Original Research Article

DETERMINATION OF CHEMICAL EXPLOSIVE REMNANTS IN SOILS OF BOKO HARAM’S AFFECTED AREAS OF GOMBE STATE NIGERIA.

ABSTRACT

Aim: The research was conducted to ascertain the level of pollution of our physical environment as a result of years of Boko Haram’s activities in Gombe State, North-Eastern Nigeria.

Study design and place of study: Samples for this research were collected from Bajoga, Nafada and Gombe metropolis and environs all in Funakaye, Nafada, and Gombe Local Government Areas respectively. Samples were taken only from places with recorded Boko Haram’s explosion activities. A control sample for each study area was taken from an area that has no record of Boko Haram attacks. Gombe State is located in the North-Eastern part of Nigeria on latitude 10°15’00’’N and longitude 11°10’00’’E bordering Yobe, Borno, Adamawa, Taraba and Bauchi states.

Methodology: The concentrations of explosive remnants (4-Nitrotoluene, 4-Propyl Benzaldehyde, 1,3-Dinitrotoluene, 2,4-Dinitrotoluene, 3,5-Dinitrotoluene, Trinitrotoluene, RDX and HMX) in the soil samples of the attacked areas were investigated using Gas Chromatography-Mass Spectrometer, GC-MS.

Result: The result indicates 4-Nitrotoluene; 0.05-0.085µg/kg, 4-Propyl Benzaldehyde; 0.07-0.19µg/kg, 1,3-Dinitrotoluene; 0.005-0.060µg/kg, 2,4-DNT; 6.16-6.86µg/kg, 3,5-DNT; 0.40-0.90µg/kg, TNT; 0.29-0.66µg/kg and RDX and HMX were not detected. All the samples in the study area had 4-Nitrotolene and 4-Propyl Benzaldehyde concentrations above those in their respective controls. 1,3-DNT in Bajoga samples, 2,4-DNT in K Police station and K/mata, 3,5-DNT in Gombe metropolis, and TNT in NFD Police station were all found to be below the concentrations in their control.

Conclusion: There is possible 4-Nitrotolene and 4-Propyl Benzaldehyde contaminations in all the studied sites and absence of pollution by 1,3-DNT in Bajoga, 2,4-DNT in K Police station and K/mata, 3,5-DNT in Gombe metropolis, and TNT in NFD Police station.

Keywords: Explosives, Remnants, Soil, Boko Haram

1. INTRODUCTION

Boko Haram (‘Western education is a sin’) was founded around 2002 in Maiduguri, the capital of Borno state and largest city in Northeast Nigeria [1]. During Boko Haram’s insurgency, bombs, explosions and mines are mounted in various locations and many casualties were recorded. The devastation to the environment and civilian population caused by cluster bombs will be a lingering and insidious nightmare against the environment and people. The bombs detonated have chemical by-products. Chemicals supporting war activities, such as Herbicides or chemical weapons, have effects that are seen for generations [2]. Warfare today uses explosives and machinery to subdue enemies and territories. The intensity of environmental damage resulting from wars has been remarkably parallel to the technological ‘advancement’ in warfare. Use of more advanced arms and ammunition means more damage to environment [2].

