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Environmental Study of Explosive Residues in Some Boko Haram Conflict Affected Areas of Konduga Borno State, Nigeria

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***Abstract**: This study aimed at assessing the explosive residues in some book haram conflict affected areas of Konduga, Borno state, Nigeria. Soil samples were collected in some bomb exploded areas for the determination of some explosive compounds like RDX, TNT, HMX, 2,4-DNT and1,3,5-TNB using SPME and GCMS analysis. The results of this study showed that, highest concentration of 1,3,5-TNB an impurity during production grade and photodegradation product of TNT have the highest value of 1.4120±0.9702 mg/kg at sample KDWS to 0.0310± 0.0207 mg/kg in sample KDES Aging tends to decrease the amount of recovery of explosives from soil samples with exception of NB. This is because analytes appear to be more tightly bound to the soil after a long period of time or to have suffered degradation While hydroxylamine a biotransformation product of 2,4-DNT have the lowest value of 0.006±0.003 mg/kg in sample KDES. USEPA has classified TNT as potential human mutagen and carcinogen. The order of energetic residue concentrations was TNT > 1,3,5-TNB > RDX > 2,4-DNT > HMX.*

***Keywords:** Explosive compounds, Residues, Soil, Mutagenic, Carcinogenic, Environment.*

INTRODUCTION

Energetic compounds, are the active chemical components of explosives and propellants which are necessary both for peaceful (e.g. demolition and mining) and military purposes. Commonly used energetic compounds include, the explosives, 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (Pitchel,2021). Nitroglycerine (NG), nitro guanidine (NQ), nitrocellulose (NC), 2,4-dinitrotoluene (DNT) and various formulations are employed in missiles, rockets and gun propellants (Jenkins, 2007).

The use of chemical weapons, although prohibited by the 1925 Geneva protocol, has been reported recently in several armed conflicts, including the Iran- Iraq war (Paul, 1992). The first explosive TNT was the first used on a significant scale during the First World War. Despite stopping TNT production in the U.S.A in the mid-1980s, contamination still largely exists since from World War 1 and 2. Moreover, TNT is still used in US munitions. Several studies have examined TNT toxicity in a variety of organisms. TNT was reported as the most toxic of the explosive contaminants. In mammal exposure may lead to skin rashes, blood disorders, and organ damage or failure. While the USEPA (2014) has classified TNT as potential human mutagen and carcinogen (Jeffrey, 2015). It is the one of the most common bulk explosives in use today both in military ordinance and mining. TNT is use as a booster for big explosive munitions and in mixtures with other energetic compounds e.g. RDX and HMX in explosive formulation. TNT is popular in military and industry because of its insensitivity to shock and friction which reduces the risk of accidental detonation (Pitchet, 2012).

In plants, RDX has been shown to suppress growth, though phytotoxicity is much lower when compared to TNT (PitcheL 2012). RDX is additionally known for its ability to translocate within plants, and therefore these compounds can accumulate in various parts of the plants. Despite its ability to translocate, RDX has been reported to have lower toxicity than TNT (Jenkins, 2012).

RDX has a lower octanol-water partition coefficients (K_{OW}), value and therefore does not firmly bind with the soil, making it more readily available and highly mobile (USEPA, 2014). For this reason, RDX contamination can spread more deeply into the soil and has a superior ability to leach into sources of drinking water. While toxic to both animals and plants, RDX is known for targeting the central nervous system when inhaled, resulting in convulsions and loss of consciousness. Furthermore, this compound has been shown to have adverse effects on the gastrointestinal and renal systems (Pitchel, 2012). It has been used previously as a rat poison (Jenkins, 2012). USEPA has it classified as a potential human carcinogen.

Rashdan, (2011) munitions (termed unexploded ordinances or UXOs) which are lost, buried, undetonated or partially detonated pose a greater ecological threat than those which properly detonate or are handled correctly. Impacts of explosive residues on vegetation can be direct via toxic effects to plants tissue. Explosives can limit the ability of vegetation to colonize, expand reproduce and grow in contaminated areas. There has been presence of TNT, RDX and HMX in soils, surface water and ground water where these explosives are being used. Most of the blasted explosives are stable in soil due to their chemical structures and easy binding to the soil organic matter, which making soil remediation difficult. TNT and HMX have resulted to decrease in terrestrial plant biomass, abnormality growth in terrestrial plants and decrease in biomass and fertility of earthworm (Jenkins, 2012).

