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Evaluation of Metal Levels in Water Samples of Some Weapon-Bombarded Areas in Borno State, Nigeria

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ABSTRACT

Heavy metal levels in water samples in some war zones of Borno State in Nigeria were evaluated. A total of 155 water samples were evaluated using Microwave Plasma Atomic Emission Spectrophotometer. The levels of these metals: Cd, Ni, Sb, Co, Pb, Mg, Mn and Cr, in water were determined. The result in µg/L showed that Cd level ranged from 0.00 to 15.38 ±0.18, Ni:0.00±0.00 to 12.65±0.13, Co:0.04±0.01 to 0.713±0.00, Pb:0.00 to 4.825±0.112, Mg: 8.928±0.066 to 471.30±2.072, Mn:0.250±0.00 to 389.6±56.83 and Cr:0.00 to 37.43+0.00. Sb was below detection limit. The descending order of the metal concentrations in the water samples were Cd > Mn > Ni >Pb > Co > Mg > Cr > Sb. A strongly positive correlation exhibited between Cd versus Ni, Co and Cr at 0.01 levels (2-tailed) as well as Cd versus Mn at 0.05 (2-tailed). Similarly, Ni showed strongly positive correlation with Cd, Co, Mg, Mn and Cr at 0.01 (2-tailed). Pb showed strongly positive correlation with Ni, Mn, Co at 0.01 (2-tailed) and weakly with Pb. Mn showed strongly positive correlation with Ni, while Cr showed strongly positive correlation with Cd, Ni, Co, Mg, and Mn at 0.01 level (2-tailed). The data indicated that the metals levels in the study areas were higher than those from the control zone. The result was found in some cases to be above the acceptable values for the WHO. The result of this study will be useful for the management and planning of the possible remediation processes that can be employed in the study area.

Keywords: Heavy metals, Water, Borno State, Evaluation, Warring Areas, Weapons**.**

INTRODUCTION

Warfare is associated with significant heavy metal contamination of the environment, due to destruction of built infrastructure which consequently releases heavy metal. Also, direct contamination from exploded ordinance and leakage from unexploded ordinance form part of the environment degradation associated to warfare. Over the last century war and natural processes have resulted in the release of large amount of toxic compounds into the biosphere. This toxic compound has led to the problem of environmental pollution and ecological degradation [1]

Heavy metals such Zn, Cu, Ni, Pb, and Cr are used extensively to coat bullets, missiles, gun barrels, and military vehicles (tanks, trucks and aircraft) [2]. Explosives harbor huge amounts of Pb and Hg [Mercury(II) fulminate] [3]. Zn, Cu, Ni, Co, Pb, and Cr are used to coat bullets, missiles, gun barrels, and military vehicles [4]. Antimony (Sb), are weapon priming compounds, [5]. In general, the use of heavy metals in weapons has increased since the end of World War II [2].

In Borno State, Nigeria, following the war, explosives and ammunitions released organic pollutants as well as toxic heavy metals into the environment. These would cause threat to the health of the animals and humans in the area. The North East has been the site of a massive environmental disruption by bombardments due to the use of bombs, bullets, improvised explosive devices (IEDs), rockets and other ammunition.

Metals are key components of bombs, bullets, and other weaponry [6]. It has been suggested that US military bases are among the most polluting operations on earth [7]. In 2009, the fight in Borno State sprang up. This later took a new turn in 2010 when the need for deployment of regimental weapon turned to deployment of armament weapons. The fight at the North East has been the sites for massive environmental disruption due to high caliber armaments in use. From 2010 till date, the war in Borno State have led to dropping of large number of bombs, rocket, cannons, and bullet on the land, which are similar situations as seen in the US fight against insurgency. Thus, the determination of the amount of cadmium, chromium, antimony, manganese, nickel, antimony, copper and lead in water samples of the war-torn areas has become necessary. Also the study will appreciate the effect of the war on the environment. It is expected that the water in that area will be affected which eventually will affect human health. It is expected that the troops will experience health challenges arising from infected injuries that would occur due to anti-microbial drug resistance caused by metals.

The hypothesis that increased war activity coincides with increased metal levels in war environment is investigated by this research work. Therefore, the aim of the research is to determine the level of heavy metals (Cd, Ni,Co, Pb, Sb, Mg, Mn and Cr)levels in war zones water samples from Borno State Nigeria using Microwave Plasma Atomic Emission

Spectrophotoscopy (MPAES). Hence the objectives of this research are:(1) To determine the level of heavy metals (Cd, Ni,Co, Pb, Sb, Mg, Mn and Cr) in water from these warring zones of Borno State. (2) To provide information on the state of water used for agricultural and domestic purposes in those selected warring areas of the research by subjecting the result of the research from the water samples to statistical analysis of variance (ANOVA) and Tukey post hoc test (3) To determine their correlation coefficient and finally, (4) To make appropriate recommendations based on the outcome of the research study on ways of improving the present situation.

MATERIALS AND METHODS

Sampling Location

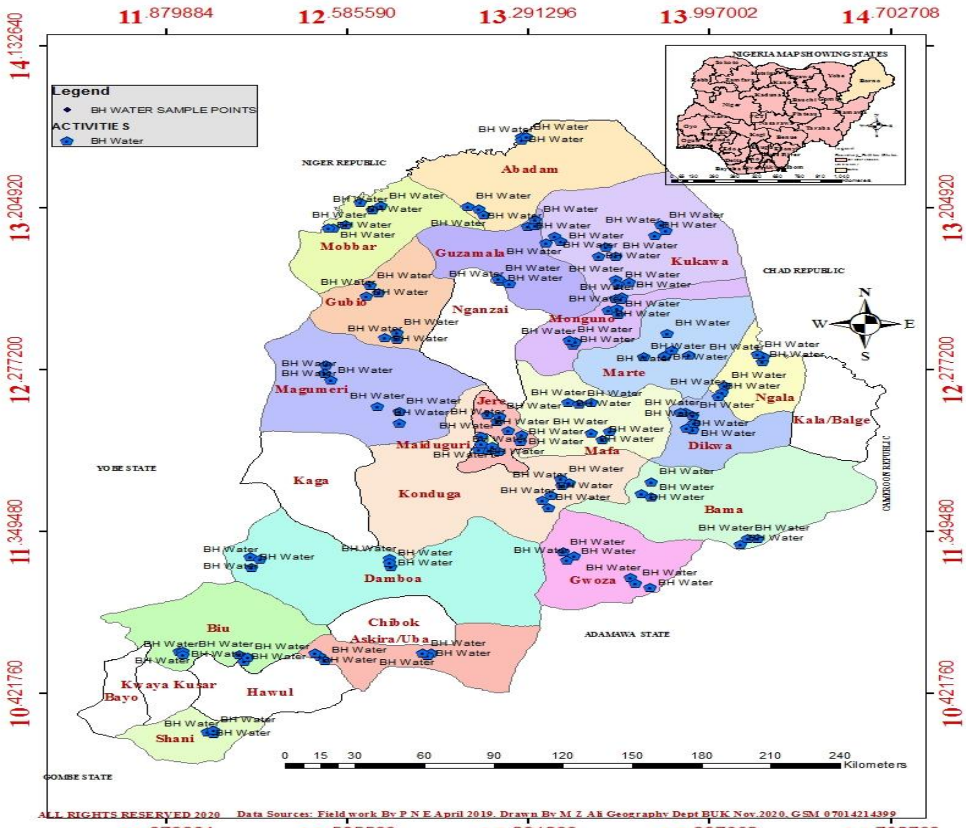

Fig 1: Map of the Study Area Showing Sampling Points for Water.

Sampling areas for water

Borno State is a state in North-Eastern part of Nigeria. Its capital is Maiduguri. Borno State has Twenty-Seven Local Government Areas (LGAs). The research work for water sampling is from 21 Local Government Areas of Borno State. These areas (Abadam, Bama, Biu, Damboa, Dikwa, Gubio, Guzamala, Kukawa, konduga, Mongonu, Jere, Mafa, Magumeri, Marte, Maiduguri, Mobbar , Marte Ngala, Baga, Shani and Gwoza) have experienced high military bombardment and explosions with the exception of Shanli LGA hence the reason why Shanli is taken as the control zone.

