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ASSESSMENT OF RESIDUAL CHEMICAL WARFARE AGENTS (CWAs) AND HEAVY METALS IN AGRICULTURAL SOIL, GRAZING LAND AND GROUND WATER IN SOME COMMUNITIES AFFECTED BY INSURGENCY IN YOBE STATE, NIGERIA

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Abstract: This research work assessed the levels of contamination of water and agricultural soil with some residual toxic chemicals that might have been used during the act of insurgency/counter insurgency in Yobe state. The research employed the use of Gas chromatography, Atomic absorption spectrophotometer and other analytical equipment to investigate the level of contamination with a view to ensure safety of the returnees. The analysis results revealed an average concentration of lead as 20.202 ±2.85mg/kg in soil and 0.818+0.08mg/L in water; the highest concentration of 75.58±4.85 mg/kg in soil was found around Goniri town followed by Wagir with 55.036±3.42 mg/kg and lowest concentration of 1.844±0.75 mg/kg at Kukareta village. Arsenic concentration of 5.82±1.06 mg/kg in soil was found around Goniri town and lowest concentration of 0.652±0.43 mg/kg at Kukareta village both of which were within the set limit in agricultural soil. Cadmium concentrations were also higher than WHO limit in some areas with 7.257 ±0.98 mg/kg, 7.214±1.11 mg/kg and 5.772±1.45 mg/kg in soils around Goniri, kukuwa and Gotala towns respectively. Concentrations of Nickel were 5.843±0.77 mg/kg and 1.153±0.63 mg/L were respectively in soil and water around Gotala village and totally absent in some communities such as Pompomari and Ajari. Copper had a concentration of 36.57±3.25 mg/kg followed by 22.257±2.09 mg/kg were respectively in soil around Gotala and Kukuwa villages; and then 2.28±0.05 and 1.399±0.74 respectively in water from same location. The values obtained in this research work indicated a high concentration of copper in both water and soil above permissible limit of 1.0 mg/L and 36 mg/kg respectively in some affected communities. GCMS analysis indicated the presence of chlooacetophenone in soil sample obtained from Buni gari, a village. These research findings revealed the presence residual toxic chemicals and heavy metals that might have been used as weapons during the act of insurgency by Boko haram insurgents and counter insurgency activities by the Nigerian Forces. The residual heavy metalswere found to be present in the soil and water in some of the affected communities; and at significant quantity that may be hazardous to health.

I. INTRODUCTION

Chemical warfare agents (CWA) are the toxic chemicals or precursors that cause sensory irritation, injury, incapacitation and death (C. W. Agent, 2017), most of which are classified as weapons of mass destruction by the United Nations, and their production and stockpiling was outlawed by the Chemical Weapons Convention of 1993. However, the application of these chemical elements in military equipment of some countries to cause or counter the act of terrorism cannot be overemphasized (Anderson, 2012).

Acetone-based and chlorine gas were used as CWAs French military World War I, and German military respectively (Szinicz, 2005) before banning in 1997 (Wiener & Hoffman, 2004). CWAs and heavy metals are still an element of equipment of some countries' military forces (Convention on the Prohibition of the Development, Production. Stockpiling and Use of Chemical Weapons and their Destruction;, 1997).

These chemicals are mainly organic compounds and can be detected by Gas chromatography (Witkiewicz *et al.*,1990) (Soderstrom, *et al.*, 1996), (Mazurek *et al.*, 2001) and (Hooijschuur *et al.*, 2002) (Hancock & Peters, 1991), (Kokko, 1993) and (Huber *et al.*, 1993)

Boko Haram insurgency against Nigerian government started in 2009 aiming at establishing “Islamic state”. The insurgents became increasingly aggressive, and started to seize large areas in northeastern Nigeria recording about 10,849 deaths in 2014 (John, 2014) and (Nossiter, 2018).

Yobe state is located on 12.2939^{0}N and 11.4390^{0}E with a population of about 2, 532, 395, an area of 45,502 sq KM and borders Bauchi, Borno, Gombe, and Jigawa State in Nigeria as well as Diffa and Zinder Regions of Niger. Yobe State has seventeen local government areas (McKenna, 2012). Eighty percent (80%) of the inhabitants are into primary production agriculture (UKaid., 2018) and dweled in the rural areas with limited access to portable water.

