DETERMINATION OF PESTICIDE RESIDUES IN POND AND EARTH DAM WATER IN GELLA USING GAS-CHROMATOGRAPHY–MASS SPECTROMETER (GC-MS)

Supported by tetfund TERTIARY EDUCATION TRUST FUND

Ismaila Yada Sudi[1,3]*, Stephen Amaechi Orji[1], Maryam Usman Ahmed[1], Priscilla Alexander[2]
[1]Department of Biochemistry, Adamawa State University, PMB 25 Mubi, Nigeria
[2]Department of Pure & Applied Chemistry, Adamawa State University, PMB 25 Mubi, Nigeria
[3]North East Zonal Biotechnology Centre of Excellence, University of Maiduguri, PMB 1069, Bama Road, Borno State, Nigeria
*Corresponding author: yada280@gmail.com

Received: December 08, 2019 **Accepted:** February 27, 2020

Abstract: This study primarily investigates the prevalence of organophophates, organnochlorines and synthetic pyrethroids alongside physicochemical properties of five ponds and one earth dam water in Gella, Mubi South local government area of Adamawa State, Nigeria using Gas Chromatography-Mass Spectrometry (GC-MS) analysis. Among the organochlorines investigated in five ponds and one earth dam water, beta BHC has the least concentration (2.03×10^{-3} mg/L) in pond 2(Tangore 2 pond) and the highest concentration (78.811×10^{3} mg/L) was aldrin in pond 4 (Girmana'a), trace amount of beta BHC in pond 5 (Kurbaca), dieldrinand heptachlor in pond 2, while heptachlor was not detected in earth dam and pond 3 (Majivua pond), beta BHC was not detected in pond 1(Tangore 1 pond) and 3. All pesticides detected in present study were above maximum residue limits (MRL). Organophosphates has a least concentration of diazinon (0.290×10^{-3} mg/L) in pond 3 and a highest maximum concentration of chlopyrifos in pond 4(97.16×10^{-3} mg/L), the maximum concentration of synthetic pyrethroid found was lambda cyhalothrin with a concentration of 92.001×10^{-3} mg/L) in pond 4 and the least concentration is deltamethrin (0.7645×10^{-3} mg/L) in pond 3, atrazine and deltamethrin were not detected in pond 1,4 and earth dam., 2,4-D was not detected in pond 2. The ponds and earth dam water samples of Gella were highly contaminated with pesticide residues and community are highly vulnerable to this pesticide pollution.

Keywords: Earth dam, Gella ponds, organophosphate, organochlorine, pyrethroid, pesticides

Introduction

The quest for clean drinking water has been one of the major challenges in recent times due to pollution from industrialization, agricultural and domestic use of pesticides as well as other related recalcitrant chemicals. The persistent use of pesticides have left tracks of pesticide residues in water bodies which serve a source of drinking water and aquatic habitat in rural areas. The unavailability of clean drinking water mostly in rural areas where ponds, dams, wells and streams are the major water sources have been the major concern to humans. In the recent years, the search for higher crop yield and longer storage life has not only left specific pesticides residues on the soil within which they are applied or in the plant but also on water bodies at concentrations that have attracted the attention of many researchers.

Contamination of ecosystems by pesticides has become a major environmental concern, (Damien *et al*., 2005). The huge amount of herbicides applied in the environment may not reach the target, but contaminate surface and groundwater due to its ability to leach into the soil profile until attaining the water table and the wells. In many cases, runoff occurs and herbicide residues pass through the walls of the wells. Water springs may also contain herbicides, because they are groundwater discharge points. Work by Sereda *et al*. (2009) indicated that pyrethroids found in human breast milk may come fromagricultural use. Bouwman and Kylin (2009) pointed out the need to include agricultural and other uses of pesticides whenevaluating risks to infants from pesticides used for vector control. It is noteworthy that water sources are commonly used for human consumption, especially in rural areas where there are no public wastewater sanitation services. Depending on the physical and chemical characteristics, there is possibility of detection of pesticide residues in wells and water springs; additionally, according to the water treatment system in cities, their detection is possible even in residential water samples (Johnen, 1999). Herbicides represent not only an environmental risk but also a health hazard (Manahan, 2000). Gas chromatography–mass spectrometry (GC-MS) is a method that identifies different substances within a test sample among others. It can also identify trace elements in test materials such as water that were thought to have disintegrated beyond identification (Rowley, 2001). Surface water could be polluted in rural set up such as Gella through non-point source (NPS) pollution (pollution as a result of diffused contamination from different sources). This type of pollution mostly arises due to the cumulative effect of small amounts of contaminants gathered from a large area (Sudi, 2017).