Table 1 is the water sample areas and sample code as seen below:

Table 1: Water Sampling Sources and Codes

Water Sample 1 from Marte Borehole Sampling Area					**Water Sample 2 from Mafa Sampling Area**				
S/N	**Area**	**Sample Code**	**General Code**	**Source**	**S/N**	**Area**	**Sample Code**	**General Code**	**Source**
1.	MAR HQ BH	MAR 1	WS1	BOREHOLE	2	MAF HQ	MAF 1	WS6	BOREHOLE
	MAR BH SEC A	MAR 2	WS2			MAF SEC A	MAF 2	WS7	
	MAR BH SEC B	MAR 3	WS 3			MAF SEC B	MAF 3	WS8	
	MAR BH SEC C	MAR 4	WS 4			MAF C	MAF 4	WS9	
	MAR BH SEC D	MAR 5	WS 5			MAF D	MAF 5	WS10	
Water Sample 3 from Jere Sampling Area					**Water Sample 4 from Konduga Sampling Area**				
S/N	**Area**	**Sample Code**	**General Code**	**Source**	**S/N**	**Area**	**Sample Code**	**General Code**	**Source**
3.	105 CG HQ BH	JER 1	WS11	BOREHOLE	**4.**	LOWCOST SEC 1	KON1	WS16	RIVER
	105 CG ACCM BH	JER 2	WS12			LOWCOST SEC2	KON 2	WS17	
	PRYCG BH	JER 3	WS13			LOWCOST SEC3	KON 3	WS18	
	PRYCG BH	JER 4	WS14			10 HSE UNIT SEC 1	KON 4	WS19	
	GOM	JER 5	WS15			10 HSE UNIT SEC 2	KON 5	WS20	
Water Sample 5 from Bama Sampling Area					**Water Sample 6 from Mobbar Sampling Area**				
S/N	**Area**	**Sample Code**	**General Code**	**Source**	**S/N**	**Area**	**Sample Code**	**General Code**	**Source**
5.	BAM IDP	BAM 1	WS21	BOREHOLE	6.	DSK HQ	DSK 1	WS26	BOREHOLE
	BAM NAF	BAM 2	WS22			DSK SEC 1	DSK 2	WS27	
	BAK IDP P1	BAM 3	WS23			DSK SEC 2	DSK 3	WS28	
	BAK IDP P2	BAM 4	WS24			DSK SEC 3	DSK 4	WS29	
	BAKARMY	BAM 5	WS25			DSK SEC 4	DSK 5	WS30	
Water Sample 7 from Mongonu Sampling Area					**Water Sample 8 from Dalori (MDG) Sampling Area**				
S/N	**Area**	**Sample Code**	**General Code**	**Source**	**S/N**	**Area**	**Sample Code**	**General Code**	**Source**
7.	MON HQ	MON 1	WS31	BOREHOLE	**8.**	IDPPNT 1	DAL 1	WS36	BOREHOLE
	MON SEC 3	MON 2	WS32			IDP PNT 2	DAL2	WS37	
	MON SEC 2	MON 3	WS33			IDP PNT 3	DAL 3	WS38	
	MON SEC 3	MON 4	WS34			IDP PNT 4	DAL 4	WS39	

	MON SEC 4	MON 5	WS35			IDP MED	DAL 5	WS40	

Water Sample 9 from Baga Sampling Area					Water Sample 10 from Maiduguri Sampling Area				
S/N	**Area**	**Sample Code**	**General Code**	**Source**	**S/N**	**Area**	**Sample Code**	**General Code**	**Source**
9.	BAG SEC 1	BAG 1	WS41	BOREHOLE	10.	MAI RGE	MDG 1	WS46	BOREHOLE
	BAG SEC 2	BAG 2	WS42			OFFR ACCM	MDG 2	WS47	
	BAG SEC 3	BAG 3	WS43			7 DIV	MDG 3	WS48	
	BAG SEC 4	BAG 4	WS44			SOGAACCM	MDG 4	WS49	
	BAG SEC 5	BAG 5	WS45			ART HQ	MDG 5	WS50	

Water Sample 11 from Gwoza Sampling Area					Water Sample 12 from Damboa River Sampling Area				
S/N	**Area**	**Sample Code**	**General Code**	**Source**	**S/N**	**Area**	**Sample Code**	**General Code**	**Source**
11.	PUK RI	GWO 1	WS51	BOREHOLE	**12.**	DAM R	DAM 1	WS56	RIVER
	PUK R2	GWO 2	WS52			DAM R	DAM 2	WS57	
	PUK R3	GWO 3	WS53			DAM R	DAM 3	WS58	
	PUK R4	GWO 4	WS54			DAM R	DAM 4	WS59	
	PUK R5	GWO 5	WS55			DAM R	DAM 5	WS60	

Water Sample 13 from from Biu Sampling Area					Water Sample 14 from Dikwa Sampling Area				
S/N	**Area**	**Sample Code**	**General Code**	**Source**	**S/N**	**Area**	**Sample Code**	**General Code**	**Source**
13.	BIU HQ	BIU 1	WS61	BOREHOLE	14.	GAJI 1	DIK 1	WS66	RIVER
	BIU SLD ACCM	BIU 2	WS62			GAJI 2	DIK 2	WS67	
	BIU OFFR ACCM	BIU 3	WS63			GAJI 3	DIK 3	WS68	
	BIU CLS	BIU 4	WS64			GAJI 4	DIK 4	WS69	
	BIU SEC	BIU 5	WS65			GAJI 5	DIK 5	WS70	

Water Sample 15 from Shanli Sampling Area									
S/N	**Area**	**Sample Code**	**General Code**	**Source**	**S/N**	**Area**	**Sample Code**	**General Code**	**Source**
15.	SHAN1	SHAN1	WS76	BOREHOLE					BOREHOLE
	SHAN 2	SHAN 2	WS77						
	SHAN 3	SHAN 3	WS78						
	SHAN 4	SHAN 4	WS79						
	SHAN 5	SHAN 5	WS80						

The control sample from Shanli was obtained at a borehole in SHANLI LGA of Borno State were no launching of ammunitions/explosives had occurred.

Water Sample 16 from Abadam Borehole Sampling Area					Water Sample 17 from Askiri /Uba Sampling Area				
S/N	**Area**	**Sample Code**	**General Code**	**Source**	**S/N**	**Area**	**Sample Code**	**General Code**	**Source**
16.	ABD HQ BH	ABD 1	WS1	BOREHOLE	17.	ASK HQ	ASK 1	WS6	BOREHOLE
	ABD BH SEC A	ABD 2	WS2			ASK SEC A	ASK 2	WS7	

	ABD BH SEC B	ABD 3	WS 3	
	ABD BH SEC C	ABD 4	WS 4	
	ABD BH SEC D	ABD 5	WS 5	

	ASK SEC B	ASK 3	WS8	
	ASK C	ASK 4	WS9	
	ASK D	ASK 5	WS10	

Water Sample 18 from Ngala Sampling Area

S/N	Area	Sample Code	General Code	Source
18.	NGA HQ BH	NGA 1	WS11	BOREHOLE
	NGA BH 1	NGA 2	WS12	
	NGA BH 2	NGA3	WS13	
	NGA BH 3	NGA 4	WS14	
	NGA BH 4	NGA 5	WS15	

Water Sample 19 from Biu Sampling Area

S/N	Area	Sample Code	General Code	Source
19.	Biu 1	BUU 1	WS16	RIVER
	Biu 2	BUU 2	WS17	
	Biu 3	BUU 3	WS18	
	Biu 4	BUU 4	WS19	
	Biu 5	BUU 5	WS20	

Water Sample 20 from Magumeri Sampling Area

S/N	Area	Sample Code	General Code	Source
20.	MAG 1	MAG 1	WS21	BOREHOLE
	MAG2	MAG2	WS22	
	MAG3	MAG3	WS23	
	MAG4	MAG4	WS24	
	MAG5	MAG5	WS25	

Water Sample 21 from Guzamala Sampling Area

S/N	Area	Sample Code	General Code	Source
21.	GUZML1	GUZML1	WS26	BOREHOLE
	GUZML2	GUZML2	WS27	
	GUZML3	GUZML3	WS28	
	GUZML4	GUZML4	WS29	
	GUZML5	GUZML5	WS30	

Water Sample 22 from Konduga Sampling Area

S/N	Area	Sample Code	General Code	Source
22.	KON HQ	KOND 1	WS31	BOREHOLE
	KON LOWCOST 1	KOND 2	WS32	
	KON LOWCOST 2	KOND 3	WS33	
	KON LOWCOST 3	KOND 4	WS34	
	KON LOWCOST 4	KON 5	WS35	

Water Sample 23 from Damboa Sampling Area

S/N	Area	Sample Code	General Code	Source
23.	DAM PNT 1	DAMB 1	WS36	BOREHOLE
	DAM PNT 2	DAMB 2	WS37	
	DAM PNT 3	DAMB 3	WS38	
	DAM PNT 4	DAMB 4	WS39	
	DAM PNT 5	DAMB 5	WS40	

