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Research Article

Determination of Heavy Metals in Soil and Water Samples from Mambilla Artisanal Mining Site and its Environs

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Abstract

Background and Objective: Environmental pollution is occurring on a vast and unprecedented scale around the globe, with mining activities been implicated. The study quantified the levels of heavy metals in soil and water samples from Mambilla artisanal mining site and its environs, to ascertain their levels compared to standard acceptable levels in soil and water. **Materials and Methods:** Eight soil and water samples were collected from the sampling points (mining site and main town of Nguroje community) in duplicate. The heavy metal quantification of Lead (Pb²⁺), Mercury (Hg²⁺), Cadmium (Cd²⁺), Arsenic (As²⁺), Iron (Fe²⁺), Chromium (Cr⁶⁺) and Zinc (Zn²⁺) was carried out using an energy dispersive x-ray fluorescence spectrometer. For the heavy metals quantified in samples, the ranges of mean values were determined in samples from mining site and main town. **Results:** There was no significant difference ($p < 0.05$) in the mean values of heavy metal concentrations in all the water samples determined. The heavy metals Pb, Cd, Fe, Hg and Cr concentrations in soil samples exceeded the standard permissible limits. From the results obtained, mining had a direct impact on the concentrations of the heavy metals determined. **Conclusion:** There is a potential for heavy metal pollution in soil and water from Mambilla artisanal mining site and its environs if not properly managed.

Key words: Heavy metals, mercury, cadmium, arsenic, chromium, energy dispersive x-ray fluorescence spectrometer

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Environmental pollution is occurring on a vast and unprecedented scale around the globe and has consequently become a worldwide problem over the years with great potential in influencing health of the human population¹. By definition, environmental pollution is the discharge of substances (solids, liquids or gases) which may be organic or inorganic, volatile or non-volatile, biodegradable or non-biodegradable into the environment in excess of normal expectancy in which bioaccumulation of these substances can cause serious deleterious effects to all life forms and adversely affect the usefulness of resources². Human activities including industrialization and agricultural practices targeted towards exploiting nature for better living conditions has contributed immensely to the degradation and pollution of the environment which have proved to be harmful to animals and man himself³. Naturally occurring heavy metals in the environment are rarely at toxic levels, but their concentrations in the environment increase due to human activities such as; artisanal mining⁴.

Artisanal and small-scale mining refers to informal mining activities carried out using low technology or with minimal machinery. Although artisanal mining helps in the creation of wealth and employment opportunities for local miners, its environmental consequences cannot be overlooked⁵. There is a wide range of environmental degradation that are associated with it such as; heavy metals pollution of soil and water bodies and occupational hazard for diggers⁵. Particularly, mining activities have been found to be the most important causes of metal pollution in the environment⁶. This was the case in Algeria with Mercury (Hg), Arsenic (As) in Namibia and South Africa, Tin (Sn), Lead (Pb), Nickel (Ni) and Chromium (Cv) in Nigeria and Copper (Cu) in Zambia⁶.

The presence of heavy metals at trace level and essential elements at elevated concentration causes deleterious toxic effects if exposed to human population⁷. Serious complications associated with heavy metals contamination were observed to include damage of the nervous system, kidney disease, heart disease and infertility⁸.

Heavy metal pollution of surface and underground water sources results in considerable soil pollution and pollution increases when mined ores are dumped on the ground surface for manual dressing⁹. Surface dumping exposes the metals to the atmosphere in air and rain thereby generating much Acid Mine Drainage (AMD). When agricultural soils and water are polluted, these metals are taken up by plants and consequently accumulate in their tissues¹⁰. Animals that graze

on such contaminated plants and drink from polluted waters as well as marine lives that breed in heavy metal polluted waters also accumulate such metals in their tissues and milk, if lactating⁹. Humans are in turn exposed to heavy metals by consuming contaminated plants and animals and this has been known to result into various biochemical disorders.

The study is geared towards quantifying the levels of heavy metals in soil and water samples from Mambilla artisanal mining site, Taraba state and its environs to evaluate the heavy metals hazard potential on the miners and the local community in general.

