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Assessment of Herbicides and Pesticides Residues in Gella Surface Water

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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ABSTRACT

Presence of pesticides residues in ponds and earth dam waters of Gella Town used by the community as a means of water source was assessed. Water samples were collected in triplicates and residual pesticides determined using high performance liquid chromatography (HPLC) techniques. The study showed presence of residual organochlorine, except for beta-BHC not detected in Tangore pond 1 (P01), Tangore pond 2 (P02), Girmana'a pond (P04), and Kurbaca pond (P05); dieldrin and heptachlor were not detected in P04 and P05; and heptachlor epoxide was not detected in P01, P02 and P04. Chlorpyriphos and dichlovos were detected in all water samples. Dieldrin was not detected in Bogga earth dam (ED) and P01. Fenitrothion was only detected in P02 and Majivu'a pond (P03); Fenthion and Malathion were only detected in P02 and P04, respectively. Pyrethroid pesticides were detected in all water samples studied except for bifentrin and deltamethrin not detected in P02, P04; and P02, respectively. Atrazine, paraquat and metalochlor were all detected in water studied, except for P01 in which metalochlor was not detected. The presence of residual pesticides in the ponds and earth dam drinking water sources of Gella is a clear indication of pollution due to anthropogenic activities. This therefore, calls for immediate intervention of Non-Governmental Organizations and both Federal and State Governments to come to the aid of Gella community and provide it with potable water. It is also pertinent that regular monitoring of this pollution factor is important to prevent occurrence of water borne epidemics in the area.

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1. INTRODUCTION

Water is a naturally occurring chemical compound covering about 75% of the total earth surface consisting of ocean water (96.5%), ground water (1.7%), glacial water (1.5%), and water vapor (0.001%). About 2.5% of the earth water is fresh water and less than 0.3% of the fresh water is from the rivers, lakes and atmosphere [1]. This fresh water serves plants and animals to maintain their metabolic activities. Water is generally regarded as polluted when it is impaired by anthropogenic contaminants which either does not support human use such as drinking, and/ or undergoes a marked shift in its ability to support its abiotic community [2]. Globally, this is a serious concern particularly in developing countries [3].

Surface water include water from the streams, rivers, swamps, ponds, dams and oceans. Surface water could be polluted in rural set up such as Gella through non-point source (NPS) pollution. NPS pollution involves diffuse contamination from different sources. It mostly arise due to the cumulative effect of small amounts of contaminants gathered from a large area. Instances include leaching out of nitrogen compounds from fertilized agricultural land, nutrient run-off in storm water over an agricultural field or forest [4]. However, the common water pollutant is the microorganisms. Most of the microorganisms in untreated water are bacteria, viruses and protozoa which causes serious diseases of clinical importance such as cholera and typhoid fever. This pose a serious concern for human health especially in the third world countries without clean potable drinking water and/ or facilities for water treatment [5]. Land clearance for rural industrial set-up and agricultural practices increases catchment run-off which contain a combination of animal wastes, fertilizers, pesticides, herbicides, and soil have been the major source of elevated sediment and nutrient loadings in estuaries and coastal waters [6,7].

Prevalent sources of water pollution are pesticides from farms which when it enters surface water source act like poison to the fauna and flora in the water which subsequently kill and endanger the aquatic life. Water pollution reduces aquatic biodiversity coupled with the fact that no species (or very few) thrive in total isolation in water, the difficulties of one species is often manifested in others [5]. Hence, water purification is inevitable for life sustenance. Herbicides and most pesticides are frequently found in urban run-off, industrial discharges, and agricultural run-off, and these contribute significantly to their high concentration in coastal water bodies [6].

1.1 Pesticides and Herbicide

German scientists under the direction of Gerhard Schrader engaged in the development of both organochlorine, organophosphorus compounds as insecticide and highly toxic nerve gases. Although these chemicals were not used during Second World War, it provided an insight for their use as the main armory in the fight against insects of importance on Agriculture, Public Health and Medicine. The immediate post-war commercial member of this group of chemicals proved very toxic to vertebrates [8].