Water Sample 24 from Dikwa Sampling Area

S/N	Area	Sample Code	General Code	Source
24.	DIKW SEC 1	DIKW 1	WS41	BOREHOLE
	DIKW SEC 2	DIKW2	WS42	
	DIKW SEC 3	DIKW3	WS43	
	DIKW SEC4	DIKW4	WS44	
	DIKW SEC 5	DIKW5	WS45	

Water Sample 25 from Gubio Sampling Area

S/N	Area	Sample Code	General Code	Source
25.	GUB 1	GUB 1	WS46	BOREHOLE
	GUB 2	GUB 2	WS47	
	GUB 3	GUB 3	WS48	
	GUB 4	GUB 4	WS49	
	GUB 5	GUB 5	WS50	

Table 26: Water Sample 26 from Mobbar Sampling Area

S/N	Area	Sample Code	General Code	Source
26.	MOBR RI	MOBR1	WS51	RIVER
	MOBR R2	MOBR2	WS52	

Table 27: Water Sample 27 from Marte River Sampling Area

S/N	Area	Sample Code	General Code	Source
27.	MARTE R 1	MARTE 1	WS56	RIVER
	MARTE R 2	MARTE 2	WS57	

S/N	Area	Sample Code	General Code	Source	S/N	Area	Sample Code	General Code	Source
	MOBR R3	MOBR3	WS53			MARTE R 3	MARTE 3	WS58	
	MOBR R4	MOBR4	WS54			MARTE R 4	MARTE 4	WS59	
	MOBR R5	MOBR5	WS55			MARTE R 5	MARTE 5	WS60	

Table 28: Water Sample 28 from from Maiduguri Samling Area					Water Sample 29 from Mafa Sampling Area				
S/N	**Area**	**Sample Code**	**General Code**	**Source**	**S/N**	**Area**	**Sample Code**	**General Code**	**Source**
28.	MAID PNT 1	MAID 1	WS61	RIVER	29.	MAFFF 1	MAFFF 1	WS66	RIVER
	MAID PNT 2	MAID 2	WS62			MAFFF2	MAFFF 2	WS67	
	MAID PNT 3	MAID 3	WS63			MAFFF 3	MAFFF 3	WS68	
	MAID PNT 4	MAID 4	WS64			MAFFF4	MAFFF4	WS69	
	MAID PNT 5	MAID 5	WS65			MAFFF 5	MAFFF 5	WS70	

Water Sample 30 from Magumeri Sampling Area					Water Sample 31 from Baga Sampling Area				
S/N	**Area**	**Sample Code**	**General Code**	**Source**	**S/N**	**Area**	**Sample Code**	**General Code**	**Source**
30.	MAGU 1	MAGU 1	WS76	BOREHOLE	**31.**	BAGA 1	BAGG 1	WS76	BOREHOLE
	MAGU 2	MAGU 2	WS77			BAGA 2	BAGG 2	WS77	
	MAGU 3	MAGU 3	WS78			BAGA3	BAGG3	WS78	
	MAGU 4	MAGU 4	WS79			BAGA4	BAGG4	WS79	
	MAGU 5	MAGU 5	WS80			BAGA5	BAGG5	WS80	

Water samples from borehole and river were collected and labeled as WS 1 to WS 155. The samples from the river were collected by grab sampling technique [9]. This was done by lowering the sampling bottle with a rope knotted at the neck of the bottle to ensure that the sample collected was not from the surface at locations where anthropogenic activities were carried out. Water was collected from drilled wells and hand dug wells after pumping for 5 - 10 minutes [9].The borehole samples were sourced from Abadam, Bama, Biu, Damboa, Dikwa, Gubio, Guzamala, Kukawa, Konduga, Mongonu, Jere, Mafa, Magumeri, Marte, Maiduguri, Mobbar , Ngala, Baga, Shanli and Gwaoza. While for the river samples were sourced from Askira/Uba, Biu, Damboa, Dikwa,Gubio, Mafa, Magumeri, Maiduguri, Marte, Mobbar , and Baga.

The samples were collected in September 2019 during rainy season and airlifted to Kano State. The experiments were carried out in the Chemistry Laboratory, Bayero University Kano (BUK), Kano State, Nigeria.

Cleaning of container for water analysis

All glass wares and the polyethylene plastic containers for collection of water sample were cleaned by washing in non- ionic detergent, and soaked in 0.5M HNO_3 for 24 hours and finally rinsed with distilled water severally prior to usage [8].

Water Sample Pretreatment

The samples for heavy metals determination were collected in 5-liter cleaned plastic containers and preserved by the addition of 5 cm^3 concentrated HNO_3 (Specific gravity 1.41) to prevent the metals from adhering to the walls of the containers used in sampling [9].

Digestion of Water Samples

A quantity of the filtered water sample was evaporated to about 100 cm^3 by transferring 500 cm^3 of the water into 1-liter pyrex glass beaker [9]. The sample was placed on a hot sand bath and evaporated. The process was repeated for about 8 times whereby all the water has been transferred into the pyrex beaker. Finally, the water was allowed to evaporate to about 100 cm^3 volumes and the heating source was removed. Then 25 cm^3 of 0.25M HNO_3 was added and allowed to boil at 85 ^oC until a clear solution was obtained. The boiling was continued until a minimum amount of sample remained in the beaker. The digested sample was allowed to cool and the sample rinsed with distilled water before filtering using ash less filter paper. It was then made up to 50cm^3 marks in 50cm^3guaged plastic container with deionised water [9]. This solution was then used for the heavy metal analysis using MPAES (Agilent technologies 4210). The MPAES machine is located at the Centre for Dry Land, Bayero University, Kano, (BUK) New site and the metal analysis was carried out in the Center for Dry Land laboratory, BUK new site. The metals which were investigated using this method are Cd, Ni, Sb, Co, Pb, Mg, Mn and Cr.

Conversion of (mgL^{-1}) to μgL^{-1}= (mgL^{-1}) x 1000 = μgL^{-1}

$$\text{Metal}(\text{mgL -1}) = \frac{\mu\text{gL -1 of metal x D}}{1000}$$

Where;

$$\text{D (dilution factor)} = \frac{\text{Total final volume in ml}}{\text{ml of sample}}$$

Preparation of Blank Solution

This consists of carrying out a separate determination, the sample being omitted under exactly the same experimental conditions as employed in the actual analysis of the sample. The aim is to find out the effect of the impurities introduced through the reagents and vessels [9]. Contamination and variation in the blank values due to interfering species, limit the determination of metal at trace levels. The interfering species may give rise to a response from the measuring system and/or mask the analyte from effective participation in the measuring process [9].

RESULT AND DISCUSSION

Table 2: Validation of Results

Serial No.	Elements	True Value	Mean Measured Value	Blank value	Mean Error	Relative Error	Percentage Error (%)
1	Cd	10	10.30	0.41	0.11	0.011	1.10
2	Mn	10	6.86	0.01	3.15	0.315	31.50
3	Sb	10	9.26	0.00	0.740	0.0740	7.40
4	Mg	10	11.43	1.52	0.09	0.009	0.90
5	Ni	10	13.38	0.00	3.38	0.338	33.80
6	Co	10	5.36	0.00	4.64	0.464	46.40
7	Cr	10	9.99	0.00	0.01	0.001	0.10
8	Pb	10	10.60	0.01	0.59	0.059	5.9

Table 3: Mean and Standard Deviation Results of Metal (μg/L) Analysis of Water Sample from Different War Zone Areas of Borno State