MATERIALS AND METHODS

Study area: This study was conducted in Nguroje community, Sardauna local government of Taraba state, Nigeria between October 2018-2019. Nguroje is a town found on the Mambilla plateau in eastern part of Nigeria as presented in Fig. 1. The Mambilla plateau is located between latitude 5° 30'-7° 18' N and longitude 10° 18'-11° 37' E with a total land mass of 3,765.2 km² forming the southern most tip of the north eastern part of Nigeria^{11,12}.

Sampling collection

Water sampling: Eight water samples were randomly collected from different points at the mining site and environs in Nguroje town using plastic bottles. Prior to this, the plastic bottles were washed with detergent then with double-distilled water followed by 2 M nitric acid, then double-distilled water again and finally with sampled water. Two samples were collected from each sampling area in which one sample of 50 mL was mixed with 4 mL of HNO₃ (Nitric acid). The bottles were filled, labeled, sealed tightly and transported in ice bags to the laboratory.

Soil sampling: Eight different soil samples (in duplicate) were collected from Nguroje town. Soil samples were collected at different distances at a depth of 10~15 cm using an auger and kept in sterile plastic bags. Each sample was labeled appropriately and transported to the laboratory in ice bags.

Sample digestion

Water digestion: This was achieved using the method described by Radojevic and Bashkin¹³.

Soil digestion: Soil digestion was carried out using the nitric acid-perchloric acid digestion method.



Fig. 1: Map of Sardauna LGA showing the sampling community (Modified local map from google Earth)

Analysis of soil and water samples: Energy dispersive x-ray fluorescence spectrometer was used to determine the levels of heavy metals in the digested soil and water samples.

Heavy metal analysis: The method described by AOAC¹⁴ was used for heavy metal analysis. The digested soil and water samples were introduced to energy dispersive x-ray fluorescence spectrometer for the analysis. The levels of Pb, Cd, Fe, Cr, Zn, Hg and As were quantitatively determined using ED-XRF (AsomaPhonix II).

RESULTS

Lead concentrations in different soil and water samples:

Figure 2 shows the different concentrations of lead in different soil and water samples with sample A1 having the highest concentration (0.274 ppm) and sample D1 having the least concentration (0.022 ppm) in soil samples while sample F1 having the highest concentration (0.663 ppm) and sample I1 having the least concentration (0.072 ppm) in water samples.

Mercury concentration in different soil and water samples:

Figure 3 shows the different concentrations of Mercury in different soil and water samples with sample E1 having the highest concentration (0.020 ppm) and sample A1 having the least concentration (0.002 ppm) in soil samples whereas

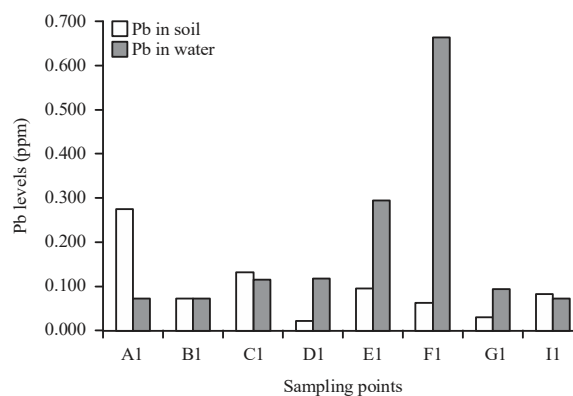


Fig. 2: Levels of Pb (ppm) from different sampling points in Nguroje

A1: Freshly dug pit at mining site, B1: Abandoned pit at mining site, C1: Abandoned pit at gate 3, mining site, D1: Stream water from mining site, E1: Running water 100 m from Hamdalla hotel, F1: Well water inside Hamdalla hotel, G1: Borehole from Gopel opposite UBA bank, I1: Well water from No 20 Galladima-Musa way

sample G1 having the highest concentration (0.706 ppm) and sample A1 and B1 having the least concentration in water samples.