1.1.1 Pesticides

These are chemicals used to control insects, diseases and other pests attacking crops in the fields [9] and are also hazardous and toxic to organisms. Even at very small concentrations, pesticides are detrimental to humans and animals health [10,11]. They are also toxic to plants [11]. These can enter human body orally through the mouth, dermally through the skin, and through inhalation into the respiratory system [12]. Pesticides can also enter human bodies via ingestion of pesticide contaminated soil, inhalation of soil dust, and dermal contact with soil [13-15]. In addition, it can enter orally due to negligence, eating during and after use without proper hygiene, exposure while mixing [12] or eating/drinking pesticide contaminated material. Dermally pesticide could enter living system when users or organisms are exposed to fumigants. Liquid or powdered pesticides also could be absorbed dermally. Inhalation of pesticides vapors, dusts, sprays particles, smoke from burning containers, and fumes of pesticides during pouring, mixing or application without protective equipment could also expose organisms including humans to dangers of pesticide contamination [12]. Depending upon the degree of exposure to pesticides, short term, acute and chronic health effects could arise. Acute health effects among others include stinging eyes, rashes, blisters, blindness, nausea, dizziness, diarrhea, and even death. Chronic health effects include infertility, immunotoxicity, and disruption of the endocrine functions [16]. A pesticide must ideally be toxic to the targeted pests, not to non-target organisms including humans [17]. The wide use of pesticides to prevent and treat plant diseases and pest in agricultural practices/products made its residual content being frequently reported in drinking and surface water sources [18]. Even herbicides that are more water soluble than organochlorines which are recalcitrant in the environment were also being detected in both surface and ground water sources since 1980s [19]. The detrimental effects of these chemicals to human, animal and aquatic life made their frequent pesticide evaluation of water bodies has become inevitable.

1.1.2 Herbicides

These are generally used in agriculture to remove weeds that would otherwise compete with the crop on farms. The most commonly used herbicides are members of the 2,4-D family, certain carbamates, triazines and also propachlor. Herbicides are classified according to their agricultural functions: foliar or soil application and control of seedling or of established weeds. The persistence of herbicides in the soil is due to their chemical nature and significantly influenced to some extent by temperature, soil type and soil microbiology. Substances with low vapor pressure and low solubilities in water than volatile or chemically unstable ones [8].

The presence of residual pesticides in surface water such as rivers, ponds, and dams ultimately ends up being used in household activities [20] and its acute toxicity to humans and animal life have drawn attention for its worldwide monitoring in drinking water supplies.

The objective of the present investigation therefore, was to explore the level of pesticide residues contamination of Gella ponds and earth dam used as source of drinking water in the area especially in the present century. The assessment result can serve as a baseline in monitoring the future changes and then predict their future effect on the biotic population in the area.

2. MATERIALS AND METHODS

2.1 Study Area

The water samples were collected from five (5) ponds (Tangore ponds 1 and 2, Majivua pond, Girmana'a pond and Kurbaca pond) and Bogga earth dam in Gella Town, Mubi South Local Government area of Adamawa State, Nigeria. It is located at the lower contour of Mandara Mountains, which separates Nigeria from Cameroon. Gella is the Headquarter Mubi South Local Government area lying at the Southern part of Mubi town, Adamawa State and located at latitude 10°15' 98.34'' N and longitude 13° 29' 97.65'' E [21,22] (Figs. 1 and 2).

2.2 Sample Collection

Water samples were collected in a clean 1 L amber bottles in triplicate from five ponds and one earth dam in Gella, Mubi South local government area, Nigeria. The water samples were immediately carried to the Animal Production Laboratory, Adamawa State University, Mubi, for analysis.

2.3 Methods

The method of Association of Official Analytical Chemists (AOAC) [23] with little modification was employed in this study. About 600 ml filtered water samples were transferred into a 1 litre separator and to each 100 ml petroleum ether was added and mixed by shaking for 2 mins and then 10 ml saturated NaCl solution added until the mixture separates. The aqueous layer was discarded and the solvent layer gently washed with two 100 ml portion of water. The solvent layer was transferred to glass stoppered cylinder and the volume recorded. Then, 15 g of anhydrous Na_2SO_4 was added and mixed by shaking. The extracts were concentrated to 10 ml by evaporation to purity.