	Source	Cd	Ni	Sb	Co	Pb	Mg	Mn	Cr
1	**MART BH**	ND	0.25±0.00	ND	0.53±0.01	2.93±0.31	113.3±2.61	75.60±0.28	0.63±0.00
2	**MAF BH**	ND	ND	ND	0.22±0.01	ND	55.23±0.49	0.25±0.00	1.13±0.00
3	**GER BH**	ND	0.25±0.00	ND	0.163±0.00	1.5±0.00	31.15±0.47	0.50±0.00	ND
4	**KON R**	ND	ND	ND	0.29±0.02	ND	307.3±1.92	0.55±0.07	0.5±0.00
5	**BAM BH**	ND	0.13±0.00	ND	0.27±0.01	0.73±0.10	54.98±0.89	4.33±0.07	0.875±0.00
6	**MOB BH**	ND	ND	ND	0.017±0.007	0.2±0.068	14.975±0.16	2.776±0.058	ND
7	**MON BH**	ND	0.25±0	ND	0.135±0.006	ND	334.7±1.41	7.38±0	0.75±0
8	**DAL BH**	ND	ND	ND	0.285±0.006	4.825±0.112	206.7±1.86	2±0	5.75±0
9	**BAG BH**	ND	ND	ND	0.14±0.00558	0.125±0	8.925±0.068	0.38±0	ND
10	**MDG BH**	ND	0.125±0	ND	0.3025±0.0056	ND	39.975±0.437	32.352±0.165	2.0±0
11	**GWOZ BH**	ND	1.375±0	ND	0.0896±0.017	ND	430.55±1.19	364.75±1.69	4.025±0.056
12	**DAM R**	ND	0.25±0	ND	0.325±0.013	ND	299.025±5.806	3.38±0	18.4±0.056
13	**BIU BH**	ND	0.5±0	ND	0.1225±0.0105	ND	471.3±2.072	127.802±0.14	2.1±0.068
14	**DIK R**	ND	ND	ND	0.22±0.007	ND	39.625±0.62	1.13±0	1.125±0
15	**SHAN BH**	ND	ND	ND	0.275±0	ND	137.22±2.199	2.38±0	0.125±0
16	**ABD BH**	4.33±0.063	0.25±0	ND	0.3375±0	ND	23.251±0.23	50.28±0.164	1.5±0
17	**ASK R**	3.68±0.05	0.5±0	ND	0.213±0	0.625±0	162.38±0	10.38±0	4.452±0
18	**NGA BH**	4.31±0.146	0.125±0	ND	0.2125±0	ND	45.32±0.49	0.5±0	0.875±0
19	**BUU R**	15.38±0.177	12.65±0.13	ND	0.713±0	ND	256.025±3.87	124.36±0.34	37.428±0.533
20	**MAG R**	4.03±0.105	ND	ND	0.4375±0.056	ND	62.6±0.789	2.13±0	0.125±0
21	**GUZML BH**	4.08±0.143	0.125±0	ND	0.2125±0	ND	26.06±0.53	2.25±0	2.75±0
22	**KON BH**	2.68±0.619	0.25±0	ND	0.2125±0	ND	10.998±0.163	17.178±0.065	11.654±0.054
23	**DAMB BH**	4.65±0.163	0.125±0	ND	0.2125±0	ND	79.45±2.524	6.75±0	2.5±0
24	**DIKW BH**	5.6±0.271	0.125±0	ND	0.3375±0	ND	89.475±1.645	2.05±0.068	3.125±0
25	**MARTE R**	4.39±0.1	0.125±0	ND	0.2125±0	ND	17.55±0.26	4.05±0.068	0.5±0
26	**MOBR R**	3.28±0.104	0.13±0	ND	0.213±0	ND	17±0.364	48.602±0.59	6.6±0.056
27	**MARTE R**	6.00±0.319	0.375±0	ND	0.4625±0	ND	108.45±2.70	111.925±0.140	3.13±0
28	**MAID R**	4.98±0.445	0.125±0	ND	0.1125±0.0559	2.7±0.056	144.825±2.01	1.00±0	ND
29	**MAFF R**	5.68±0.34	0.25±0	ND	0.3375±0	1.75±0	145.525±2.31	50.026±0.375	0.375±0
30	**MAGU BH**	5.30±0.142	0.125±0	ND	0.2125±0	ND	19.48±0.37	5.00±0	ND
31	**BAGG R**	5.6±0.104	0.125±0	ND	0.3375±0	ND	44.15±1.01	4.63±0	2.625±0
	WHO PERMISSIBLE LIMIT (μg/l)	**3.0**	**6.0**	**6.0**	**50.0**	**10.0**	**20,000**	**100**	**50.0**

Cadmium (Cd) in Water Sample

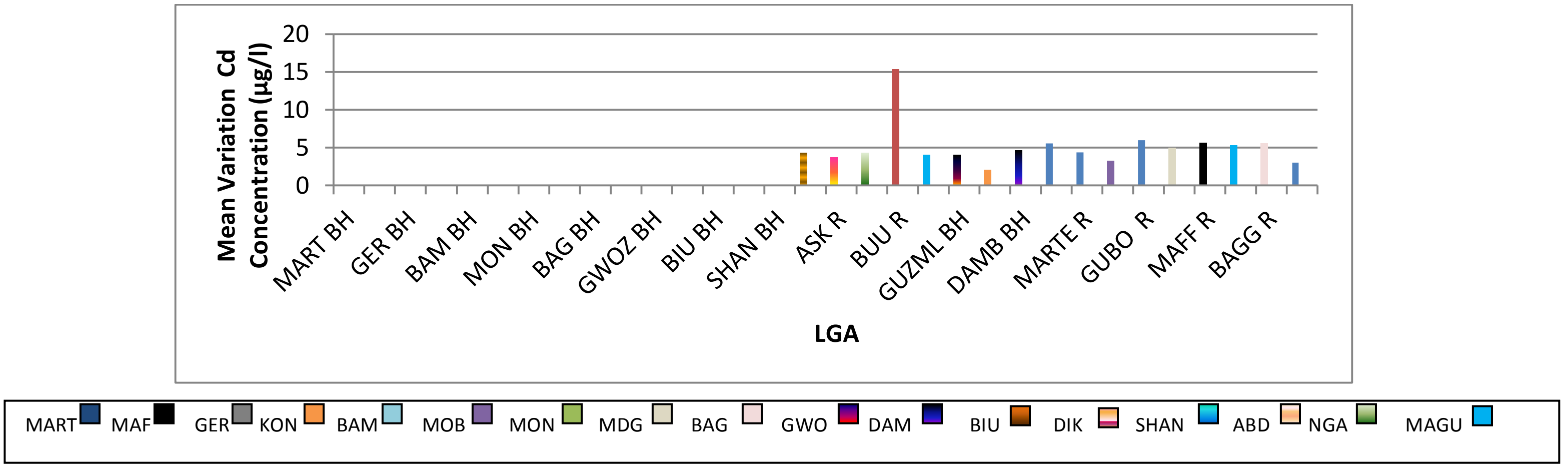

Fig. 2: Mean Variation of Cd Concentration (µg/L) in water samples of the Borno State War Zones

Figure 2 shows the mean values of Cd in the water samples for metal analysis and post hoc test readings. The results ranged from 0.00 to 15.38 ±0.18 µg/L with the highest concentration found in the samples collected from WS 19 (15.38 ± 0.18µg/L). and WS 27 (6.00±0.319 µg/L) (Table 3). WS 1 to WS 15 values were below detection limits (BDL). The mean Cd level of the water samples were all above the permissible limits of 3.0µg/L set by WHO [10]. Tukey post hoc test revealed that the level of Cd in WS 1 -15 were statistically not significant as these were BDLs (Table 3)

Statistical analysis revealed that there was significant difference between levels of Cd in WS 22 and WS 26 at P<0.05. Similarly, the levels in WS 17 and 20 were not significant but were significantly lower compared to those of WS 21, WS 18 and WS 16. Those three were significantly lower than WS 25. Similarly, WS 25 were significantly difference from WS 23 which was lower than WS 28. WS 30 was significantly different from WS 24 which in turn was different from 31. Also levels of Cd in WS 29 were different from those of WS 27 and were lower than those of WS 19. The ANOVA for Pb in decreasing order in the sample is WS 19,>27>29>31, 24>28>23>25>16,18,21>20,27>26 >22. While those of WS 1 – 14 are BDL Figure 2 shows that the mean values of Cd in both borehole and river water samples for metal readings and post hoc test respectively. The extremely high levels of Cd found in some samples in the area, could be attributed to the combustion of gasoline used in mortars and tanks deployed in war. Cd is found to be contained in gasoline [11]. In addition, the explosives of ammunition and bullets which release Cd must have largely contributed to the high level of Cd in the environment. The levels of Cd in the water samples were above the limit permissible in water for use in both domestics and agricultural purposes [12]. The levels obtained for cadmium in all the sites (except WS 1- 15) were higher than those reported for Hengshishu wetland of Northern China [13]. However, the level of cadmium (0.029 mg/L) observed by Honggang *et al*. [14] were higher than values recorded in this study but were similar to the values reported by Yusuf *et al* [15]. Additionally, the levels of cadmium in this study were above those reported by Pavithrapriya. *et a*l. [16] which ranged from 0.2mg/L to 0.7mg/L for Combatore in India. Concentration of cadmium in Maiduguri was found to be BDL to 0.07mg/L) [17] which is below the value obtained in this present study. The control was also found to be within the permissible limit of WHO [10]. The result showed that the Cd levels are building up due to the warring activities. The implication therefore is that the higher levels of Cd in the water samples can bioaccumulate in man and animals that consume the contaminated water in the war zones and can lead to nervous system break down [18].