Major soil contaminants found in army depots, ammunition evaluation facilities, artillery ranges, and ordnance disposal sites include composition B (Comp B), which is a commonly used military formulation, consisting of the toxic explosive compounds 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (Jeffrey, 2015).Their recalcitrance to degradation, toxic, and mutagenic effects has made explosive contamination a matter of concern.

As with other contaminants, explosive compounds can influence ecological and environmental processes. Munitions (termed unexploded ordnances or UXOs) which are lost, buried, undetonated, or partially detonated pose a greater ecological threat than those which properly detonate or are handled correctly (Pichtel, 2012). The most commonly used and studied explosives are RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and TNT (2-methyl-1,3,5-trinitrobenzene.

TNT toxicity has been demonstrated using earthworm reproduction tests and studies with *Vibrio fischeri* have established TNT as being “very toxic” to aquatic organisms. Mutagenicity studies have been carried out using TNT and its metabolites on *Salmonella* strains and mammalian cell lines. TNT w

Via *et al.,* (2014) soil types where munitions are present play a large role in migration and bioavailability of explosive compounds. Clay soils adsorb more explosive compounds than sandy soils, and humic soils bind more TNT than other soil types. As organic material in soil decreases, so does binding potential, increasing bioavailability of explosive compounds as found to be mutagenic, with some metabolites more so than the TNT itself.

Zellmer, (2009) who uses GCMS analysis with acetonitrile extract of soil sample and propellant grains and confirmed the presence of dibutylphthalate, 1,3,5-TNB, butylphthalate ,4-ADNT along with high concentration of 2,6-DNT. The aim of the research was to determining the explosive residues in some Boko haram conflict affected areas of Konduga, Borno state, Nigeria that may cause a deleterious effect to plants and animals in that environment.

MATERIALS AND METHODs

Sampling Location

The sampling sites of this work were the three soil samples located within Konduga Borno state namely; Konduga south soil(KDSS), Konduga east soil (KDES) and Konduga west soil (KDWS). The three soil samples were collected within the vicinity of bomb exploded; rocket propelled granite (RPG) lunched areas. The soil samples were collected and harmonized at various locations of the sites.