The detection and determination of the residues were carried out by injecting 1 µL of the 1.0 cm^3 purified extract into the injection port of a Buck Scientific BLC10/11 – model HPLC Las Vegas USA equipped with UV/VIS Detector set at 200 – 700 nm 338 nm. The stainless steel column (250 mm × 4.0 mm i.d.) was packed with Inertsil ODS-3v (5 *µ*m particle diameter, GL Sciences, Las Vegas USA). The column temperature maintained at 30°C. The gradient system consisted of a mixture of acetonitrile and 20 mM

KH_2PO4. The flow rate was 1 mL/min. The initial composition of the mobile phase, consisting of 7% (v/v) solvent A (100% acetonitrile) and 93% (20 mM KH_2PO4), maintained for 7 min. Solvent phase was then increased linearly to 10% at 20 min, 15% at 25 min, 20% at 30 min, and 25% at 45 min to 70 min. Programming was then continued in the isocratic mode as follows: 40% A at 70.1 to 75.0 min and 7% A at 75.1 to 90.1 min. The run time was 17 mins. Identification of pesticide residues was accomplished using mix AB #2 Restek USA reference standards and relative retention time technique while the residues were determined by comparing the peak heights of the samples with the corresponding peak heights of the reference standards of known concentrations. The concentrations of organochlorines were calculated directly by the chromatograph.

3. RESULTS AND DISCUSSION

3.1 Results

The level of organochlorine residues in Gella earth dam and ponds used as source of drinking water (Table 1) shows that all the pesticides studied were present in various concentration at different sources. Aldrin residue presence was recorded for all sources with range between 63 and 92.5 (x 10^{-3} mg/L); alpha-BHC residues ranged between 61.5 and 82.5 (x 10^{-3} mg/L); beta-BHC residues ranged between 34.5 and 42.5 (x 10^{-3} mg/L); dieldrin residues ranged from

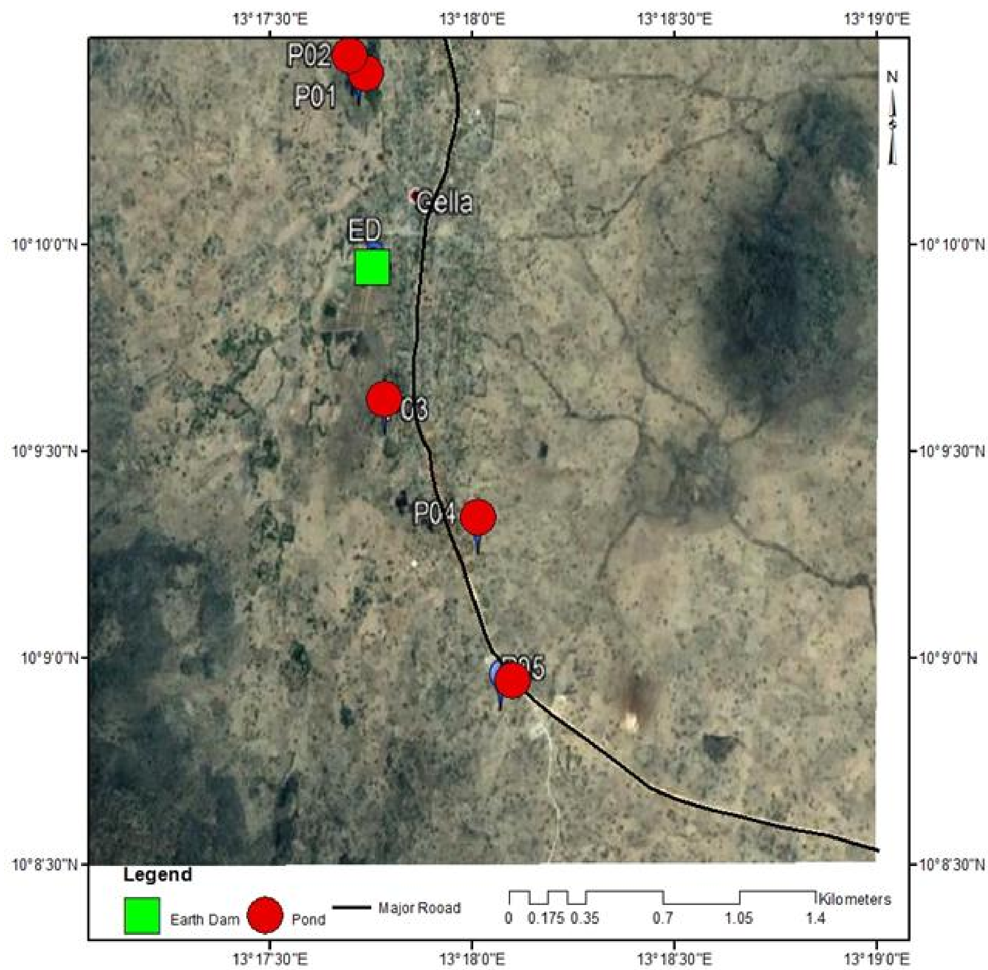

Fig. 1. Google earth map sketch of the earth dam and pond sites at Gella, Mubi South Local Government Area, Adamawa State, Nigeria

