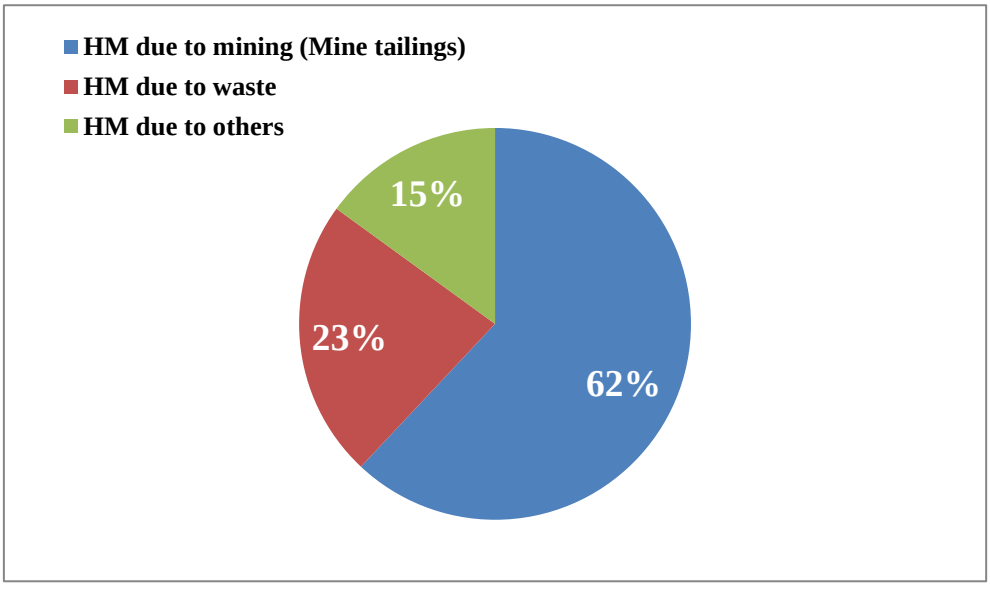

Figure 2. Percentage of major source of HM within the study area.

4. CONCLUSION

The rate at which HMs affect human, plants, aquatic organism and even the environment within the study area is a major source of concern. Hence, there is an urgent need to constantly re-evaluate HMs status at regional scale, in order to avert several damages that HM pose to human, plants and aquatic organisms and if possible reinstate water resources and soil to its natural state. Findings from study suggested that water resources especially groundwater is affected by leaching of HMs from mining and other anthropogenic and geogenic activities within the study area and that HMs such as Hg in take in human is linked to human eating fish with such metal.

Recommendations

- To avert HM in soil and water attributed to waste disposal, it advised that waste management and recycling is highly recommended in order to avert further pollution of HM in soil and water

- ❖ The Public sensitization programs should be proposed by government and non-governmental organizations to sensitize the inhabitants on water source contamination.
- ❖ Miners should be properly enlightened on the dangers associated with exposure to heavy metals to prevent them from polluting water bodies

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