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CONCENTRATIONS OF LEAD, CADMIUM AND COPPER IN SOIL SAMPLES AT A SHOOTING RANGE IN NASINTA, KATSINA, NIGERIA

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ABSTRACT

Over the last century, war and other military activities have resulted into the release of large amounts of toxic compounds into the biosphere leading to environmental pollution. Soil samples were collected from a shooting range in Katsina, Nigeria and analysed using Atomic Absorption Spectrometry (AAS). The mean concentration of soil samples range for Pb, Cd and Cu were found to be BDL to 54.30±13.2, BDL to 0.9±0.14, BDL to 55.86±1.53, respectively. It was discovered that the mean concentrations at the target point (berm) of the shooting range was more polluted than the other sampling points within the range. The mean concentrations of the heavy metals at the sampling points analyzed were however within World Health Organisation (WHO)'s tolerable limit. Factors responsible for the tolerable concentrations of the heavy metal within the range, apart from some few exceptions, can be directly attributed to the gap of usage (once in a year) of the range. Additionally, heavy rainfall witnessed around the period the samples were collected could also reduce the heavy metal concentration in the shooting range soil due to leachate migration.

Key words: Berm, concentration, heavy metals, leachate, soil, shooting range

INTRODUCTION

Soil quality is a measure of the condition of soil relative to the requirements of one or more biotic species and or to any human need or purpose [1]. Ultra-acidic soils (pH < 3.5) and very strongly alkaline soils (pH > 9) are rare [2].

Military range management has become extremely important in recent years, in order to comply with the standards imposed by national and international environmental regulations. The presence of contaminants as energetic materials (EM) and heavy metals (Pb, Cu, Cd), with a heterogeneous distribution on the range and concentrated in the impact and firing line areas was studied [3]. A large number of military ranges have been targeted for investigation and/or clean-up in recent years under various environmental regulations [4].

A number of studies [5- 7] has evaluated the environmental impact of contaminants from the firing of bombs, rockets, projectiles, and pyrotechnics, on the quality of soil, ground water and surface water. Contaminants from a range may lead to important health hazards to wildlife and people who are exposed to the affected environment [3, 7]. Environmental agencies frequently conclude that the contaminated site is, in fact, the entire active area of the base [8, 9]. In the case of munitions firing, it has been shown [10] that over 99.99% of the Energetic materials are turned into gases.

Several studies have been published which examined Pb concentrations and mineralization in shooting range sands but fewer papers exist which examine other metals [11-14]. The transport of Pb and other metals from shooting range soils has been experimentally examined [15, 16].

Factors which have been observed as influencing heavy metals chemistry in firing range sand include pH [11, 12, 14 & 17], mineralogy [12], natural organic matter and water content [14]. Shooting ranges are the main source of environmental heavy metals pollution after battery industry [18].

Soil is a complex mixture of minerals, nutrients, organic matter and living organisms upon which all other terrestrial trophic systems are dependent [19]. Pb is mainly found in the core of bullets and shots while Cu, Zn, Sb and Cd are constituents of bullet ore heads and cartridges [20]. The aim of this research is to evaluate the concentrations of Lead, Cadmium and Copper in soil samples at a shooting range in Katsina, Nigeria.

MATERIALS AND METHODS

Reagents and materials used in this research work were obtained from the Department of Chemistry, Ahmadu Bello University (ABU), Zaria, Nigeria; Cardinal Scientific and Chemical Company Kwangila, and Multi User Research Laboratory Chemistry Department, ABU, Zaria. They were collected in pure and standard states. Deionized water was used to prepare all the standard solutions

Soil sampling

Soil samples were collected quarterly (four times) within a period of a year from soils in the shooting range of a military Barrack in Katsina. The samples were collected at several distances of 10 m, 20 m and 50 m from the shooting point. At each distance, three samples were collected. The soil samples were kept in well labeled polythene bags.