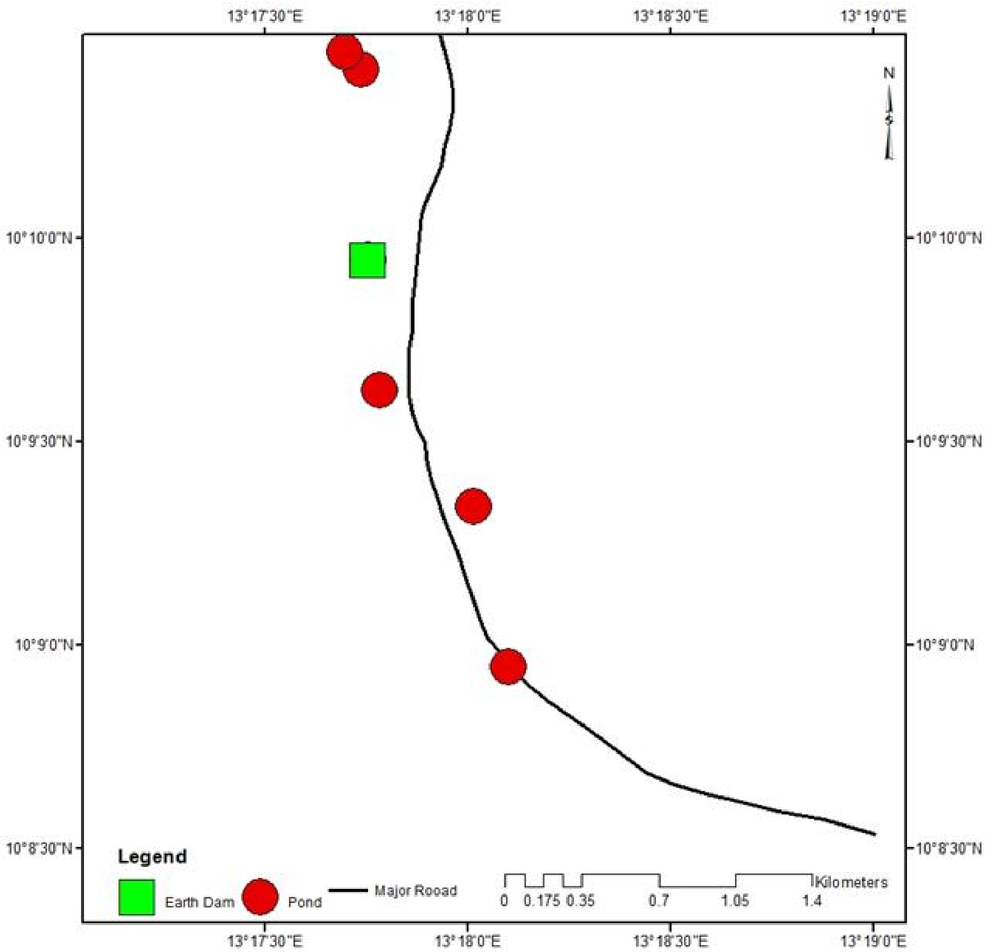

Fig. 2. Earth dam and pond sites at Gella field work 2017

Table 1. Organochlorine pesticide residues in Gella drinking surface water (x 10^{-3} mg/L)

Pesticide residues (mg/L)	E D	P 01	P 02	P 03	P 04	P 05
Aldrin	65.5	74.5	87.5	63.0	92.5	88.5
Alpha-BHC	78.5	61.5	68.5	81.5	82.5	69.5
Beta-BHC	34.5	ND	ND	42.5	ND	ND
Dieldrin	83.0	ND	57.5	75.0	65.0	ND
Endosulfan I	31.5	14.5	22.0	43.5	22.0	48.5
Endosulfan II	22.5	18.0	27.5	15.5	26.0	20.0
Endosulfan sulfate	26.5	37.5	31.5	33.5	29.0	26.5
Heptachlor	11.5	14.5	15.5	22.0	27.5	ND
Heptaclor epoxide	14.5	ND	ND	32.0	ND	24.5

ED = Bogga earth dam; P01 = Tangore pond 1; P02 = Tangore pond 2; P03 = Majivu'a pond; P04 = Girmana'a pond; P05 = Kurbaca pond; ND = Not detected

57.5 and 83 (x 10^{-3} mg/L); endosulfan I and II residues ranged between 14.5 and 48.5 (x 10^{-3} mg/L) and 15.5 and 27.5 (x 10^{-3} mg/L) respectively, while endosulfan sulfate residues ranged between 26.5 and 37.5 (x 10^{-3} mg/L); heptachlor and heptachlor epoxide residues ranged between 11.5 and 27.5 (x 10^{-3} mg/L) and 14.5 to 24.5 (x 10^{-3} mg/L) respectively.