Cadmium concentrations in different soil and water samples:

Figure 4 shows the different concentrations of Cadmium in different soil and water samples with sample D1 having the highest concentration (0.088 ppm) and sample

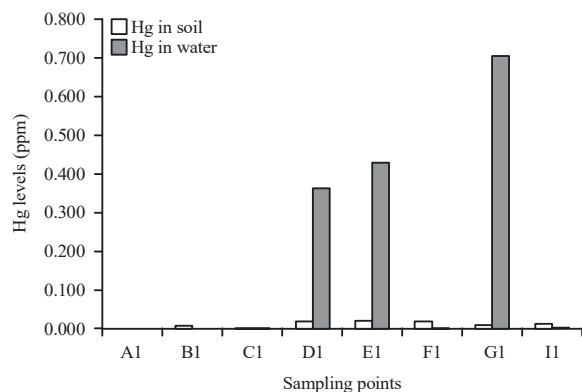


Fig. 3: Levels of Hg (ppm) from different sampling points in Nguroje

A1: Freshly dug pit at mining site, B1: Abandoned pit at mining site, C1: Abandoned pit at gate 3, mining site, D1: Stream water from mining site, E1: Running water 100 m from Hamdalla hotel, F1: Well water inside Hamdalla hotel, G1: Borehole from Gopel opposite UBA bank, I1: Well water from No 20 Galladima-Musa way

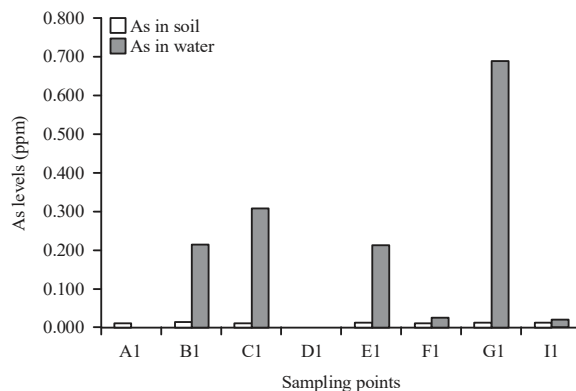


Fig. 5: Levels of As (ppm) from different sampling points in Nguroje

A1: Freshly dug pit at mining site, B1: Abandoned pit at mining site, C1: Abandoned pit at gate 3, mining site, D1: Stream water from mining site, E1: Running water 100 m from Hamdalla hotel, F1: Well water inside Hamdalla hotel, G1: Borehole from Gopel opposite UBA bank, I1: Well water from No 20 Galladima-Musa way

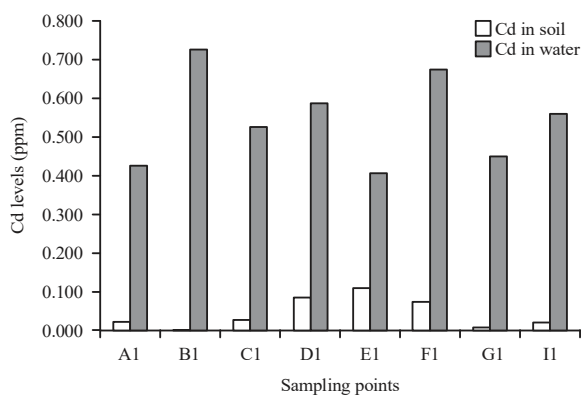


Fig. 4: Levels of Cd (ppm) from different sampling points in Nguroje

A1: Freshly dug pit at mining site, B1: Abandoned pit at mining site, C1: Abandoned pit at gate 3, mining site, D1: Stream water from mining site, E1: Running water 100 m from Hamdalla hotel, F1: Well water inside Hamdalla hotel, G1: Borehole from Gopel opposite UBA bank, I1: Well water from No 20 Galladima-Musa way

B1 having the least concentration (0.003 ppm) in soil samples while sample B1 having the highest concentration (0.727 ppm) and sample E1 having the least concentration (0.409 ppm) in water samples.