Sample Pre-treatment

The soil samples were allowed to dry at room temperature for a period of eight days to attain a stable weight and large object such as glass, stones and polythenes were hand-picked from them. The air dried samples were pounded in a ceramic mortar with a pestle made of porcelain. The samples were passed through a 2 mm sieve to maintain the integrity of the samples. The 2 mm air-dried samples were kept in polythene bags and stored under dry condition until the time of analysis.

Digestion of soil samples

The digestion of the soil sample was carried out as reported by Jeng and Bergseth [21]. Two grams of each of the soil samples were weighed and transferred into 100 cm^3 glass beakers. To the samples in the dry beakers, 15 cm^3 concentrated HCl and 5 cm^3 concentrated HNO_3 were added. The samples were swirled gently and left to stand overnight. The beakers were placed on a hot plate heated at 100 ºC under reflux condition for two hours. Refluxing was stopped but boiling continued until the solution almost dried, with the avoidance of caking. The samples were cooled and the residues dissolved in 5 cm^3 concentrated HNO_3. The digested samples were transferred into 50 cm^3 volumetric flask and deionized water added to 50 cm^3 mark. The solution was filtered with whatman No. 2 filter paper and transferred to a clean 100 cm^3 propylene bottle. Copper, Lead and Cadmium metals in the digests were determined using atomic absorption spectrometry (AAS) (model AA 6800 pro, Shimadzu, Japan) at National Institute of Chemical Technology (NARICT), Zaria, with appropriate standard prepared in a similar matrix [21].

SAMPLE ANALYSIS

The digested samples were analyzed using atomic absorption spectrometry at the National Institute of Chemical Technology (NARICT) Basawa, Zaria.

RESULTS AND DISCUSSION

Table 1: Mean concentration (mg/kg) of soil sample at the vicinity of a shooting range in Katsina (October 2018).

Sample	Pb(mg/kg)	Cd(mg/kg)	Cu(mg/kg)
1	3.04±1.03	0.13±0.02	0.70±0.001
2	13.85±2.10	0.11±0.02	18.62±1.23
3	11.56±0.02	BDL	0.21±0.06
4	9.24±0.03	0.29±0.02	37.97±6.54
5	6.62±o.54	0.06±0.01	0.91±0.06
6	18.12±0.01	0.13±0.01	0.51±0.004
7	20.18±4.02	0.35±0.03	0.20±0.012
8	12.07±0.01	0.02±0.00	0.06±0.11
9	15.36±2.04	0.14±0.01	0.67±0.32
CTR	20.18±0.01	0.07±0.01	0.30±0.01
WHO (mg/kg)	85	0.8	36

Key: BDL= below detection limit, CTR= control

Table 2: Mean concentration (mg/kg) of soil sample at the vicinity of a shooting range in Katsina (February 2019)

Sample	Pb(mg/kg)	Cd(mg/kg)	Cu(mg/kg)
1	20.44±1.21	0.08±0.02	55.86±1.53
2	9.05±0.03	0.90±0.01	55.53±0.34
3	BDL	0.09±0.001	55.43±5.34
4	BDL	0.12±0.04	55.54±0.27
5	BDL	0.11±0.03	54.83±0.38
6	2.70±0.02	BDL	54.14±0.42

7	0.84±0.03	BDL	54.64±4.23
8	0.73±0.05	BDL	53.85±0.05
CTR	4.36±0.012	BDL	53.81±3.12
WHO(mg/kg)	85	0.8	36

Key: BDL= below detection limit, CTR= control

Table 3: Mean concentration (mg/kg) of soil sample at the vicinity of a shooting range in Katsina (June 2019)

Sample	Pb(mg/kg)	Cd(mg/kg)	Cu(mg/kg)
1	27.00±7.63	0.24±0.03	49.83±3.12
2	15.05±1.02	0.90±0.04	49.33±4.34
3	5.60±0.64	0.69±0.05	48.57±2.32
4	54.30±13.2	0.12±0.03	45.40±5.03
5	BDL	0.11±0.04	46.83±3.23
6	2.70±045	BDL	42.14±1.05
7	0.97±0.02	BDL	41.64±7.04
8	4.73±1.54	BDL	43.85±4.41
9	4.36±0.33	BDL	43.81±5.43
CTR	17.62±1.85	0.10±0.00	0.00
WHO(mg/kg)	85	0.8	36