While efforts were being put in place to improve Water supply, Sanitation and Hygiene (WASH) through various funded projects, the population suddenly displaced following the Boko Haram insurgency in 2013 (UNDP, 2016) and (World Bank, 2017). The residents remain in exile for almost two years (2013-2015) leaving their homes and farmlands at the disposal of Boko Haram insurgents. The insurgents indiscriminately use every available space to store their weapons and plant a lot of improvised explosive devices on roads and other footpath to prevent military from accessing their locations. A relative peace was restored in 2016 and the displaced persons returned to their communities. Agricultural activities especially crop production gradually picked up which led to a good bumper harvest in 2018 (Babagana *et al.*, 2018).

The deposition of such toxic warfare chemical agents may be washed away by rain water into agricultural lands, grazing lands, rivers and underground water sources thereby contaminating the source and adversely affecting agriculture and water resources in the affected areas.

The three (3) most affected Local Governments include Damaturu, Gujba and Gulani. After being displaced by boko haram in 2013, the community is currently resettling and reoccupying the lands hence the need for proper assessment of these toxic chemicals and heavy metals is necessary to prevent health hazard in those communities.

Figure 1: Map of Nigeria, showing Yobe State

Source: (YSSB, 2017) and (NBS, 2019).

3.0 **METHODOLOGY**

The study area covers Gujba, Gulani and Damaturu Local Governments Areas with population of about 184, 200, 103, 510 and 124, 500 respectively. Gulani is located on 11^{0}00’N and 11^{0}43’E, covering a land boarder of 2,090Km^2. Gujba is on 11^{0}29’52”N and 11^{0}55’51”E and area of 3, 239 Km^2. Damaturu is located on 11^{0}44’49.09”N and 11^{0}57’38.99”E.

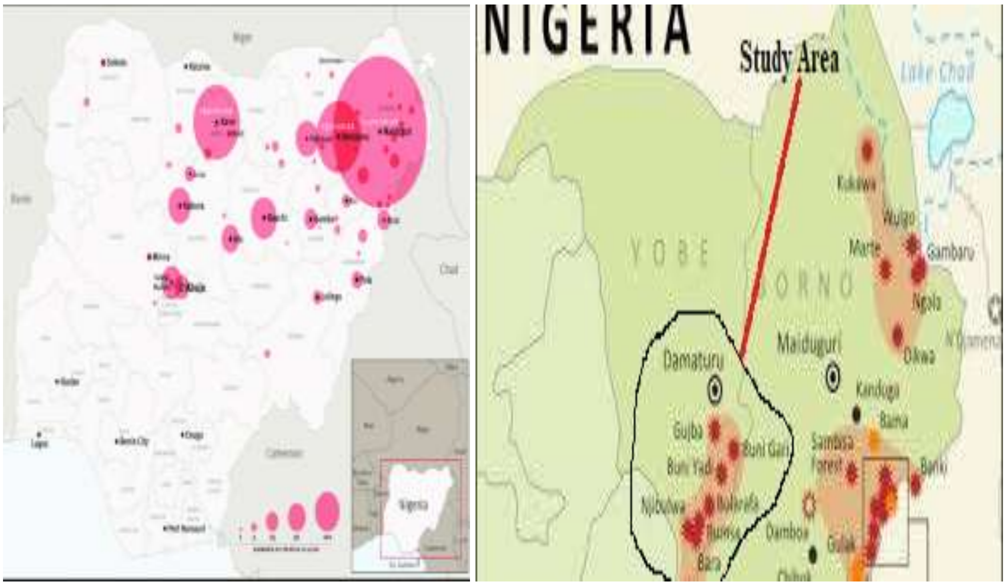

Figure 2: Map of Yobe State (Nigeria) showing areas affected by Boko Haram insurgency

The target communities for this research include Kukuwa, Shishiwaji, Bularafa, Bumsa, Bursali and Gulani town in Gulani LGA; Gujba town, Goniri, Gotala, Wagir, Buni gari and Kukuwa gari in Gujba LGA; Pompomari, Ajari and Kukareta in Damaturu LGA.

3.0 Materials/Equipment;

3.1 Sample collection

Water Samples Collection and Pre-Treatment

Water samples were collected in plastic (inert) containers, stored in an ice cold box and transported immediately to the laboratory. The samples were extracted via liquid–liquid extraction (LLE) and purified by solid-phase extraction (SPE) methods (Rosenfeld *et al.*, 1984) and (Stanisław & Zygfryd, 2009) (Thomas & Charles, 2020).