This study is aimed at determination of pesticide residues using GC-MS and physicochemical parameters in ponds and earth dam water in Gella town, Mubi South Local Government Area of Adamawa State, Nigeria.

Materials and Methods

Study area

Gella was earlier described by Sudi *et al.* (2017) as the Headquarter of 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(GEP, 2017).

Sample collection

Water samples were collected in 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.

Sample extraction

The method of Association of Official Analytical Chemists (AOAC, 2000) described by Sudi (2017) was employed. Six hundred (600) ml filtered water samples was transferred into a 1 liter separator and to each 100 ml petroleum ether was added, mixed by shaking for 2 minutes and 10 ml saturated NaCl solution was added until the mixture separates. The aqueous layer was discarded and the solvent layer gently washed with 100 ml portion of water twice. 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 extract was concentrated to 10 ml by evaporation to purity.

Sample preparation

Sample extract resulting from the phase separation of sample preparation supernatant was transferred into a vial tube of graphite carbon, after which each sample was shook for a minute and then centrifuged for 4 – 5 min at 3500 rcf. After which the centrifugation was stopped, and the supernatant used for GC-MS analysis.

Ogah and Coker (2012) pointed that the limit of detection (LOD) of GC-MS equipment used for each pesticide was determined by running an air blank sample under the experimental conditions to obtain the detector baseline noise. A detectable ion should produce a signal that is at least three times the baseline noise. Individual pesticides LOD was estimated by serially running diluted solutions of the pesticide standard and recording the baseline noise ratio (signal-to-noise = 3).

Identification and quantification of pesticide residue

Ogah and Coker (2012) pointed out that identification of pesticide residues could be achieved by matching the retention times and CAS codes to those of the standards. In addition, quantification was done by the external standard method of correlative peak areas with those of pesticide standards under the same treatment. Pesticide residue content for each sample were then analyzed.

$$\text{Pesticide Content} = \frac{\text{As} \times \text{Vf}}{\text{Wt} \times \text{CF}}$$

Where: As = peak area of sample; Vf = final volume of clean extract; Wts = weight of sample extracted; CF = calibration factor = Peak Area of Standard /Total Amount of Standard Injected

All pesticide residues were determined using GC-MS as described by Shinggu *et al.* (2015). Helium (He) flow through the column was set at 1.2 ml/min, injections of 1 µl was done with injector at 275°C in pulsed split-less mode flow rate of 1.0L/min. The MS was operated in electron impact, at an oven temperature maintained at 40°C for 1 min, fitted with a detector voltage of 600-700V, and emission current of 150 µV. The transfer line was from the GC to MS. The MS was operated in electron ionization (EI) mode and data collected atselected ion monitoring (SIM) mode.

Results and Discussion

The analysis of water samples from five ponds namely P1 (Tangore 1), P2 (Tangore 2), P3 (Majivua), P4 (Girmana'a), P5 (Kurbaca),and one earth dam, showed variations which could be attributed to some factors such as location, activities of indigenous inhabitants and season of the year (Table 1). The highest concentration of aldrin (78.811 x 10^{-3} mg/L) was in Girmana'a pond (P4) and trace level in earth dam. Beta BHC was not detected in Tangore 1 (P1), Majivua (P3) ponds, only trace level in Kurbaca (P5) and highest concentration (10.189 x 10^{-3} mg/L) was in earth dam which could be attributed to the nature of its water source (stream). Stream water flows into the dam leaving behind in the dam pesticide residues and debris when it overflows. Dieldrin was found in high concentration (67.748 x 10^{-3} mg/L) in Kurbaca pond (P5) and trace in Tangore 2 pond (P2). Highest concentration of heptachlor (13.022 x 10^{-3} mg/L) was in Kurbaca pond (P5), trace level in Tangore 2 pond (P2), and below detectable limit (ND) in Majivua pond (P3) and Earth dam.