Nickel in Water Samples

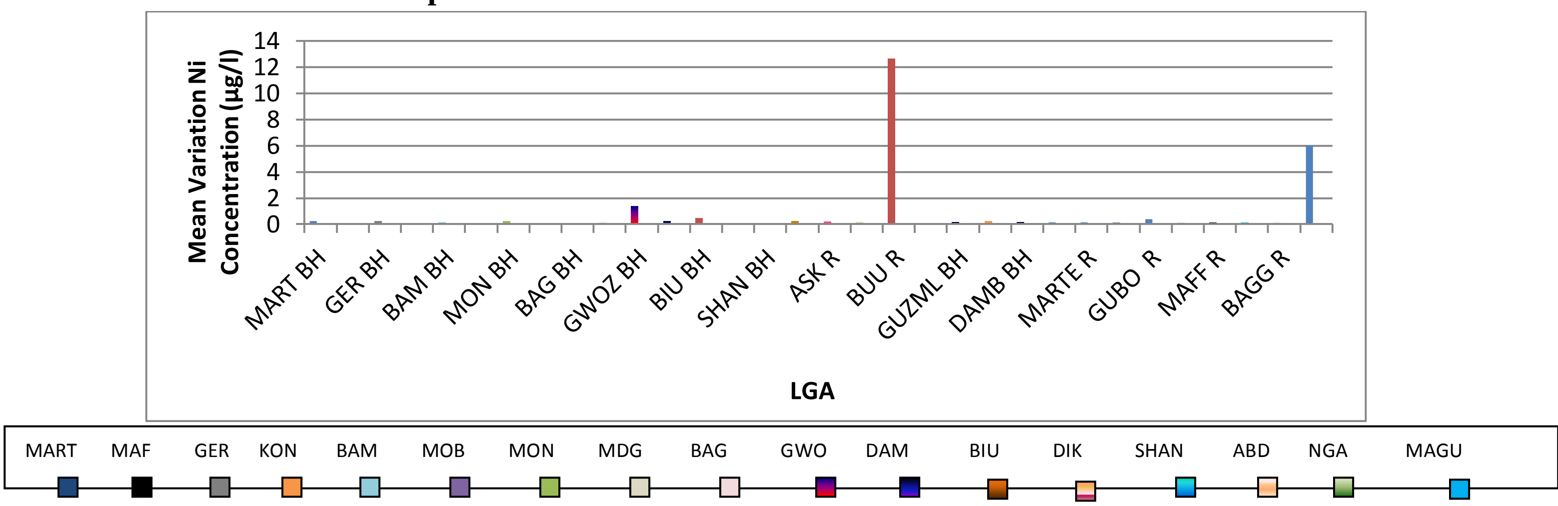

Fig. 3: Mean Variation of Ni Concentration (µg/L) in water samples of the Borno State War Zones

Figure 3 shows that the mean values of Ni in the water samples for metal analysis and post hoc test readings. The result ranged from 0.00±0.00 to 12.65±0.13µg/L with the highest concentration found in the samples collected from WS 19. However, WS 2, 4, 6,8,9,14,15 and WS 20 had the lowest value and were below detection limits (Table 3). The mean Ni levels of all the water samples were all below permissible limit of 6.0µg/L set by WHO [10] except WS19 Biu LGA (12.65±0.13µg/L). Also sample from Gwoza (WS 11) was also high (1.40

µg/L) compared to other samples. The control was also found to be below detection limit of the machine.

Statistical analysis of the data tukey post hoc test revealed that the levels of Ni were significantly similar in WS 5,10,18,21,23,24,25,28,30 and 31 while others were slightly different at $P<0.05$. Analysis for Ni in decreasing order is WS 19>11>17>13>27>29, 22 16, 12, 7, 3, 1> 26, 31, 30, 28, 25, 24, 23, 21, 18, 10, 5. While sample 20, 15, 14, 8, 6, 4 were BDL of the machine. The bombardment of the farmlands with ammunition and explosives may be a contributing factor of Ni level. The mean Ni level in WS 19 is greater than the study by Hengshiu of Manyin [13]. However, the ranges for nickel reported ranged from 0.6 – 2.21µgL^{-1} were above the average of those Ni found in the study [19]. The highest level of Ni determined in WS19 can be attributed to the several wars fought in Biu (12.65µg/L). However, the value of Ni level (0.20 – 8.80 µg/L) recorded in Kubuwa [20] was higher than the concentration determined in this study. Though the level of Ni present in this study can bioaccumulate in the human brain and would affects nervous system [21]. The level of Ni (0.013 µg/L) determined in the study by Honggang [14] was similar to some of the lower limits of this study (0.00 – 12.65 µg/L but Honggang result was below those determined by Priya study [22] which was 0.70µg/L to 3.3 µg/L.

Antimony in Water Samples

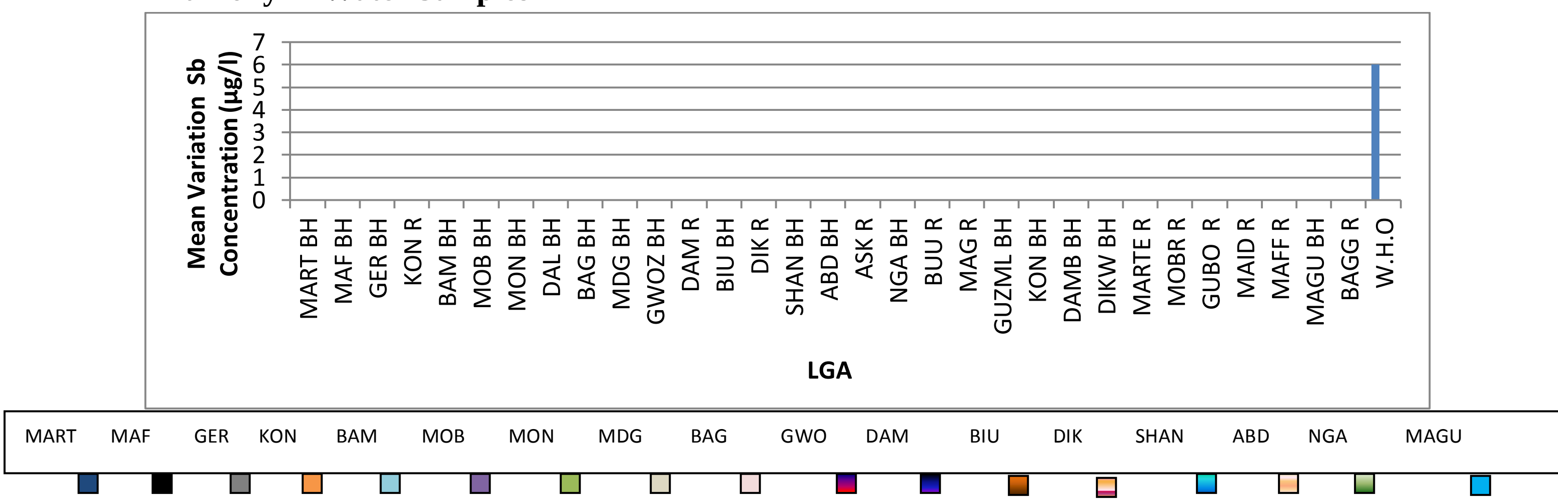

Fig. 4: Mean Variation of Sb Concentration (µg/L) in water samples of the Borno State War Zones

Figure 4 shows that the mean values of Antimony (Sb) in the water samples for metal analysis were below detection limit of the machine. The result therefore suggested that the Sb do not have significant presence in the water studied. Also in study of Odiba [23] Sb level was not detected (Table 3).