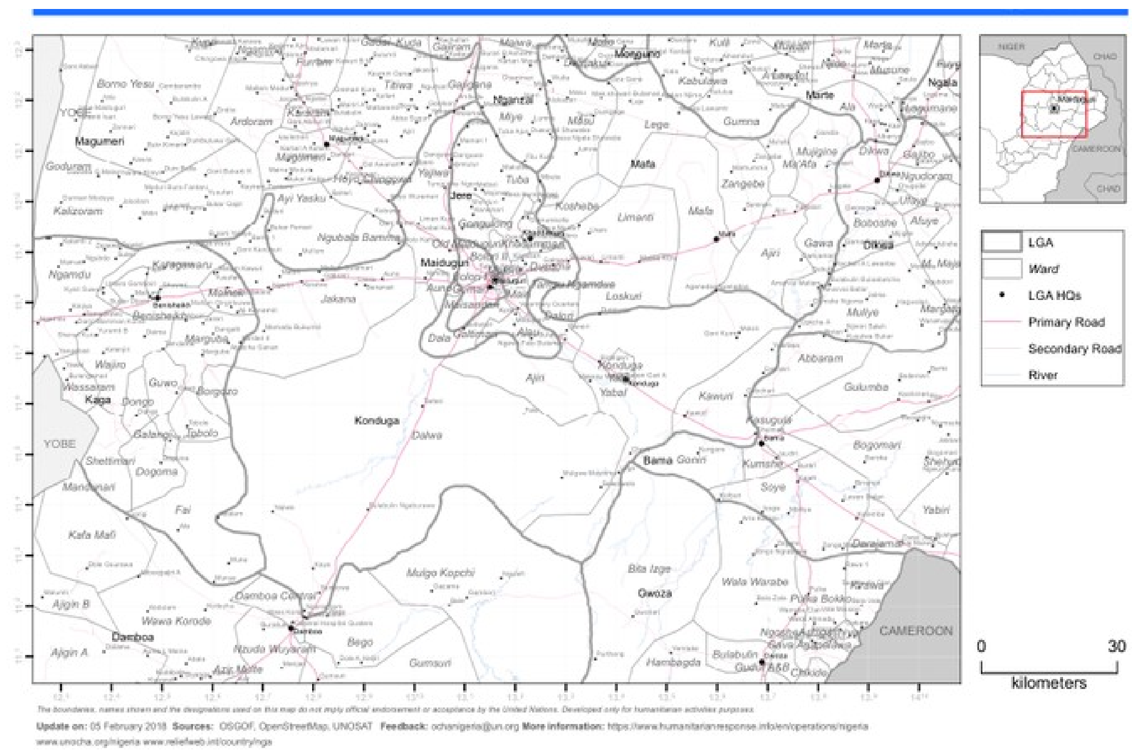

Fig. 1: Map of Konduga showing sample areas

Sample Collection

Zellmer, (2019) 5 g of soil samples was taken by means of a stainless- steel spoon at different locations and stored in polyethylene bags. The bags were immediately stored on ice in coolers in the dark to avoid photodegradation of light sensitive compounds. The soil samples were collected from Konduga from different points with fifty (50) meters between each sampling point and was collected at 25 cm deep.

Soil sample extraction and cleanup for Explosive Residues

According to Anol, (2011), soil samples were prepared by taking 5 g of soil, sonicated for 30 min with 25-ml acetonitrile solvent. Different amounts of the stock solutions were utilized to obtain the required concentration in the soil samples.

Anol, (2011) SPME was used to clean up the extracts. Samples were then loaded, elated (5 ml acetonitrile) and collected into 10-ml graduated tubes. The sample was concentrated to 1.0 ml under nitrogen gas, and ready for GCMS analysis.

Results and Discussion

Results of some Explosive Residues TNT, RDX, HMX, 2,4-DNT and 1,3,5-TNB in Soil Samples of Konduga Local Govt. Area

Fig 1. shows the mean concentrations of some explosive residues found in the soil samples obtained from bomb exploded areas of Konduga local government, Borno state. Among the explosive compounds studied in the soil samples, dibutyl phthalate, 2,6-DNT and 1,3,6-TNB, and all are transformation products of TNT were the predominant compounds found in the soil samples. The detectable levels of dibutyl phthalate ranges between 0.0340±0.1492 mg/kg at sample KDWS to 0.0137±0.0092 mg/kg at sample KDES. While 2,6-DNT ranges between 0.3011±0.4481mg/kg in sample KDWS to 0.1500±0.1 mg/kg in sample KDES, and 1,3,5-TNB ranges between 1.4120±0.9702 mg/kg in sample KDWS to 0.0310±0.0207 mg/kg in sample KDES. 4-nitroso-2,4-nitro-2,4-diazabutanal a transformation product of HMX ranges between 0.0068±9,9678 mg/kg in sample KDWS to 0.0021±0.0374 mg/kg in sample KDES. While methylenedinitramine a biotransformation product of RDX ranges between 0.0225±0.1224 mg/kg in sample KDWS to 0.0029±0.28 mg/kg in sample KDES.