The concentrations of organophosphorus pesticide residues in Gella earth dam and pond water used by the community shows that chlorpyriphos residues in all water sources with various concentration ranging between 12.5 and 55.0 (x 10^{-3} mg/L). Diazinon residues was not detected in ED (Bogga earth dam) and P01 (Tangore pond 1) but found in other sources at various concentration ranging from 11.5-31.0 (x 10^{-3} mg/L). Dichlovos residues was found in all water sources studied ranging from 23.5 to 65.5 (x 10^{-3} mg/L). Fenitrothion residues was only detected in P02 (Tangore pond 2) and P03 (Manjivu'a pond) at a concentration of 14.0 (x 10^{-3} mg/L). Similarly fenthion residues was detected in only ED and P02 and concentrations of 23.0 and 11.5 (x 10^{-3} mg/L) respectively; and malathion was only detected in P04 at concentration of 22.5 (x 10^{-3} mg/L) (Table 2).

The levels of pyrethroids pesticides studied in Gella drinking water (Table 3) shows that bifenthrin was not detected in P02 and P04 but was found in other sources within the range of 2.40 – 21.50 x 10^{-3} mg/L. The cypermethrin residues was detected in all the water samples analyzed within the range of 25-61.50 x 10^{-3} mg/L. The highest level of cypermethrin was in P04 (61.5 x 10^{-3} mg/L) and the lowest in P03 (25 x 10^{-3} mg/L). Delta methrin was not detected in water source P02 but in other sources, the levels ranged from 12.5-37.5 x 10^{-3} mg/L. The highest level of delta methrin was in water source P05 (37.5 x 10^{-3} mg/L) and lowest in ED (12.5 x 10^{-3} mg/L). The level of permethrin residual concentration observed in water sources studied ranged from 22.5-62.5 x 10^{-3} mg/L with highest concentration in P05 (62 x 10^{-3} mg/L) and lowest in P02 (22.5 x 10^{-3} mg/L).

The levels of atrazine, metachlor and paraquat herbicides residual concentration in surface drinking water sources studied is presented in Table 4. The levels of atrazine residue in surface water sources studied ranged from 25-86 x 10^{-3} mg/L; with the highest concentration in P04 (86 x 10^{-3} mg/L) and lowest in P05 (25 x 10^{-3} mg/L). Metalachlor residue was not detected in water source P01 but was found in other sources within the range of 24.5-62 x 10^{-3} mg/L. The highest residual level of metalachlor was in P05 (62 x 10^{-3} mg/L) and lowest in P02 (24.5 x 10^{-3} mg/L). Paraquat residual concentration was found in the range of 63.5-87.5 x 10^{-3} mg/L. The highest residual concentration paraquat was in P05 (87.5 x 10^{-3} mg/L) and the lowest in P01 (63.5 x 10^{-3} mg/L).

Table 2. Organophosphorus pesticide residues in Gella drinking surface water (x 10^{-3} mg/L)

Pesticide residues (mg/L)	ED	P01	P02	P03	P04	P05
Chlorpyriphos	41.5	55.0	23.5	12.5	51.5	41.5
Diazinon	ND	ND	11.5	14.5	24.5	31.0
Dichlovos	65.5	34.5	51.5	45.5	23.5	47.5
Fenitrothion	ND	ND	14.0	14.0	ND	ND
Fenthion	23.0	ND	11.5	ND	ND	ND
Malathion	ND	ND	ND	ND	22.5	ND

ED = Bogga earth dam; P01 = Tangore pond 1; P02 = Tangore pond 2; P03 = Majivu'a pond; P04 = Girmana'a pond; P05 = Kurbaca pond; ND = Not detected; NA = Not available

Table 3. Pyrethroids pesticide residues in Gella drinking surface water (x 10^{-3} mg/L)