Cobalt in Water Samples

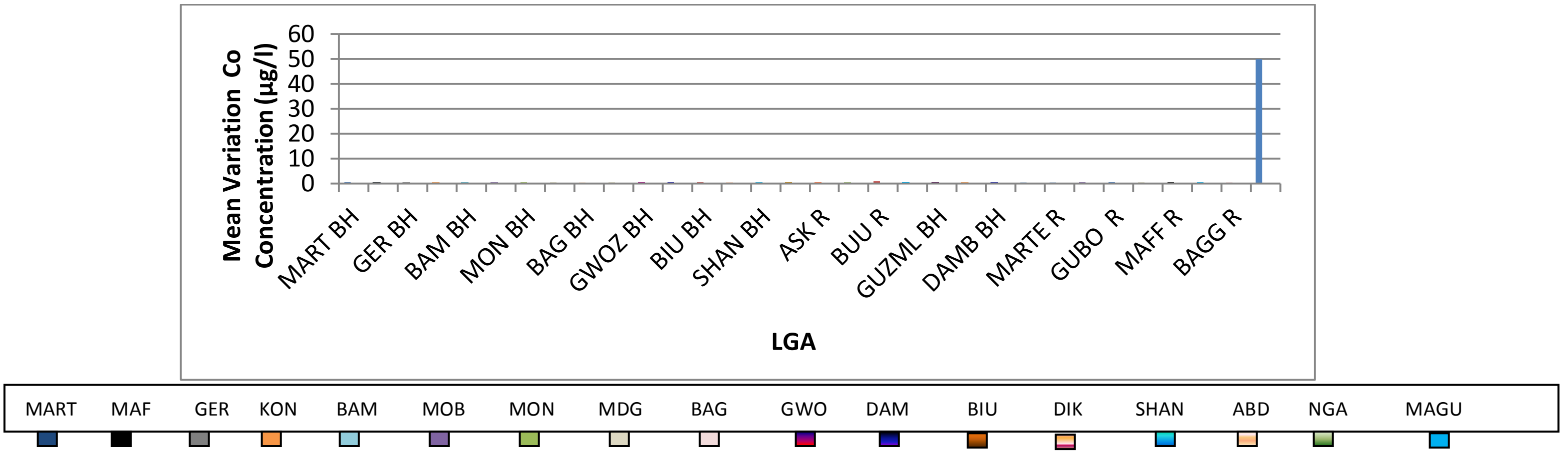

Fig. 5: Mean Variation of Co Concentration (µg/L) in water samples of the Borno State War Zones

Figure 5 shows that mean values of Cobalt (Co) in the water samples and post hoc test readings ranged from 0.017±0.007 to 0.713±0.00 µg/L. The highest value was found in WS 19 and lowest values in WS 6 (Table 3). The mean Co levels of the water samples including the control were all below permissible limits of 50.0µg/L set by WHO [10]. The tukey post hoc test revealed that level of Co in WS 1- 31 were below WHO permissible limits at a confident limit of $p< 0.05$. However, WS 13,7,9,3 and 6 were significantly similar but lower than WS 11. This was in turn lower than WS 28, 14, 2 and 5 respectively. WS 4, 10, 15, 17, 18, 21, 22, 23, 25, and 30, were similar but significantly lower than WS 12. While WS 16, 24, 29 and 31 were similar but significantly lower than WS 20 and 27 with WS 19 as the least with Co concentration. ANOVA for Co in decreasing order for water sample study gives that WS 19 > 27 , 1 , 20 > 31 , 29 , 24 , 16>12 >4, 8, 10 , 15, 18, 21, 22, 23, 25, 26 , 30 >5>2>14>28>11>3, 6, 7, 9, 13. The bombardment of the farmland with ammunition and explosives may be the contributing factor of Co. Comparisons of reported result of this study with that of Oladeji [24] showed that Co level (377.00 – 1520.00µg/L) was far higher than that obtained in present study. However, in Bangladesh study of surface water for Co level (0.01-0.40µg/L) shows that the level of Co in the study is lower than recorded in this present [25].

Lead in Water Samples

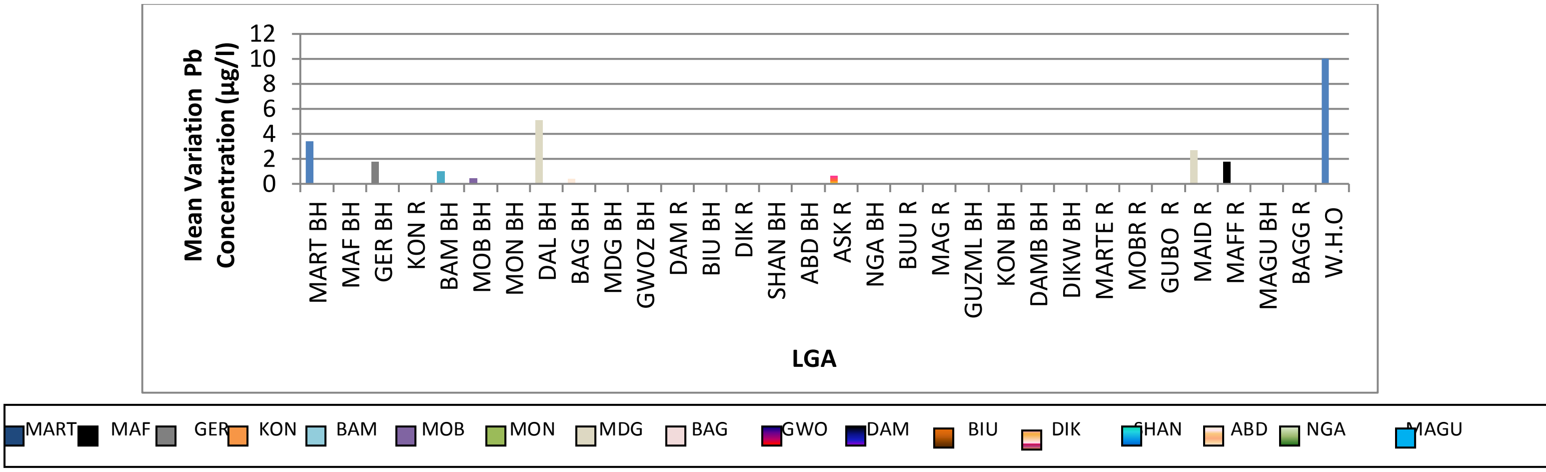

Fig. 6: Mean Variation of Pb Concentration (µg/L) in water samples of the Borno State War

Figure 6 shows the mean values of Pb in the water samples analysed which ranged from 0.00± 0.00 to 4.825±0.112 µg/L with the highest level of concentration found in the sample collected from WS8 (Table 3). The lowest values were found in WS 2,4,7,10,11,12,13,14,15,16,18,19,20,27,30, and 31, which were all below acceptable limits of WHO (5.00µg/L for infant, 10.00µg/L for Adult) [10]. However, WS 8 (4.825±0.112µg/L) was almost closing up to the permissible limit for infant. The control was also found to be within the permissible limit of WHO [10]. The concentration of Pb in borehole water samples from Maiduguri was found to be present as 0.04 to 0.14 µg/L [17] which was below the present study and shows that Pb is building up due to the war activities as seen in Maiduguri sample of Pb 2.7±0.056µg/L. Also in the study of Pb in borehole in Calabar [26] Pb (1.00 µg/L) recorded are lower than the present study. Dam from Pakistan results revealed that lead level was 0.00 µg/L [27] which is in line with those of the present study with Pb level of 0.00 µg/L. In the study of Odiba *et al* [23], Pb level was not detected and in some cases were detected even higher than in this study. Furthermore, a study conducted on water from Ghana revealed the concentration of Pb was 0.038 µg/L [28]. The upper limit of the study never the less was lower than result reported for Bantaji water samples, whose result recorded higher in concentration of Pb as 14.5µg/L which is higher than the upper limits of this study. Pb had mean differences that were statistically significant at $P<0.05$. The presence of Pb in warring weapons and ammunition around the water sources can wash into the water bodies from soil. Pb which is present remarkably in the study area have been reported to bio accumulate in vital body organs and can also affect fetus, infants resulting in lowering of intelligent quotient even at lowest dose [21]. The tukey test reveals that the mean concentration of lead shows slightly significant difference at $P<0.05$. ANOVA of lead in the decreasing order is WS 8 >1>28>29, 3>5>17>6, 9, while the rest samples were BDL of the machine.