Key: BDL= below detection limit, CTR= control

Table 4: Mean concentration (mg/kg) of soil sample at the vicinity of a shooting range in Katsina (September 2019)

Sample	Pb(mg/kg)	Cd(mg/kg)	Cu(mg/kg)
1	2.15±1.43	0.10±1.32	0.50±0.01
2	12.84±5.30	0.80±0.74	13.62±1.20
3	10.53±2.33	BDL	0.17±0.03
4	7.26±0.03	0.24±0.01	27.97±3.11
5	5.34±1.05	BDL	0.81±0.01
6	14.12±0.43	0.90±0.14	0.43±0.04
7	18.17±2.31	0.27±0.01	BDL
8	9.07±1.21	BDL	0.01±0.00
9	12.46±0.04	0.90±0.02	0.57±0.04
CTR	20.18±2.02	0.01±0..00	0.30±0.02
WHO(mg/kg)	85	0.8±	36

Key: BDL= below detection limit, CTR= control

As presented in Tables 1 and 4, the mean concentrations of Pb, Cd and Cu in the analyzed soil samples during the rainy season (October, and September) generally revealed significantly higher concentration of Pb as compared to the rest of the analyzed metal ions, with few exceptions.

However, the lowest concentrations among the analyzed metal ions were found to be Cd. On comparing the levels of the analyzed metals determined with WHO [22] recommendations they were all found to be lower than the WHO tolerable limit with the exception of Cd in samples (2, 5 and 6) during the rainy season for the period of June and September, respectively as reflected in Tables 3 and 4.

Generally, the trend observed for the metal ion concentration during the rainy season was Pb>Cu>Cd. This order of decreasing mean concentration of heavy metals in the soil samples from the shooting range is in accord with the work of Rodríguez-Seijo [23] where the trend of Pb>Cu>Cd was found. On comparing the levels of the metal ions obtained in the analyzed soil samples in the rainy season with those of the dry season it was discovered that the concentrations of Pb and Cd were lower during the dry season than the rainy season. This might be attributed to the shooting exercise that was carried out in the sampling points. Other activities carried out close to the shooting range which is majorly agricultural practices normally occur during the rainy season also affects the concentrations.

It should be noted that Tables 2 and 3 when the operation was carried out in June during the wet season, the concentration of the analyzed metals have significantly increased to a much higher concentrations especially Pb and Cd with few exceptions this relates to similar studies where firing of ammunition can translate immediately to the increase in the concentration of heavy metals [7]. This clearly indicates that the exercise carried out at the sampling points significantly lead to environmental pollution, and consequently to the pollution of the underground water used by the villagers around the area.

Consumption of contaminated water generally lead to serious health problems associated with heavy metal poisoning such as liver and kidney dysfunction. Overall, the heavy metal concentration trend that was observed from the soil sample during the dry season was as follows: Cu>Pb>Cd.

On comparing the levels of the analyzed heavy metals determined during the dry season, it was found that the concentrations of Cu was above tolerable limit (36 mg/kg) without an exception as reflected in Table 2, while those for Pb, and Cd were found to be lower than the [22] tolerable limit as shown in the same Table. 2

CONCLUSION

The mean concentration of heavy metals in the analyzed soil samples at the berm showed higher level of heavy metal compared to the other sampling points. This emphatically indicates that the berm which is the target point at the shooting range is more polluted than the other sampling points within the range. Although, the mean concentration of all the sampling points analyzed when compared to the USEFA tolerable limit seems to be within tolerable limit. A closer analysis of the factors responsible for the tolerable quantity of the heavy metal presence within the range apart from some few exceptions can be directly attributed to the annual use of the range. Additionally, the heavy rainfall witnessed around the period these samples were collected can also directly affect the heavy metal concentrations in the shooting range soil.

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