The organophosphates pesticide residues in Gella ponds and earth dam waters (Table 2) showed variations of concentrations for their sources. Chlorophyrifos highest concentration (97.160 x 10^{-3} mg/L) in Girmana'a pond (P4), lowest level (17.020 x 10^{-3} mg/L) in the earth dam water, and diazinon residue was below detectable limit in Kurbaca pond (P5). The highest concentration of dichlovos was in Tangore 2 pond water (67.804 x 10^{-3} mg/L) and lowest in Majivua pond water (6.061 x 10^{-3} mg/L). Fenitrithion residue was detected in Girmana'a pond water (P4) (0.517 x 10^{-3} mg/L), trace amount in Majivua pond water, and below the detection limit (of the GC-MS instrument used) in the remaining water sources investigated.

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

OC pesticides	LOD	P1	P2	P3	P4	P5	ED	WHO Standard
Aldrin	0.002	43.321	17.044	6.332	78.811	39.094	trace	0.0003
Beta BHC	0.004	ND	4.811	ND	2.030	Trace	10.189	0.0006
Dieldrin	0.002	37.119	trace	31.162	30.420	67.748	34.040	0.0003
Heptachlor	0.003	3.660	trace	ND	7.338	13.022	ND	0.0006

OC = organochlorine, ED = earth dam, Tangore = P1, Tangore = P2, Majivu'a = P3, Girmana'a = P4,Kurbbaca = P5, ND = below detectable limit,LOD = Limit of Detection by the instrument used.

Table 2: Organophosphate pesticide residues of water samples in Gella drinking surface water (x 10^{-3} mg/L)

OP pesticides	LOD	P1	P2	P3	P4	P5	ED	WHO Standard
Chlorpyrifos	0.003	31.292	48.716	62.055	97.160	ND	17.020	0.03
Diazinon	0.004	0.311	0.411	0.290	0.310	ND	Trace	0.02
Dichlovos	0.002	40.228	67.804	6.061	31.120	20.208	16.553	0.001
Fenitrithion	0.003	ND	ND	trace	0.517	ND	ND	0.01

OP = organophospates, ED = earth dam, Tangore = P1, Tangore = P2, Majivu'a = P3, Girmana'a = P4, Kurbbaca = P5, ND = below detectable limit, LOD = Limit of Detection by the instrument used

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

Pyrethroids pesticides	LOD	P1	P2	P3	P4	P5	ED	WHO Standard
lambda-Cyhalothrin	0.002	13.104	0.827	1.761	92.001	ND	ND	0.005
Cypermethrin	0.003	72.330	70.645	1.160	98.300	3.712	Trace	0.001
Deltametrin	0.002	ND	Trace	0.733	21.810	ND	ND	0.001
Atrazine	0.004	ND	Trace	3.210	84.170	ND	ND	0.1
2,4-D	0.002	Trace	ND	31.701	79.331	2.571	2.307	0.0006

ED = earth dam, Tangore = P1, Tangore = P2, Majivu'a = P3, Girmana'a = P4, Kurbbaca = P5, ND = below detectable limit, LOD = Limit of Detection by the instrument used