3.2 Soil sample collection and Sample Pre-treatment

Soil samples were collected from different locations in plastic zip lip bags, air dried and then sieved through a 1.0 mm sieve prior to use.

3.3 Soil Extraction Procedure

Water (Cold) pH 7/4 ^{0}C were used for the extraction process using ultrasonic vibration for about 15-20 minutes. The extracts were centrifuged at 2500 rpm for 5 minutes and the supernatant were recovered for purification. The extraction processes were repeated twice and the total extracts collected in a single container and purified via liquid-liquid extraction as in water sample. The pure extracts were stored in at 20^{0}C prior to analysis.

3.4 Sample Analysis

Agilent gas chromatography (GC 7890B) coupled with Mass Spectrometer detector (MSD 5977A) was used for the analysis of the organic components while Atomic absorption spectrophotometer were used for the heavy metals.

3.5 Chromatographic Condition

A chromatographic Column 30m x 0.25 mm id x 0.25 μm film thickness and 15.5 psi helium carrier gas were set constant pressure mode. Oven program 40 °C (0.4 min); 10 °C/min to 280 °C; hold 4 min Splitless mode, injcetion temperature, 250 °C; 1 μL liquid injection

3.6 Analysis of Heavy Metals

Sample Pre-Treatment/Digestion (soil samples)

The samples were allowed to dry using hot oven (Model 30GC lab oven) and then ground into fine powder by using a porcelain mortar and pestle. 100mg of each sample was weighed in to thoroughly clean plastic container (microwave tube) and 6ml of 65% HNO_3 and 2ml of H_2O_2 (and 2mL of HF for soil samples only) were added and allowed and to stand for a while. The plastic container (microwave tube) was then covered and placed in to microwave digester (Master 40 serial No: 40G106M) and 150^{0}C for 40mins.

3.8 Determination of metal contents of each sample

Concentrations of the metals present in the samples were determined by reading their absorbance using AAS (Buck scientific model 210GP) and comparing it on the respective standard calibration curve. Three replicate determinations were carried out on each sample.

4.1 Results and Discussion

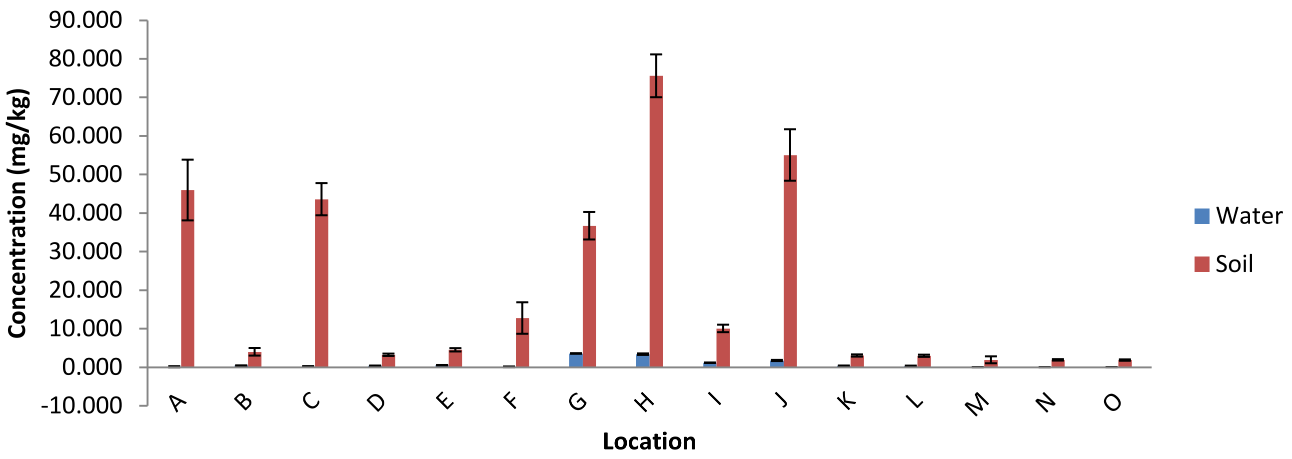

Figure 3: Concentration of Lead in soil and water from areas affected by insurgency in Yobe, Nigeria

Figure 3 revealed the concentration of lead from areas affected by insurgent activities in Yobe State, Nigeria. The average concentration is 20.202 mg/kg in soil and 0.818 mg/L in water. Highest Lead concentration of 75.58 mg/kg in soil was found around Goniri town followed by Wagir with 55.036 mg/kg and lowest concentration of 1.844 mg/kg at Kukareta village. Lead is most often used as solder, alloys, lead-acid batteries, lubricating agent, anti-knock agents and in ammunitions. These applications often lead to concentrations of the lead in air, food and drinking-water.