Arsenic concentrations in different soil and water samples:

Figure 5 shows the different concentrations of Arsenic in different soil and water samples with samples B1 and I1 having the highest concentration (0.015 ppm) and sample D1 having the least concentration (0.001 ppm) in soil samples while in water samples, sample G1 is having the highest

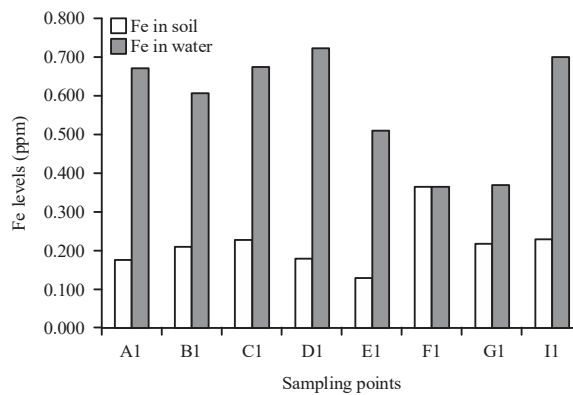


Fig. 6: Levels of Fe (ppm) from different sampling points in Nguroje

A1: Freshly dug pit at mining site, B1: Abandoned pit at mining site, C1: Abandoned pit at gate 3, mining site, D1: Stream water from mining site, E1: Running water 100 m from Hamdalla hotel, F1: Well water inside Hamdalla hotel, G1: Borehole from Gopel opposite UBA bank, I1: Well water from No 20 Galladima-Musa way

concentration (0.689 ppm) whereas samples D1 had the least concentration (0.001 ppm).

Iron concentration in different soil and water samples:

Figure 6 shows the different concentrations of Iron in different soil and water samples with sample F1 having the highest concentration (0.367 ppm) and sample E1 having the least concentration (0.130 ppm) in soil samples while sample D1 had the highest concentration (0.726 ppm) and sample F1 and G1 having the least concentration (0.367 ppm) in water samples.

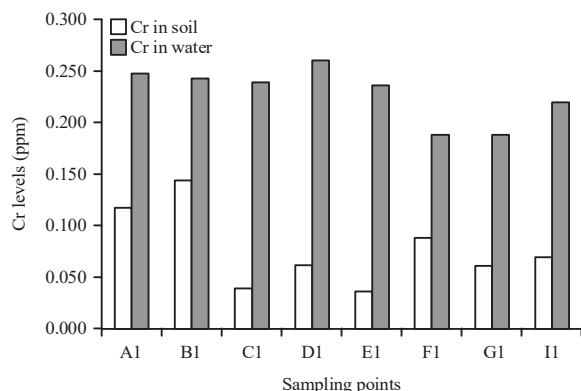


Fig. 7: Levels of Cr (ppm) from different sampling points in Nguroje

A1: Freshly dug pit at mining site, B1: Abandoned pit at mining site, C1: Abandoned pit at gate 3, mining site, D1: Stream water from mining site, E1: Running water 100 m from Hamdalla hotel, F1: Well water inside Hamdalla hotel, G1: Borehole from Gopel opposite UBA bank, I1: Well water from No 20 Galladima-Musa way

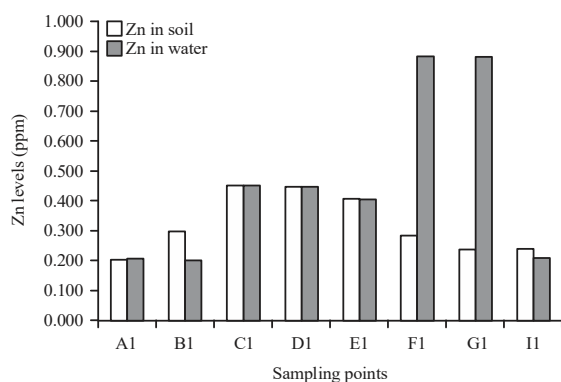


Fig. 8: Levels of Zn (ppm) from different sampling points in Nguroje

A1: Freshly dug pit at mining site, B1: Abandoned pit at mining site, C1: Abandoned pit at gate 3, mining site, D1: Stream water from mining site, E1: Running water 100 m from Hamdalla hotel, F1: Well water inside Hamdalla hotel, G1: Borehole from Gopel opposite UBA bank, I1: Well water from No 20 Galladima-Musa way

Chromium concentrations in different soil and water samples:

Figure 7 shows the different concentrations of Chromium in different soil and water samples with sample B1 having the highest concentration (0.144 ppm) and sample E1 having the least concentration (0.037 ppm) in soil sample, while sample D1 had the highest concentration (0.262 ppm) and sample F1 and G1 having the least concentration (0.189 ppm) in water samples.