Pyrethroid residues (mg/L)	ED	P01	P02	P03	P04	P05
Bifenthrin	2.40	18.5	ND	12.5	ND	21.5
Cypermethrin	37.5	26.5	46.0	25.0	61.5	48.0
Deltamethrin	12.5	23.0	ND	18.5	33.5	37.5
Permethrin	41.5	45.5	22.5	34.0	37.0	62.0

ED = Bogga earth dam; P01 = Tangore pond 1; P02 = Tangore pond 2; P03 = Majivu'a pond; P04 = Girmana'a pond; P05 = Kurbaca pond; ND = Not detected

Table 4. Level of herbicide residues in Gella drinking surface water (x 10^{-3} mg/L)

Herbicide residues (mg/L)	ED	P01	P02	P03	P04	P05
Atrazine	79.0	63.5	53.5	32.5	86.0	25.0
Metalachlor	42.5	ND	24.5	36.5	53.5	62.0
Paraquat	72.0	63.5	81.5	76.0	82.5	87.5

ED = Bogga earth dam; P01 = Tangore pond 1; P02 = Tangore pond 2; P03 = Majivu'a pond; P04 = Girmana'a pond; P05 = Kurbaca pond; ND = Not detected

3.2 Discussion

Organochlorine pesticides (OCPs) have been found to pose greater risks to the aquatic biota mainly due to their recalcitrance in the environment and its magnification along the food chains [24], birds, and marine mammals may also be impacted lethally or sub-lethally [25]. Apart from bacteriological water pollution, residual pesticides in water are also another water contamination index. The presence of OCPs observed in all the water sources studied in Gella earth dam and ponds indicates that there is a case of pollution of the water either through indiscriminate use of the pesticide or through leaching/runoff into the water sources. The most concentrated pesticide residues were aldrin, dieldrin and alpha-BHC. These pesticides belong to class of OCPs, whose accumulation in the environment is due to their chemical nature and physical properties (polarity and solubility in water) makes them recalcitrant [26]. The toxicity to OCPs is dangerous and could lead to carcinogenesis due to polychlorocyclodienes that form epoxides during their biotransformation [27].

The levels of organophosphate pesticides (OPP) observed in water sources studied also indicates pesticide pollution. The high levels of chlorpyriphos and dichlovos could be attributed to the indiscriminate use of the parent chemicals by the community. OPP are easily biodegradable by cytochrome P_{450} enzymes generating more toxic metabolites than the parent compound [28]. They can pose serious danger to biota on exposure to high concentration due to its high toxicity [3].

Pyrethroid insecticides belong to a class of synthetic compounds extracted from chrysanthemum flowers that are noted to “knock-down” insects. They are stabilized to increase persistence in fields applied and /or increase their toxicity [29].

Pyrethroid residual concentrations observed in Gella surface water sources points at the levels of contamination. The high levels of permethrin and cypermethrin in the water samples studied indicates pyrethroid water contamination in Gella. This is detrimental to mammals and insects health. All pyrethroids exert the same mechanism of action in insects and mammals by disrupting the muscular system thereby altering the normal functioning of the voltage-dependent sodium channels. The interaction of pyrethroids with sodium channel makes the cell to operate in an abnormal state of hyper excitability which culminates into depolarization and blocks conduction of the action potential until the situation in the cell becomes unsustainable [30].

High levels of herbicides residues in earth dam and pond waters in Gella indicates either leaching or runoff of the herbicides into the water sources occurred. The persistence and presence of residual herbicides in the water samples could be attributed to their chemical nature. It could also be influenced to some extent by temperature, soil type and soil microbiology [8]. The presence of residual herbicides observed in this study could be attributed to the fact that there is agricultural activities around the water sources every year. The farming activities around the water sites mostly involves herbicides application. This is partly possible due to low awareness of the dangers of indiscriminate use of herbicides in the area.

Li and Jennings [31,32] have evaluated the World wide pesticide standard values (including drinking water), their work hopefully could help Adamawa State and Federal Government develop a systematic pesticide regulation to protect public health.

4. CONCLUSION

The presence of pesticide and herbicide residues in Gella ponds and earth dam indicates water contamination by their residues though at varying concentrations is still of health significance. The Adamawa State and Federal Governments are called upon to come to the aid of people of Gella and provide them with potable drinking water. The non-governmental organizations are also called upon to help the community in whatever means to provide a clean and safe drinking water for Gella community. In addition, Adamawa State and Federal Governments are implored to come up with the regulatory guide values for pesticides.

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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