Though rarely present in tap water as a result of its dissolution from natural sources but may be introduced through plumbing systems containing lead in pipes, fittings and solder.(WHO, 2003). The results revealed some affected areas such as Goniri, Gotala and Kukuwa have their soil and water contaminated with lead above the WHO permissible limit of 0.1mg/kg (agricultural soil) mg/kg 0.01 mg/L (Goffery, et al., 2020)

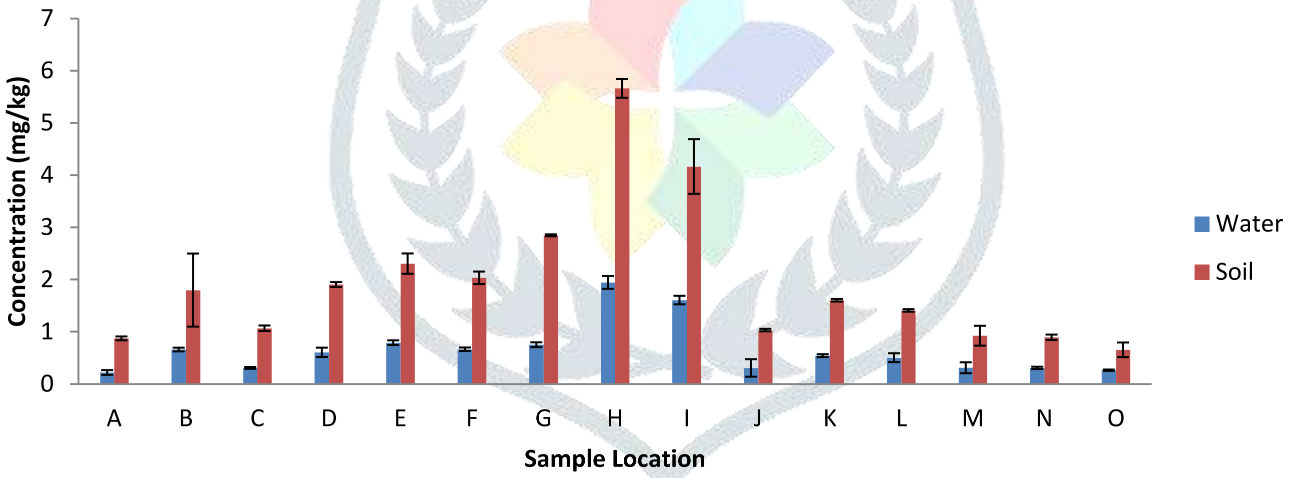

Figure 4: Concentration of Arsenic in soil and water from areas affected by insurgency in Yobe, Nigeria

Figure 4 shows the concentration of Arsenic in soil and water from areas affected by insurgent activities in Yobe State, Nigeria. Highest Arsenic concentration of 5.82 mg/kg in soil was found around Goniri town and lowest concentration of 0.652 mg/kg at Kukareta village. The concentrations of the toxic elements in water samples also follow the same trend. Arsenic concentration was also higher than WHO permissible limit of 0.01 mg/L in water (WHO, 2004), and falls within the set limit of 20 mg/kg in agricultural soil by European Union (EU) (Rahman *et al.*, 2013)