Zinc concentrations in different soil and water samples:

Figure 8 shows the different concentrations of Zinc in different soil samples with sample C1 having the highest concentration

(0.453 ppm) and sample A1 having the least concentration (0.206 ppm) in soil samples while sample F1 had the highest concentration (0.887 ppm) and sample B1 having the least concentration (0.204 ppm) in water samples.

DISCUSSION

Heavy metal quantification was carried out in the present study to ascertain the levels of metals exposure to animals, plants and humans caused by artisanal mining activities. Lead concentrations in soil and water samples from Nguroje (mining site and main town) had a mean value ranging from 0.022-0.274 ppm in soil and 0.072-0.663 ppm in water. Lead concentrations in the samples were above the WHO¹⁵ accepted limits of 0.01 ppm in water while only samples A1 (0.274 ppm) and C1 (0.132 ppm) exceeded the standard value of 0.10 ppm in soil. Bolawa and Adelusi¹⁶ suggested that Lead contamination of the ground water may be the result of entry from industrial effluents, old plumbing, household sewages, agricultural run-off and mining activities as well as human and animal excreta. In addition to the symptoms found in acute lead exposure, symptoms of chronic lead exposure could be allergies, arthritis, hyperactivity, mood swings, nausea, memory loss, numbness, lack of concentration, seizures and weight loss as well as hearing and learning disabilities.

The concentrations of Mercury in the water samples analyzed varied enormously with a minimum and maximum mean value between 0.002-0.02 ppm in soil samples and 0.001-0.706 ppm in water samples. Mercury toxicity depends on the chemical form of ingestion. Inorganic forms of mercury cause spontaneous abortion, congenital malformation and gastrointestinal disorders⁹. Poisoning by its organic forms, which include monomethyl and dimethylmercury presents with stomatitis, neurological disorders, total damage to the brain and CNS and are also associated with congenital malformation⁹.

Cadmium concentrations determined in the study were seen to have high means in all samples analyzed. These means ranged from 0.001-0.015 ppm in soil and 0.409-0.727 ppm in water, with B1 (abandoned pit at mining site) having the highest value in water samples. WHO¹⁵ permissible limit for the presence of Cadmium in water is 0.003 ppm while that of soil is 0.01 ppm. This implies that all the samples determined for Cadmium levels in water were above the accepted limit while only sample B1 was found to be below WHO¹⁵ permissible limits in soil. The presence of this metal in the water samples analyzed may be due to the anthropogenic or artisanal activities at top gear in the region. Among the sources of Cadmium in the environment, mining and smelting

of metal ores, fossil fuel combustion and also phosphate fertilizers are mostly common¹⁷. The exposure of Cadmium and especially chronic exposure can cause renal dysfunction, calcium metabolism disorders and also increased incidence of some forms of cancer¹⁸.

Arsenic concentrations in the water samples were determined and the means of the samples recorded showed that samples A1 and D1 have a minimum value of 0.001 ppm while sample G1 had the highest mean value of 0.689 ppm in water while samples B1 (0.015 ppm) and I1 (0.015 ppm) contains the highest concentrations of Arsenic and D1 (0.001 ppm) contain the least amount. Among of all samples analyzed, A1 and D1 showed negative compliance with WHO¹⁵ acceptable limit (0.01 ppm) for Arsenic levels in water while all samples determined for Arsenic in soil samples showed positive compliance, falling below the acceptable limit of 1.50 ppm. Studies shows that agents of denudation, leaching or mining activity may be responsible for the high concentration in water sample obtained from point G1. Arsenic is very toxic and carcinogenic. Sankhla *et al.*⁹ reported that humans may encounter Arsenic by natural means, industrial source or from unintended sources. Health effects associated with Arsenic toxicity include anti-immune disorder that occurs when the body's immune system mistakenly attacks part of the PNS resulting in nerve inflammation that causes muscle weakness, formation of complexes with cofactors inhibiting metabolism of Adenosine Triphosphate (ATP) during respiration as well as death.