1,3,5-TNB an impurity during production grade and photodegradation product of TNT to have the highest value of 1.4120±0.9702 mg/kg at sample KDWS to 0.0310± 0.0207 mg/kg in sample KDES. Aging tends to decrease the amount of recovery of explosives from soil samples with exception of NB (Sonia et al., 2013). This is because analytes appears to be more tightly bound to the soil after a long period of time or to have suffered degradation (Sonia *et al*., 2013). This study is in conformity with the research carried out by (Pitchel, 2012) who detected 54% of 1, 3, 5-TNB in soils contaminated with explosive compounds. HMX and RDX was having the lowest value, this may be because dissolved RDX and HMX does not strongly interact with soils and can migrate to the vadose zone to ground water resources (Ali et al.,2014). This is consistent with the lower soil/water partitioning coefficient (Kow) of HMX and aerobic degradation after 100 days incubation 61% of HMX was mineralized to CO_2 (Pichtel, 2012) Decreased in HMX correspond to release of CO_2 and accumulation of 4-nitroso-2,4-dinitro-2,4-diazabutanal. The source of the higher number of transformation products and their concentrations in soil samples obtained from KDWS than KDES, could be because KDWS sample was obtained from unexploded ordinance (UXO) disposal site and blow in place (BIP) operation site. While the source of some high concentrations of TNT in sample KDES may be thought to be the tritonal used as high explosives in air force bombs. The order of energetic residue concentrations was TNT > 1,3,5-TNB > RDX > 2,4-DNT > HMX.

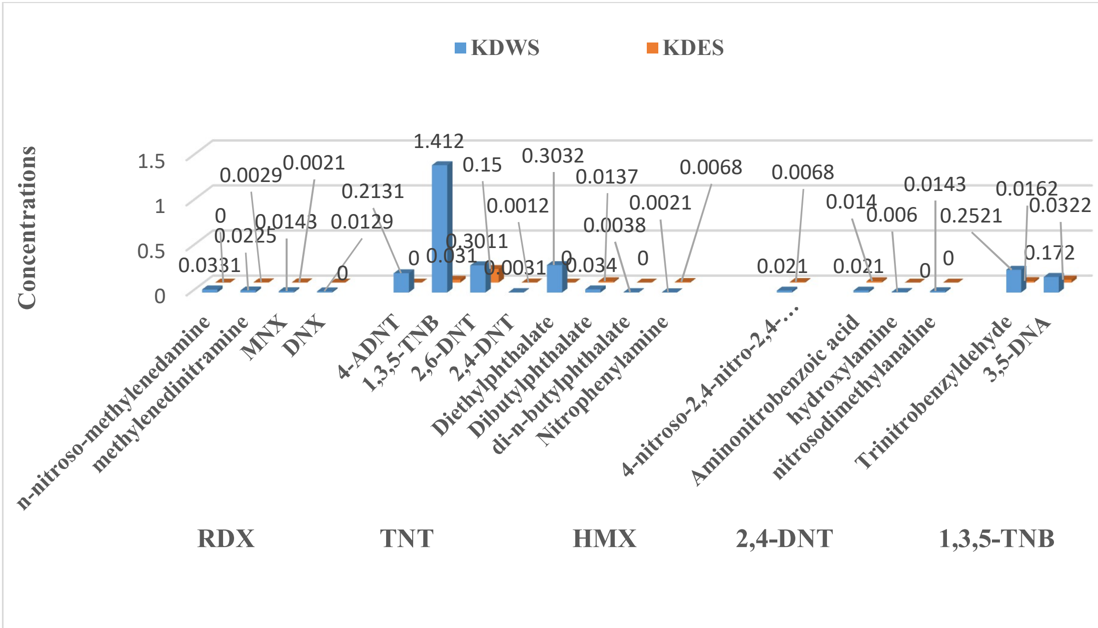

Fig .2: Mean Concentrations of some Explosive Residues detected in Soil Samples of Konduga Local Govt Area

CONCLUSION

Energetic compounds undergo varying degrees of chemical and biological transformations depending on the compounds involved and environmental factors. While TNT and its transformation products was predominant and found most frequently in the soil samples, which could be due to their high octanal water partitioning coefficient which make them to bind to soil particles. Base on the results of this study, it was observed that the concentrations of TNT, RDX, HMX, 2, 4-DNT and 1, 3, 5-TNB in soil samples were within the permissible limit of WHO (2014). The results of this study implies that continuous monitoring has to be carried out to ascertain whether or not the presence of these explosives in this area. TNT was reported as the most toxic of the explosive contaminants. In mammal exposure may lead to skin rashes, blood disorders, and organ damage or failure. While the USEPA (2014) has classified TNT as potential human mutagen and carcinogen (Jeffrey, 2015). The order of energetic residue concentrations was TNT > 1,3,5-TNB > RDX > 2,4-DNT > HMX.

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