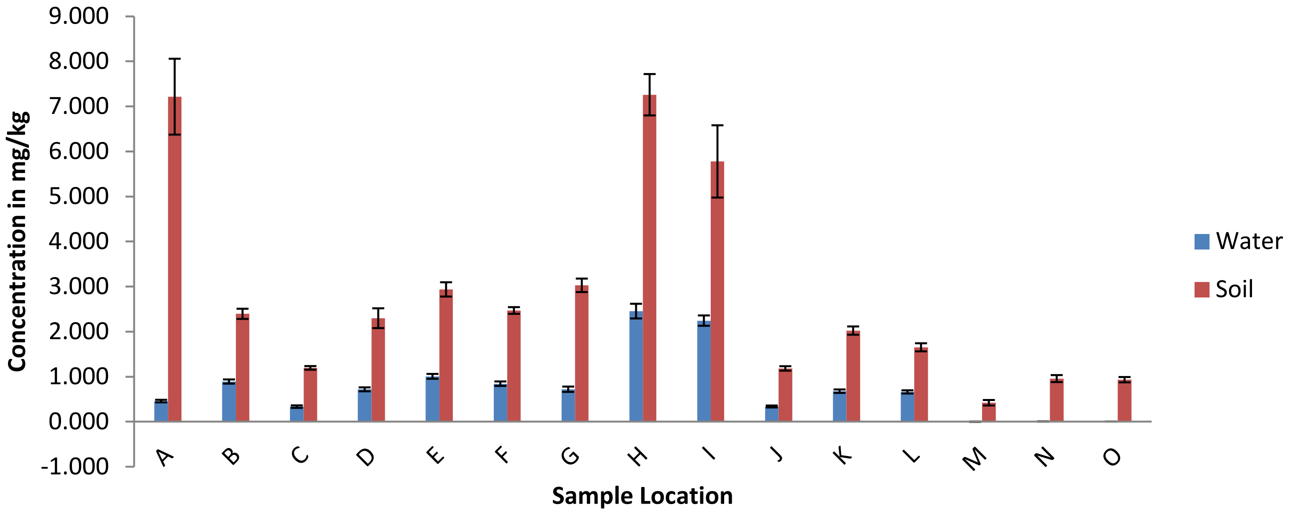

Figure 5: Concentration of Cadmium in Soil and Water from areas affected by insurgency in Yobe, Nigeria

Figure 5 revealed the concentration of Cadmium in soil and water from areas affected by insurgent activities in Yobe State, Nigeria. Highest concentrations of 7.257 mg/kg, 7.214 mg/kg and 5.772 mg/kg in soils were found around Goniri, kukuwa and Gotala towns respectively. The lowest concentration of 0.420 mg/kg was found at Pompomari area. The concentrations of cadmium in this research work, especially those from three areas listed were higher than the limits set by WHO.

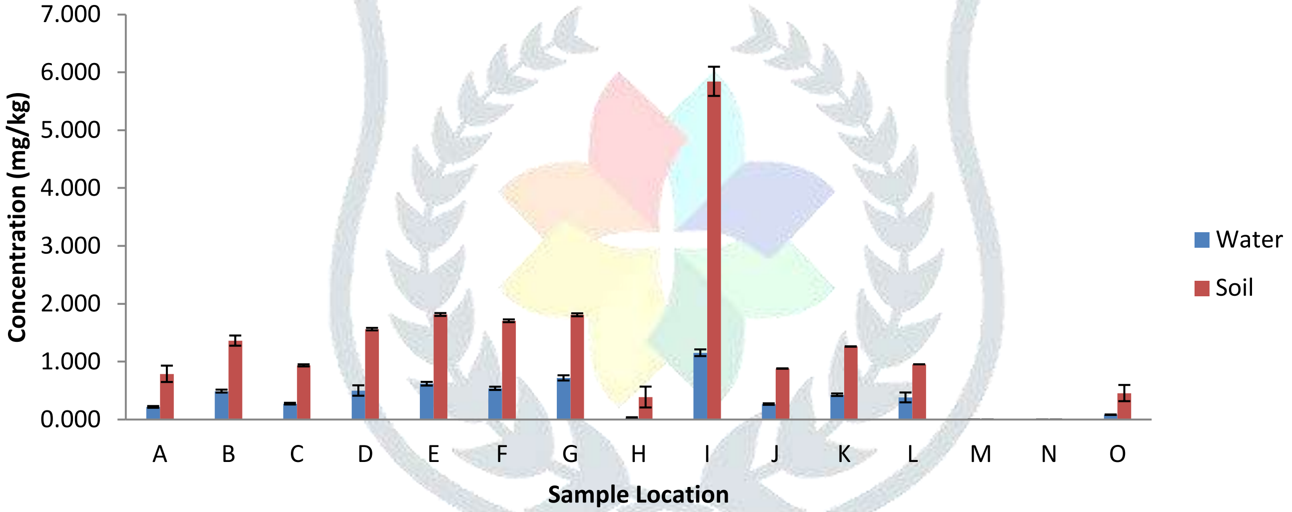

Figure 6: Concentration of Nickel in Soil and Water from areas affected by insurgency in Yobe, Nigeria

Figure 6 revealed the concentration of Nickel in soil and water from areas affected by insurgent activities in Yobe State, Nigeria. High Nickel concentration of 5.843 mg/kg and 1.153 mg/L were respectively found in soil and water around Gotala village. No nickel detected at Pompomari and Ajari areas. According to WHO 1996, the permissible limit of Nickel in soil is 35 mg/kg, while that of water is 0.02 mg/L. the results of the analysis revealed that most of the water samples were contaminated, however the soils samples were within the set limit.