The concentrations of pyrethroids residues in Gella ponds and earth dam waters (Table 3) also similar to organophosphate levels which showed variations of concentrations in their sources.All pyrethroids studied showed their highest concentrations in Girmana'a pond water at different levels. Lambda-cyhalothrin residue concentration detected was high in all samples. The highest concentration was in Girmana'a pond water (92.001 x 10^{-3} mg/L), lowest in Majivua pond water (1.761 x 10^{-3} mg/L) and it was below detection limit in Kurbaca pond and earth dam water sources. The highest level of cypermethrin residue (98.300 x 10^{-3} mg/L) was in Girmana'a pond water followed closely by Tangore 1 and 2 pond water (72. 330 and 70.645 x 10^{-3} mg/L, respectively), and trace in earth dam water. Deltametrin residue concentration observed was higher in Kurbaca water (21.810 x 10^{-3} mg/L) than in Majivua pond water (0.733 x 10^{-3} mg/L), trace in Tangore 2 pond water, and not detected in the remaining water sources. Similarly, highest level of atrazine residue level in Girmana'a pond water (84.170 x 10^{-3} mg/L), lowest in Majivua water pond (3.210 x 10^{-3} mg/L), trace in Tangore 2 pond water, and not detected in the remaining water sources. The level of 2,4-D residue in Gella ponds and earth dam waters was high. The highest level was in Girmana'a pond water (79.331x 10^{-3} mg/L), lowest in earth dam water, trace in Tangore 1 pond water, and not detected in Tangore 2 pond water.

The quest for a pure and clean drinking water clear of pollutants is one of the most challenging tasks in the world. Among environmental pollutants of water bodies are pesticides, organic solvents which on getting into the biological system exert toxic effect at various levels.

Significant concentrations of various studied organochlorines, organophosphates and pyrethroids which are of biological implication were recorded in Gella pond and earth dam waters. Highest average residue concentration of organochlorine (aldrin) pesticide (78.811x10^{-3} mg/L) was observed in pond 4(Girmana'a pond water) which is in consonance with reportof Sudi (2017) and a lowest average (2.030 x 10^{-3} mg/L) value in pond 3(Majivua pond water) and the remaining water sources have trace concentrations. Organochlorines (aldrin, beta BHC, dieldrin, heptachlor) studied showed significant levels of various organochlorine residues. The prolonged half-life and bio accumulative ability makes this class of pollutants biologically important, due to their toxic effect as many derivatives of these pesticides have been banned (USEPA, 2016). OCPs are lipophilic with low vapor pressure, OCPs are known to degrade slowly as such, they penetrate easily and persist. Pond 4 (Girmana'a pond water) has aldrin concentration that may bio-accumulate with persistence and cause adverse effect. OCPs in water samples in drinking-water sources are at concentrations of health concern. Organophosphate residue showed highest (chlopyrifos) average residue concentration of 97.160 $\times 10^{-3}$mg/L in pond 4 and the lowest average residue concentration of diazion 0.230$\times 10^{-3}$ mg/Lin pond 3. Among the organophosphate (chlorpyrifos diazinon dichlovos fenitrithion) pesticides residues screened in water samples;chlopyrifos was observed at concentrations of biological significance. Chlorpyrifos though mainly metabolized enzymatically to highly reactive chlorpyrifosoxon by oxidative desulfuration, and further metabolized to diethylphosphate and 3,5,6-trichloropyridinol (WHO, 2004); its lipophilic nature may form bonds with vital proteins and disrupt homeostasis. Owing to non-polar nature of chlorpyrifos, it is only slightly soluble in water and great tendency to partition from aqueous into organic phases in the environment. dichlovos is present at considerable concentration. Diazinon and fenitrithion are present at low concentrations. Organophosphate residues observed in Gella pond and earth dam drinking-water sources are at concentrations that pose a potential risk of high bioaccumulation.