Energetic compounds, defined as the active chemical components of explosives and propellants, are necessary both for peaceful and military purposes. Commonly used military energetic compounds include the explosives 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) [3]. In missile, rocket, and gun propellants,
nitroglycerin (NG), nitroguanidine (NQ), nitrocellulose (NC), 2,4-dinitro toluene (DNT), and different perchlorate formulations are used [4]. Many energetic compounds and their byproducts have contaminated the environment as a result of military actions, incorrect management, and disposal procedures, to the point that the health of people, animals, wildlife, and ecosystems is in danger. In people, TNT is associated with abnormal liver function and anemia, and both TNT and RDX have been classified as potential human carcinogens [5]. TNT and its metabolites have been used in investigations on the mutagenicity of Salmonella strains and mammalian cell lines [6]. It was discovered that TNT and several of its metabolites were both mutagenic. Convulsions are a common feature of RDX’s effects on mammals. After being exposed to RDX, factory workers in Europe and the US experienced convulsions, unconsciousness, vertigo, and vomiting [7]. There are a variety of ways energetic molecules can reach the soil environment, including the following: (i) Ammunition manufacturing facilities, such as wastewater lagoons and filtration pits; (ii) Packing or storage facilities; (iii) Facilities for waste disposal and destruction, such as open landfills, burn pits, and incinerators; (iv) Weapons firing ranges; and (v) Weapon impact zones [8]. Soil contamination by energetics at manufacturing sites, conflict areas, and military ranges is an international concern. Numerous military installations are reported as being contaminated by energetic chemicals in the US [9]. Bombing and other training exercises have an impact on roughly 50 million. There could be even more polluted locations throughout Europe and Asia [10]. Military agencies in the US, Canada, and many European and Asian countries have been forced to identify sites of energetic contamination and assess the effects of military activities on the quality of soil, groundwater, and surface water over the past 20 years due to an increase in environmental awareness.

2. MATERIAL AND METHOD

2.1 Study Area

This research was conducted on samples collected from Bajoga, Nafada and Gombe and environs all in Funakaye, Nafada, and Gombe Local Government Areas respectively. Samples were taken only from places with recorded Boko Haram’s explosion activities. A control sample for each study area was taken from an area that has no record of Boko Haram attacks.

2.2 Sampling

Soil sampling was carried out according to the method described by Aluko et al. [11]. From each sampling location, five replicate samples were collected. These were thoroughly mixed to give a homogenous sample, out of which 500g was packaged in tagged polythene bags. Control samples were obtained 1km off the sampling sites. All collected samples were properly tagged and identified by their sampling locations. Furthermore, the coordinates were obtained, using a Global Positioning System (GPS) receiver. The collected soil samples were taken to the Defence Industries Corporation of Nigeria (DICON) laboratory for analysis.

2.3 Sample Preparation

The soil samples were dried and sieved through a metal sieve (4-mm opening size) before fortification. The blank sample was analyzed to determine the background level of the analytes. It showed no presence of the target chemicals. The soil samples (20 g) were fortified with a stock mixture of standard chemicals in 100-150 mL of methanol-acetonitrile (1:1, v/v) and were thoroughly mixed. After the solvent was evaporated with a rotary evaporator, the soil was allowed to sit in a fume hood for 24h at room temperature. The fortified soil was then stored at 2-4°C for later use. A portion of this spiked soil was set aside and aged at room temperature (25°C ± 2°C) prior to extraction. The spiking level was 2.5 µg/g for each analyte. Also, the same level of the explosives was spiked directly on top of the Ottawa sand in the extraction cells as a control for the extraction processes. All the fortification samples were in triplicates.
2.4 Extraction procedure

A Dionex ASE 200 extractor was used for all extractions. The bottom of each 22-mL extraction cell was fitted with two cellulose filters covered with 2–3 cm² sand. Each sample was mixed with 1–5 g of sand as a dispersion agent and was loaded into the cell. The sand was used to fill up the cell. The cell was loaded onto the ASE 200 extractor. An extraction cycle began with the filling of the cell with a mixture of methanol-acetonitrile (1:1, v/v), then a 5-min preheating time, followed by a 5-min static extraction. The extract was flushed out of the system with a 60-s nitrogen purge into a glass collection vial. The sample extract (~30 mL) was concentrated with a rotary evaporator and brought to 4–5 mL for GC–MS.

2.5 GC–MS analysis

All the extracts were analyzed with a Varian 3800/4000 gas chromatograph mass spectrometer equipped with an Agilent equipped with a splitter split/split less. A DB-1 capillary column (J&W Scientific, Folsom, CA) was used, with dimensions of 10-m length, 0.18-mm i.d., and 0.4-μm film thickness. It is necessary to use a shorter column (10 m, rather than 30 m) with a thicker film (0.4 μm, compared with 0.25 μm) to minimize degradation of the very active analytes during separation processes. The injection port liner was the Stichrom type (Roštek, Belfelont, PA) and held at 210°C. The GC–MS transfer line and ion-trap temperatures were 200°C and 210°C, respectively. The GC oven temperature started at 80°C for 1 min, was ramped at 20°C/min to 140°C, then at 6°C/min to 200°C. The final temperature (200°C) was held for 16 min. The helium flow was 1.4 mL/min. The MS was operated in electron ionization (E) and full scan modes to monitor a 100–650-amu range. The total analysis time from extraction to complete GC–MS run was as approximately 40 min/sample.