The levels of Iron in the different water samples analyzed were extremely high. The minimum and maximum mean values in water were seen in samples F1 and D1 to be 0.367 and 0.726 ppm, respectively. Sample F1 (0.367 ppm) has the highest concentration of Fe in soil. In all water samples for Fe concentrations, sample F1 was found to be above 0.30 ppm permissible limit for Iron in both soil and water samples set by WHO¹⁵ and Standard Organization of Nigeria (SON)¹⁹. The presence of this metal may be due to the mining activity in the region. Samples A1, B1, C1 as well as D1 (obtained from mining site) recorded higher mean values for Fe in water than the other samples from the main town. The level of Iron could be the result of clay deposits in the area. The presence of iron is responsible for the brownish-red colour of the water when allowed to stay for some min, it can also stain laundry and induces incrustation, brownish and rusty colouration^{20,21}. Excess of Iron will also influence the presence of bacteria (Iron-reducing) in ground water. Iron is an essential element to the human body, hence higher iron concentration does not pose a serious threat to the human health although high concentration is associated with Tetanus²¹.

Result shows a significant difference ($p > 0.05$) between the concentrations of Chromium and Iron in sample D1 (stream water from mining site) and sample F1 in water. Chromium levels in soil and water in this study did not exceed 0.05 ppm limits by WHO¹⁵ and SON¹⁹. The prevalence of Chromium in drinking water above 5 mg L⁻¹ results in bleeding of the gastrointestinal tract, cancer of the respiratory tract, ulcers of the skin and mucus membrane²². The sources of Chromium include water erosion of rocks, power plants, liquid fuels, brown and hard coal and industrial and municipal wastes.

Zinc concentrations determined in the different water samples showed mean values distributed across the various samples analyzed to have a minimum and maximum values of 0.204 and 0.887 ppm, respectively. All samples analyzed for Zinc concentrations in soil were below the permissible limit in soil. The high concentrations of Zinc in water samples F1 and G1 indicates translocation either by leeching or erosion of the element²³. Soil and water levels of industrial activities, such as mining, coal and waste combustion and steel processing²⁴. Zinc toxicity is rare but at concentrations of up to 40 mg L⁻¹, it may induce toxicity characterized by symptoms of irritability, muscular stiffness and pain²⁵. Zn can interrupt activity in soils as it negatively influences the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter²⁶.

Comparing the levels of the heavy metals analyzed in soil samples and water samples, no significant difference ($p < 0.05$) in concentrations of lead between soil and water in sample B1 while soil samples A1, C1 and I1 had significant difference ($p < 0.05$) in lead levels than water samples. The decreased concentrations determined in the various soil samples could be due to its transformation into various mobile forms before ending into the environmental²². Zinc determined in this study interestingly revealed that samples A1, C1, D1 and E1 have equal mean values in both water and soil samples while samples B1 and I1 have higher values for Zinc in soil than water and samples F1 and G1 having much more higher values of Zinc in water compared to those analyzed in soil samples. This levels of these metallic elements at much higher levels in water samples compared to soil can be attributed to mining and anthropogenic activities as well as transportation by erosion and other agents of denudation or leached into aquifers and eventually into streams, rivers and other water sources downstream thereby leading to contamination.

CONCLUSION

The study has demonstrated high levels of heavy metals in water samples and relatively elevated levels in soil samples obtained from Mambilla artisanal mining site and its environ. This signifies potential toxicity in this environment. From the studies carried out, heavy metal concentrations in the study area were much higher than the standard permissible limits especially in water samples. The levels of these metallic elements at much higher levels in water samples compared to soil can be attributed to the anthropogenic activities as well as transportation by erosion and other agents of denudation or leached into aquifers and eventually into streams, rivers and other water sources downstream thereby contaminating the same. The contaminated water is consumed on regular basis by humans or is taken up by plants and animals which directly or indirectly expose them to the toxic effects of the heavy metals. Efforts should therefore be made to reduce contamination of the community. Moreover, it is occupied by the local community who are prone to be affected by the presence of these heavy metals.

SIGNIFICANCE STATEMENT

This study has further buttressed various literature reports that mining activities are a major route via which toxic heavy metals are released into the food chain leading to various deleterious health effects. This study has also brought to light the fact that continues artisanal mining activities over the years has led to the release of toxic heavy metals at the mining site and its environment, hence it's a wake-up call to the Nigeria environmental protection agency to swing into action.

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