Magnesium (Mg) in Water Sample

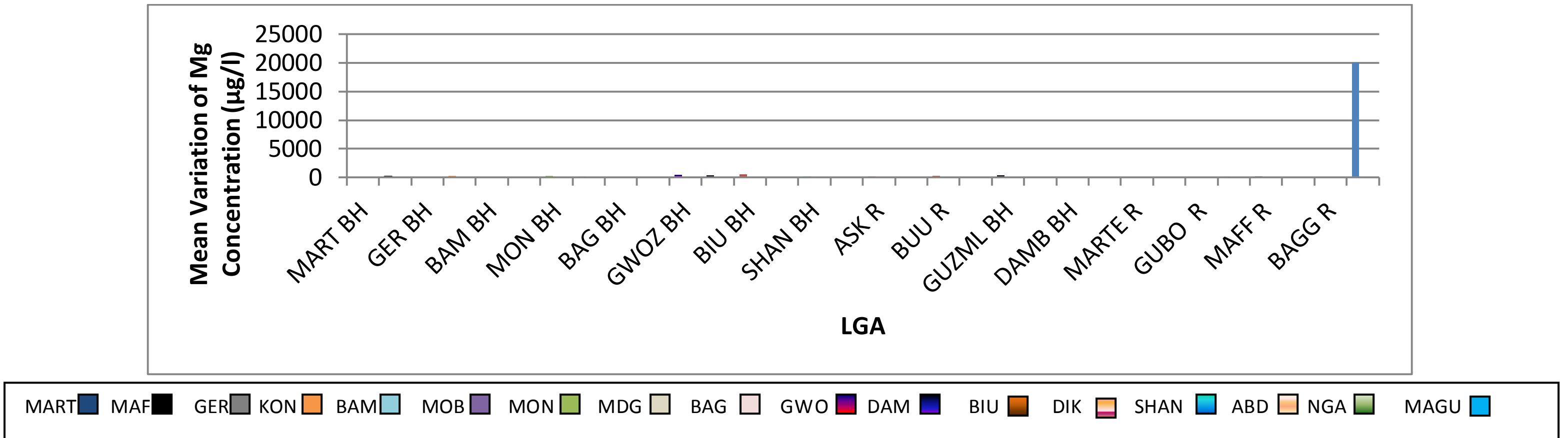

Fig 7: Mean Variation of Mg Concentration (µg/L) in water samples of the Borno State War Zones

Figure 7 shows the mean values of Mg in water sample analysis and post hoc test reading which ranged from 8.928±0.066 to 471.30±2.072 µg/L (Table 3), with the highest concentration found in WS 13 and lowest value in WS 9 all of which were below acceptable limits of WHO (20,000µg/L). The tukey post hoc test revealed that there is slightly significant difference for the samples at $P<0.05$. The WS 9 and WS 22 were similar but significantly lower than WS 6 which in turn is lower than WS 25, 26, and 30. ANOVA of the sample in decreasing order is WS 13 >11>7>4>12>21>19>8>17>29,28>15>1>27>24>23>20>2,5>18>31,10,14>3>16>30,25,26>6>22 > 9. Mathew study shows that Mg for three well waters were 61560.00 µg/L, 513.00 µg/L and 194.00 µg/L, which were far above the values of these study except for 194.00µg/L which was low [20]. Shill's study showed that Mg values for three borehole water gave 33750.00, 9160.00 and 11460.00 µg/L all of which values were higher than this present study [29]. Aremu carried out assessment of Mg in stream water of Kubuwa, F.C.T, Nigeria, on three stream samples. The study recorded 3167.00, 1174.00 and 3725.00 µg/L respectively and the Mg values were far above the present study [30]. Also all values of Mg obtained in this present study were below acceptable limit. The control was also found to be within the permissible limit of WHO [10]. Mg is a necessary mineral in life [29]. Shill also reported that people who drink water deficient in Mg generally appears more susceptible to cardio vascular disease. Deficiency in Mg (as in the case of this present study) is called hypomagnesaemia. It can lead to nausea, health rhythm enzymes Alzheimer disease, fatigue [29].

Manganese in Water Samples

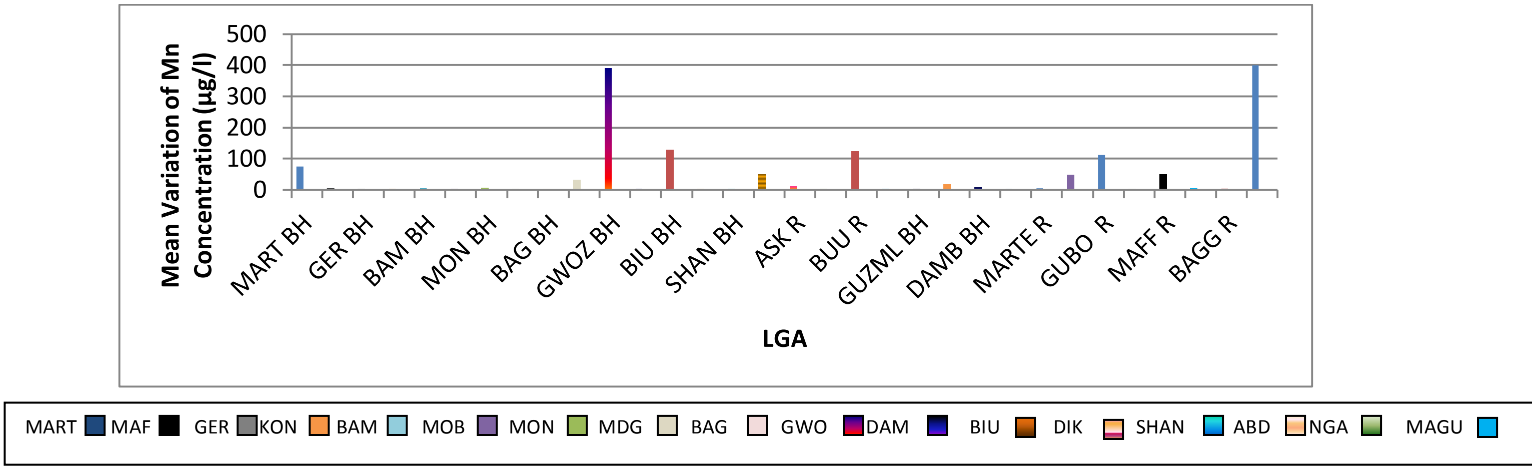

Fig. 8: Mean Variation of Mn Concentration (μg/L) in water samples of the Borno State War Zones

Figure 8 shows the mean values of Mn in water sample analysis of this study which ranged from 0.250±0.00 μg/L to 364.75 ± 56.83 μg/L, with the highest concentration, found in WS 11 and lowest in WS 2. All of the samples (Table 3) were below acceptable limits of WHO (400 μg/L) [10]. Also the upper limit of the present study was below to the WHO acceptable high value [10]. The tukey post hoc test revealed no significant difference at $P<0.05$. The mean concentration of WS 2, 3, 4, 5, 6, 7, 9, 12, 14, 15, 17, 18,20, 21, 22, 23, 25, 30, 31, were similar but slightly different from WS 10.

The ANOVA of this study for Mn concentration in decreasing order is WS 11 >13,19 27 >1, 16 , 29 ,26 > 10 >31, 30, 28, 25,24, 23, 22, 21, 20, 18, 17 ,16, 15, 14, 12, 9, 8, 7, 6, 5, 4, 3, and 2. The concentration of Mn in borehole water samples from Kebbi was found to be 100 μg/L [31] which is below the higher limit of this present study, but higher than the lower limit of the present study. Also in a study in South Saudi, Mn mean concentration on ground water samples was 100μg/L [32]., This value was higher than the lower limit of the Mn determined in the present study. The increase and accumulation of Mn above permissible WHO limits have gross health implication if their presence is more than acceptable level [23]. Often time Mn are transported from one point of contamination to another in form of dissolved species in streams and river or embedded as part of suspended matter [23]. Odiba, further reported that Mn at

160µg/L was obtained [23]. While Njar *et al* [26] reported 20 µg/L and were far lower than present study. On comparing the past studies with the present study, it was observed that most of the sample from the present study, (though within permissible WHO limit) were higher than the level of Mn in the past study sited. This high Mn could be attributed to the increase in war around the sampled areas and this has gross health implication if not treated. Additionally, Mn is used in the manufacturing of weapons used for explosives. Its application is to impact hardness to iron and is currently substituting antimony in weapon production on the said purpose [32].