Organic compounds in the sample were identified in Wiley’s NIST 08 Mass Spectral Library if the obtained comparison scores were higher than 95%. Otherwise, fragmentation peaks of the compounds were evaluated, and the compounds were identified using the memory background for the identification of the compounds that appeared in GC/MS chromatograms. Contents of individual compound in the extract were given in percent of the total compound in the sample. This was the standard way to quantify most organic compounds in the honey samples. The chromatograms obtained from the total ion count (TIC) were integrated without any correction for co-eluting peaks and the results were expressed as total abundance. All the peaks were identified based on mass spectral matching (≥ 90%) from both the NIST and Wiley libraries. Only compounds with 90% or greater spectral matching accuracy are reported. No response factors were calculated.

3. RESULT AND DISCUSSION

The concentration of explosive remnants in the soil samples from Boko Haram’s explosion sites in Gombe metropolis were estimated using GCMS and the results are presented in Table 1 while Table 2 shows the concentration of the remnants in the soil samples collected from Bajoga and Nafada. 4-Nitrotoluene with a molecular weight of 137 g/mole was detected by GC-MS analysis in the soil of the study area at a retention time of 11.80 minutes with a percentage peak area of 4.20–4.51. The concentration of 4-Nitrotoluene was found to range from 0.005–0.085 µg/kg. Soil sample collected from Military Quarter guard recorded the highest concentration while the lowest concentrations were recorded by K/mata and Main market soil samples. The distribution of the 4-Nitrotoluene in the samples were observed to be in the order: Quarter guard> Dadin kow a Park> Gombe Division> K. Police station, Timber market> K/mata and main market. All the soil samples in Gombe metropolis were found to have higher concentrations of the 4-Nitrotoluene than the control sample which recorded a concentration of 0.0008 µg/kg. This indicates possible contamination with 4-Nitrotoluene in all the sampling sites within the metropolis. Nafada Police Station and Nafada Mosques samples had 4-Nitrotoluene’s concentrations of 0.006 and 0.008 µg/kg. These concentrations are above that obtained in the Nafada Control sample (0.003 µg/kg). All the soil samples collected from Bajoga had 4-Nitrotoluene concentrations greater than that obtained in Bajoga control samples. The concentrations in Bajoga samples were in the order: Ashaka Junction- GRA/Union Bank>Bajoga Police Station with concentrations of 0.007, 0.006, 0.006, and 0.005 µg/kg respectively.
<table>
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<th>GDS</th>
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<th>DPS</th>
<th>K/MATA</th>
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<th>MMS</th>
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<td>0.39</td>
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</tr>
<tr>
<td>RDX</td>
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<td>ND</td>
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<tr>
<td>HMX</td>
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</table>

4-Nitrotoluene was not listed on the HEAST cancer table and was not classifiable as [9] human carcinogenicity because of inadequate evidence in humans and animals, and limited evidence for genotoxicity in mammalian systems [12].

4-Propyl Benzaldehyde was detected at a retention time of 14.00 minutes and a percentage peak area of 5.41 – 5.91%. The concentration of propyl benzaldehyde in the soil samples from Boko Haram's explosion sites in Gombe metropolis ranged from 0.12µg/kg in Timber and Main markets to 0.18µg/kg in Quarter guard soil sample. The concentrations in all the soil samples analyzed from the sampling sites in Gombe metropolis were found to be above that obtained in the control Sample with 0.011µg/kg.
concentrations were in the order: Quarter guard > D/kowa Park > Gombe Division > K/Mata > Kwadon Police Station > Timber market and Main market.