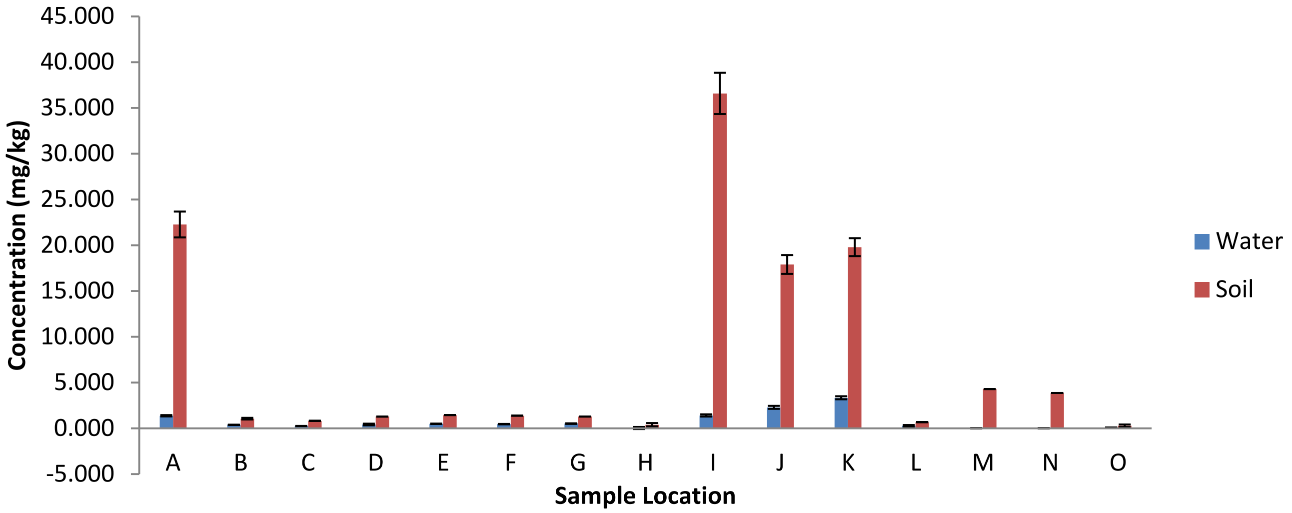

Figure 7: Concentration of Copper in Soil and Water from areas affected by insurgency in Yobe, Nigeria

Figure 7 revealed the concentration of Copper in soil and water from areas affected by insurgent activities in Yobe State, Nigeria. Highest concentrations of 36.57 mg/kg followed by 22.257 mg/kg were respectively found in soil Gotala and Kukuwa villages. The concentrations in water were also high the same locations, with values of 2.28 and 1.399 respectively. The values obtained in this research work indicated a high concentration of copper in both water and soil above permissible limit of 1.0 mg/L and 36 mg/kg respectively in some affected communities.