Chromium in Water Samples

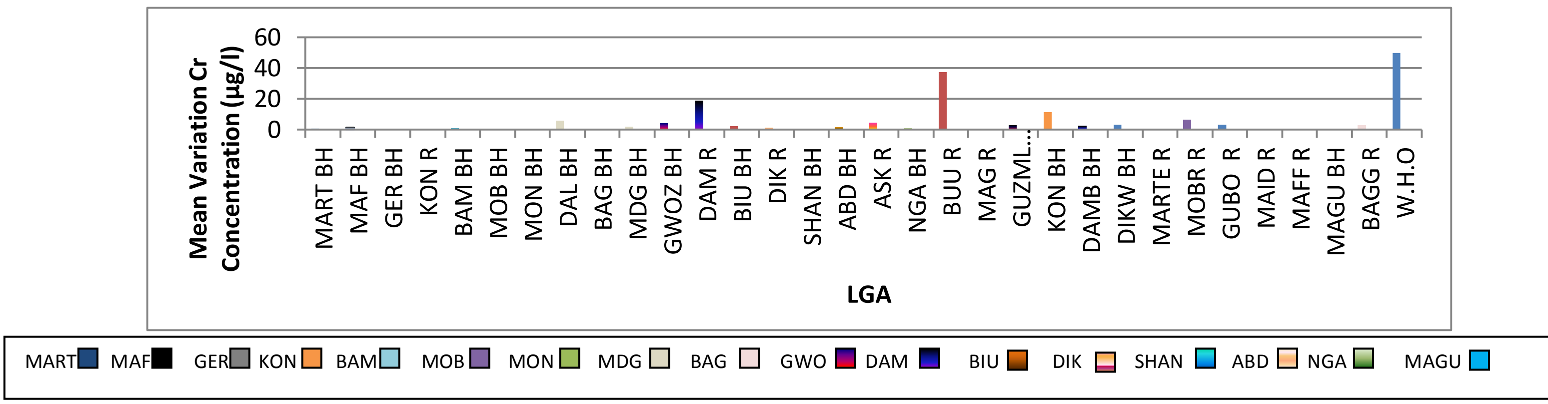

Fig 9: Mean Variation of Cr Concentration (µg/L) in water samples of the Borno State War Zones

Figure 9 shows the mean values of Cr in water samples analysis of this study which ranged from 0.00 to 37.43+0.00 µg/L (Table 3). The highest concentration is found in the WS 19 and lowest level recorded was those below detection limits (BDL) of the machine (Table 3). WS 3,6, 9, 28 and 30 were BDL of the machine. The control was also found to be within the permissible limit of WHO [10]. The tukey post hoc test reveal that at $P<0.05$ the mean concentration of WS 3, 6, 9, 28 and 30 were similar. ANOVA of this study for Cr concentration in decreasing order gives that WS 29>25>4>1>7>18>5>14>2>16>10>13>23>31>21> 24 > 27 > 11 > 17 > 8 > 26 > 22 > 12 and 19 respectively. All the samples were below the acceptable limits of WHO (50.0µg/L) [10]. However this study shows that at WS 3, 6, 9, and WS 20, Cr was not detected and thus may imply that Cr is more readily bound to sediments than other elements. Also low Cr concentration may be due to high Dissolved Organic Nitrogen, Dissolved Oxygen and

Dissolved Organic Phosphorus [15]. The increase in Cr in WS 19 and other zones recorded maybe attributed to the liberation of metals from the sediment to the overlying water under the effect of both high temperature and organic matter decomposition [33]. Meanwhile, the deposition of the metals on those sediments may be from the war activities which involved deployments of high caliber ammunition on the soil. This is possible following detonation and explosives from aircraft, motors and tanks which are known to bear Cr. However, it has been reported that significant amount of Cr, were atmospherically deposited [33]. The level of Cr obtained in Hengshuihu (8.5µg/L) was lower than those reported by this study [13]. The value of Cr in Manyin's study is still far below those reported by Pavithrapriya *et al.* [16] which ranged from 30.00 µg/L to 51.80 µg/L. Pavithrapriya's study was above the level of Cr in this study. Also Cr was observed between BDL and 10.00mg/l [25] which was below the upper limits of this study. Wuana and Okieiman, [21] reported that bio accumulation of Cr in vital organs was possible and that chromium when accumulated in organs can also affect the kidney and central nervous systems. The implication therefore is that building up Cr in amount higher than permissible limits in the bodies of man and animals that drink the contaminated water source is dangerous. There is need to find means of removing this heavy metals (Cr) which might make crops and water unsuitable for human consumption in future by providing appropriate remediation method for metals from the bodies [12]

Correlation of Water Metals

Generally, the levels of concentration of metals in the war bombarded areas sampled were found in the following order: Cd> Ni>Pb> Mn>Co>Mg>Cr>Sb. Pearson correlation analysis (Table 4) was conducted on the levels of heavy metal to assess if there are similarities in the origins. Cd shows strongly positive correlations with Ni, Co, Cr at 0.01 (2 – tailed). Cd also showed correlation with Mn at 0.05 (2- tailed). Ni showed strongly positive correlation with Cd, Co, Mg, Mn, and Cr at 0.01 (2- tailed). Pb showed strongly positively correlation with Ni, Mn, Cr at 0.01 (2-tailed) and also weak correlation with Pb. Mn showed strongly positive correlation with Ni, while Cr showed strongly positive correlation with Cd, Ni, Co, Mg and Mn at 0.01 (2- tailed). Following the extensive deployment of weapons/ ammunition on the war zones with no extensive farming ongoing, this indicates that the metals could mainly originate from warring activities. Weapons are known to bear these metals: Cd, As, Ni, Cr, Mn, Mg, Co, Sb. [11]. It is therefore no doubt that the war is the major contributing factor of those metals following the strong positive correlation between the metals studied. In addition, the high content of these metals found in some samples indicated water pollution via metals (Ni, Cr, Mn, Mg, Co, Cd) presence. However, Sb was below detection limit of the machine. The result of this study when compared to the control zone led to indication of the water quality of the war zone water sampled to have become contaminated due to war deposits. The high correlation therefore shows that the parameters are derived from same sources [34].

Table 4: Correlation of Metals in the Water Samples

		Cd	Ni	Sb	Co	Pb	Mg	Mn	Cr
Cd	Pearson Correlation	1	.694**	.b	.599**	-.143	-.118	.080	.573**
	Sig. (2-tailed)		.000	.	.000	.076	.145	.322	.000
	N	155	155	155	155	155	155	155	155
Ni	Pearson Correlation	.694**	1	.b	.558**	-.091	.257**	.332**	.858**
	Sig. (2-tailed)	.000		.	.000	.261	.001	.000	.000
	N	155	155	155	155	155	155	155	155
Sb	Pearson Correlation	.b	.b	.b	.b	.b	.b	.b	.b
	Sig. (2-tailed)	.	.		.	.	.	.	.
	N	155	155	155	155	155	155	155	155
Co	Pearson Correlation	.599**	.558**	.b	1	.100	-.167*	-.020	.399**
	Sig. (2-tailed)	.000	.000	.		.215	.038	.804	.000
	N	155	155	155	155	155	155	155	155
Pb	Pearson Correlation	-.143	-.091	.b	.100	1	.065	-.081	-.094
	Sig. (2-tailed)	.076	.261	.	.215		.418	.318	.245
	N	155	155	155	155	155	155	155	155
Mg	Pearson Correlation	-.118	.257**	.b	.167*	.065	1	.570**	.274**
	Sig. (2-tailed)	.145	.001	.	.038	.418		.000	.001
	N	155	155	155	155	155	155	155	155
Mn	Pearson Correlation	.080	.332**	.b	-.020	-.081	.570**	1	.232**
	Sig. (2-tailed)	.322	.000	.	.804	.318	.000		.004
	N	155	155	155	155	155	155	155	155
Cr	Pearson Correlation	.573**	.858**	.b	.399**	-.094	.274**	.232**	1
	Sig. (2-tailed)	.000	.000	.	.000	.245	.001	.004	
	N	155	155	155	155	155	155	155	155

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

b. Cannot be computed because at least one of the variables is constant.

CONCLUSION

This environmental assessment of level of metal research in the water samples of Borno State war zone will be useful for the management and planning of the protection of water sources in the warring zones. The metals from these water samples (WS) of war zones were found to be in decreasing order of Cd>Mn>Ni> Pb>Co>Mg>Cr>Sb. The level of metals in the water samples were found as follows: 0.00 to 15.38 ±0.18µg/L (Cd),0.00±0.00 to 12.65±0.13µg/L (Ni), Sb where below detection limit of the machine. 0.00±0.00 µg/L to 0.713±0.00µg/L (Co), 0.380 ± 0.00 to 5.07± 0.11µg/L (Pb), 8.928±0.066 to 471.30±2.072 µg/L (Mg), 0.25±0.00 µg/L to 364.75 ± 1.69µg/L (Mn) and 0.00 to 37.43+0.00 µg/L (Cr). Correlation matrix reveal that warring activities could be the anthropogenic source of Cd, Mn, Ni, Pb, Co, Mg, Cr, in the water samples as most agricultural activities have seized due to war. However, a comparison with previous studies in Maiduguri of Borno State shows accumulation and increase in the metals over time. The strong correlation between metals in the sampled waters further shows that contamination could mainly originate from one source of anthropogenic activity which is war. This is believed to be so because control zone have metals levels all below WHO permissible limit despite the agricultural activities on going in its environment. Presence of Cd, Mn and Ni needs to be looked into as this can cause challenges to humans following direct consumption of the polluted water.

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