In Nafada and Bajoga samples, the concentrations of 4-propyl benzaldehyde ranged from 0.07µg/kg to 0.19µg/kg as shown in Table 2. The highest concentrations of propyl Benzaldehyde in Nafada and Bajoga were observed in samples from NFD-Police Bajoga police station respectively while the lowest concentrations were observed in NFD-Mosque and Ashaka Junction samples respectively. All the samples recorded higher concentrations than their respective controls. This indicates possible propyl benzaldehyde contamination in the soils of the study area.

The concentration of 1,3-DNT in the soil samples was detected at the retention time of 24.95 minutes with a peak area of 18.0 - 18.71%. The concentration of 2,4-DNT in soil samples from Gombe metropolis ranged from 6.16µg/kg – 6.66µg/kg. K. Police Station and K/Mata soils have concentrations of 6.66 µg/kg which was greater than the concentration in the Gombe control soil sample (6.44 µg/kg). The control sample had concentration above all the soil samples from Gombe metropolis except K. Police Station and K/Mata soil samples indicating possible pollution only in these locations.

NFD-Police Station and NFD-Mosques have concentrations of 6.66µg/kg and 6.33µg/kg respectively which are both above the concentration in the NFD-Control (6.13µg/kg). This indicates pollution of the sampling location by 2,4-DNT in Nafada Samples. All the Samples from Bajoga have almost the same 2,4-DNT concentrations including the Control Sample. This shows there is no evidence of 2,4-DNT pollution in Bajoga Soil Samples.

The concentrations of 1,3-DNT in soil samples from NFD-Police Bajoga police station, Ashaka Junction, GRA and Union Bank were: 0.71, 0.58, 0.51 and 0.60µg/kg respectively. The concentration in the control was 0.60 µg/kg which was higher than that in Ashaka Junction and GRA but less than that in Bajoga Police station and GRA. All the Samples from Bajoga have almost the same 2,4-DNT concentrations including the Control Sample. This shows there is no evidence of 2,4-DNT pollution in Bajoga Soil Samples.

The concentration in the control was 0.60 µg/kg while NFD-Mosques sample recorded 0.58µg/kg 3,5-DNT concentration of <1µg/kg was found at the Donnelly Training Area (AK) [14]. Concentration of 2,4-DNT in US and Canadian Artillery ranges were reported to decreased from 9.6mg/kg in the top 0-3cm to 0.56mg/kg at 10-20cm [4].

The retention time of 3,5-Dinitrotoluene was 25.26 minutes with a peak area of 9.33 - 10.11%. The concentration of 3,5-Dinitrotoluene was found to be evenly distributed in the soils of Boko Haram’s explosion sites in Gombe metropolis ranging from 0.40µg/kg – 0.60µg/kg. The distribution of this remnant was in the order: D/Kowa Park > Quarter guard > K/Mata > Gombe Division > K. Police Station > Main Market > Timber Market, it was observed that all the concentrations in the affected areas were less than the concentration in the control sample which recorded 0.62µg/kg. It can therefore be suggested that there is no evidence of 3,5-DNT pollution from Boko Haram’s activity within the study area.

In Nafada soil samples, NFD-Police station has 3,5-DNT concentration of 0.90µg/kg which was greater than 0.60µg/kg recorded by the NFD-control sample while NFD-Mosques sample recorded 0.58µg/kg 3,5-DNT control which was closely above the NFD Control. These indicate possible 3,5-DNT pollution from Boko Haram’s attack on NFD-Police Station.

The concentration of 3,5-DNT in soil samples from Bajoga Police Station, Ashaka Junction, GRA and Union Bank were: 0.71, 0.58, 0.51 and 0.60µg/kg respectively. The concentration in the control was 0.60 µg/kg which was higher than that in Ashaka Junction and GRA but less than that in Bajoga Police station and GRA.