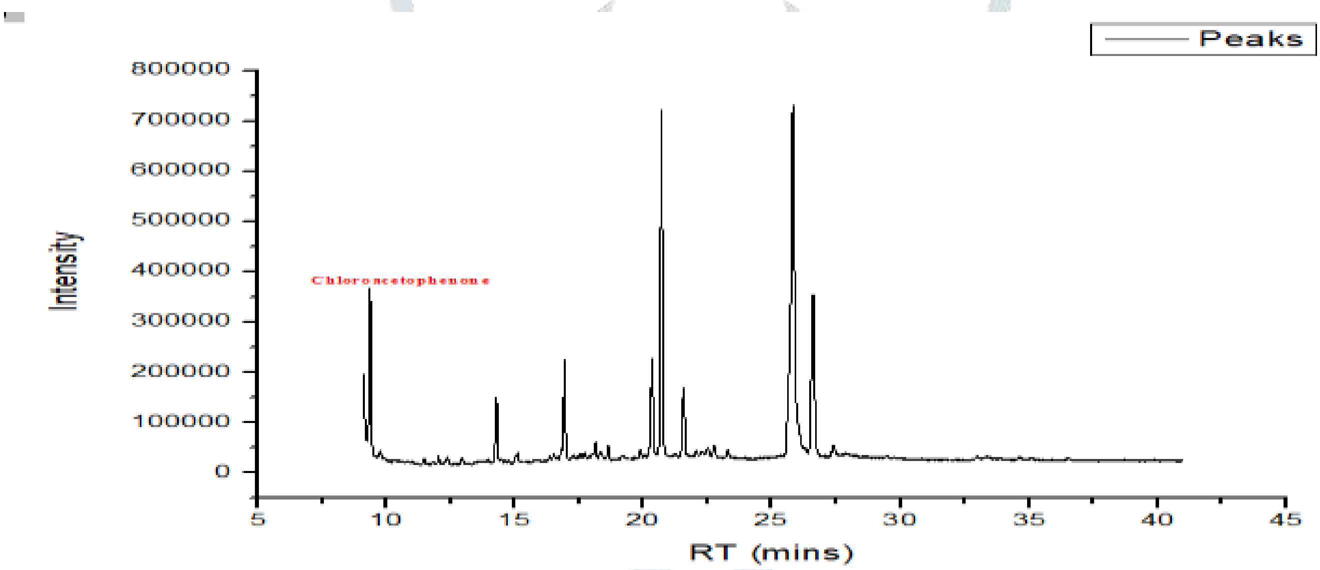

Figure 8: GCMS result showing the presence of chloroacetophenone in some affected areas

Figure 8 shows the GCMS chromatogram of chlooacetophenone (CN) detected in soil sample obtained from Buni gari, a village frequently attacked by Boko Haram insurgents

Soil in most cases becomes contaminated by Toxic elements through the industries (Hinojosa *et al.*,2004) resulting to adverse effects on crop yield, size and quality and microbial activity in the soil (Yao *et al.*, 2003). Toxic elements such as Cd, Hg, As, and Pb that do not have a known physiological function in plants are considered non essential for plants growth (Khan *et al.*, 2008) (Garrido *et al.*, 2002) (Rascio & Izzo, 2011).

Considering food-chain implications, cultivation of plants on contaminated soil constitute a potential health risk due to the fact that pant tissues can accumulate heavy metals (Jordao, Nascentes, Cecon, Fontes, & Pereira, 2006). Heavy metals toxicity in human body arises when they are not fully metabolized by the body, leading to accumulation in soft tissues(Sobha *et al.*, 2007)

Lead (Pb) is toxic to humans physiologically and neurologically. Acute Pb poisoning can results into dysfunctions of kidney, liver, reproduction system, and brain leading to death (Odum, 2007).

Arsenic coagulates protein and forms complexes with coenzymes and inhibits the production of adenosine triphosphate (ATP) during respiration. It is carcinogenic and high exposure can cause death. Cadmium is known to be toxic to kidneys, liver, placenta, lungs, bones and brain depending on the severity of exposure (Duruibe *et al.*, 2007). Excessive human intake of copper may leads to hepatic and renal damages, central nervous system irritation and depression (Argun *et al.*, 2007).

Chloroacetophenone (CN), is used in riot control or as tear agent by the military and other law enforcement agents. It can be dissolved in a solvent and has a very sharp irritating odor. When sprayed into air, it can contaminate water and food. As an aerosol, it can to contaminate agricultural soil and products. This tear agent can be absorbed into human body through inhalation and ingestion, leading to irritation of the gastrointestinal tract (GIT), respiratory tract, and skin or eyes.
(CDC, 2011)

Conclusion

These research findings revealed the presence residual toxic chemicals and heavy metals that might have been used as weapons during the act of insurgency by Boko haram insurgents and counter insurgency activities by the Nigerian Forces. The residual heavy metals and other toxic elements were found to be present in the soil and water in some of the affected communities; and at significant quantity that may be hazardous to health. Among the toxic elements studied; Lead, Arsenic, Nickel, Copper and Cadmium, the mean concentrations found in the both the soil and water samples were within the allowable limits set by WHO. However, individual communities such Goniri, Gotala and Kukuwa and Wagir were slightly above the set limit. This may be related to frequent attack and counter attack by both the insurgents and Nigerian Forces as both parties battle to have control of the areas. The uptake of these elements by plants from the soil may reduce the crop productivity in the affected communities by inhibiting the plants' physiological metabolism.

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