DNTs are widely used in manufacturing explosives and propellants as [14] gelatinizing, plasticizing and waterproofing agents in industries such as the munitions and mining industry. It is also used as a modifier for smokeless gunpowder in the munitions industry. DNT mixtures are predominantly used in the production of polyurethane polymers. These mixtures are also used as an intermediate in the production of dyes, plastics, herbicides and automobile airbags [15,16].
DNT is commonly deposited through live-fire and blow-in-place detonations at military ranges and found in waste streams and soil near munitions manufacturing and processing facilities [17]. Trinitrotoluene, TNT with a molecular weight of 227g/mole was detected at a retention time of 30.02 minutes with a peak area of 6.12 – 6.82%. The concentration in the soil samples from affected areas of Gombe Metropolis were found to be; 0.32, 0.45, 0.30, 0.29, 0.29, 0.45 and 0.36µg/kg in Gombe division, Quarter guard, K. Police station, D/Kowa Park, K/mata, Timber Market and Main Market respectively (Figure 1). The concentration of the TNT in the control Sample, 0.19µg/kg was found to be lower than the concentration in all the samples in the study sites indicating no possible remnant contamination in the study sites.

The concentration in Nafada soil samples as shown in Table 4 were 0.66, 0.41 and 0.44µg/kg in NFD-Police Station, NFD-Mosque and NFD-Control respectively while that of Bajoga soil samples were; 0.52, 0.40, 0.39, 0.42 and 0.31µg/kg in BJG-Police Station, Ashaka Junction, GRA, Union Bank and BJG-control respectively. This suggests presence of remnant pollution in all sampling sites from Bajoga and NFD-Police station.

TNT makes up around 99% of military grade TNT in most cases and additional components including 2,4-DNT, 2,6-DNT, 1,3-DinitroBenzene and 1,3,5 TNB can also exist [18]. TNT concentration of 358mg/kg was reported in soil taken from a nearby M72 rocket explosion at the depth of 0 - 0.5cm and this concentration decrease to 1.7mg/kg at the depth of 6 – 10cm [4]. Residues of TNT at a concentration of <1- 314mg/kg were also found at the Donnelly training area, AK [14]. At the cold Lake Air weapon, Pennington et al., [4] reported a TNT concentration of 3-408mg/kg. 2,4,6-Trinitrotoluene has been detected in surface soil samples at an average concentration of 13,000 mg/kg at the U.S. Department of Energy’s Weldon Spring site in St. Charles County, Missouri [19]. At the West Virginia Ordinance Works located in Mason County, West Virginia, 2,4,6-trinitrotoluene and other nitroaromatics have been detected in surface soils at burning sites in concentrations of up to 4% (40,000 mg/kg). Nitroaromatics, principally 2,4,6-trinitrotoluene, were detected at up to 20,000 mg/kg within 5-10 meters of the foundations of processing and refining facilities [19].

These literatures reported far greater concentrations than those reported in the soils of this study. HMX and RDX were not detected in all the samples investigated in this study. Many literatures reported HMX and RDX in varying concentrations in soils. An RDX concentration in the range of <1mg/kg – 50mg/kg and HMX of <1mg/kg – 9.1mg/kg were reported at the 23 Millitary installation in US and Canada [4]). At the grenade impact zones of Fort Lewis (WA) and Fort Richardson, RDX concentration of 51.2mg/kg and <0.1-0.5mg/kg respectively were reported by Jenkins et al.,[20]. HMX concentration of up to 10,400mg/kg was obtained in the soil from a nearby M72 rocket explosion at 0-5cm [4]

4. CONCLUSION

The concentrations of explosive remnants in the soil of the study area (4-Nitrotoluene, 4-Propyl Benzaidehyde, 1,3-Dinitrotoluene, 2,4-DNT, 3,5-DNT, RDX and HMX were investigated. All the samples in the study area had 4-Nitrotoluene and 4-Propyl Benzaidehyde concentrations above those in their respective controls. This indicates possible remnant contaminations in these locations. 1,3-DNT in Bajoga samples, 2,4-DNT in K Police station and K/mata, 3,5-DNT in Gombe metropolis, and TNT in NFD Police station were all found to be above the concentrations in their control indicating absence of pollutions from the remnants in these locations.

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