Highest average pyrethroids concentration was observed due tocypermetrin residue in pond 4 water (98.300$\times 10^{-3}$ mg/L) and a lowest average value of 0.733 $\times 10^{-3}$ mg/L in pond 3 water. Pyrethroids residue was observed in all water samples among the synthetic pyrethroids (lambda cyalothrin cypermethrin, deltamethrin, permethrin and atrazine with 2,4-D) investigated. Cypermethrin shows highest concentration of 98.30 $\times 10^{-3}$ mg/L in pond 4 water (Girmana'a pond water). Cypermethrin concentration observed in pond 4 is slightly above the maximum residue level (MRL). This prevalence may be due to pesticide use and leaching into ponds from contaminated soil or both. At chronic levels, symptoms after exposure to cypermethrin may include brain and locomotory disorders, polyneuropathy and immuno-suppression, and may resemble multiple chemical sensitivity syndromes; it is among the genotoxic pollutant in mouse inducing chromosomal aberration and sister chromatid exchange. It induces systemic genotoxicity in mammals by causing DNA damage in vital organs like brain, liver, kidney, apart from that in the hematopoietic system. It is also a mutagen inducing dominant lethal mutations in male germ cells of mice. It induces chromosomal aberrations and single stranded breaks in DNA in the cultured human lymphocytes (Akan *et al*., 2014).

Deltametrin showed 60.81 $\times 10^{-3}$ mg/L in pond 4 and only trace amount in pond 2. Cyalothrin was observed in ponds 1,2,3 and 4, and completely not detected in pond 5 and ED (below LOD). This relative rareness may results from degradation or its application is not pronounced within the area. However, subsequent application over time may lead to bio magnification. Atrazine showed concentration of 84.17 $\times 10^{-3}$ mg/L in pond 4 and 3.21$\times 10^{-3}$ mg/L in pond 3. Traces of atrazine were found in pond 2 but completely not detected in pond 1,5 and ED. 2,4-D showed concentration of 79.33$\times 10^{-3}$ mg/L in pond 4 but only trace concentration in pond 1 and completely not detected in pond 2.

The various levels of pesticide observed in present study could be due to annual agricultural activities and the use of pesticides and additionally the land location in relation to that of ponds is prone to run offs causing easy flow into these ponds.

Conclusion

The effect of agricultural activities have not only impacted on target pests and weeds but have proceeded to cycles that affect non-target organism with time, this agricultural activities have interfered with ground water bodies as a result of this, it contributes to the unavailability of clean drinking water. From this study, it can be concluded that water sample from five ponds and one earth dam showed various concentrations of pesticide residues. Organochlorines, organophosphorus and synthetic pyrethroid pesticides (though at tolerable concentrations) are of biological implication. Concentration of residues from ponds and earth dam most especially dieldrin, chlopyrifos, cypermethrin and 2,4-D are above stipulated maximum residue levels (MRLs). This implies poor water quality. Water samples from study area showed presence of pesticide residues, despite bans and restrictions on the usage of some of these pesticides in Nigeria, which are still in use and can have been detected in natural water sources. The prevalence of the studied pesticides (organochlorine, organophosphorus and synthetic pyrethroid) in water samples from Gella Mubi North LGA implies that this pollutant either persists in the environment or are still in continues usage.

Values above MRLs are prone to toxic effect on bioaccumulation. Again there is a tendency that ''cocktail effect'' may occur in the body. Both effects may concomitantly exert a synergistic effect. This implies that even at safe levels pesticides maybecome highly toxic, as a result of bioaccumulation of various pesticides in the body (Hernández *et al.,* 2013).

The water samples investigated in present study were highly contaminated with pesticide residue and consumers are highly vulnerable to risk of exposure. This calls for proper measures to be adopted. It is therefore recommended that proper public sensitization on the hazards associated with the use of pesticides should be conducted regularly. Government should encourage "farmer education" on the side effect of unguided use of pesticides. Proper boiling and sieving of water is a necessity that should also be emphasized and encouraged among the community.

Conflict of Interest

Authors declare there is no conflict of interest related to this study.

References

Akan JC, Sodipo OA, Maohammed Z & Abdulrahaman FI 2014. Determination of organochlorines, organophosphorus and pyrethroids pesticides residues in water and sediment samples by high performance liquid chromatography (HPLC) with UV/Visible detector. *J. Anal. Bioanal. Tech.,* 5(6): 226 doi:10.4172/2155-9871.1000226

Association of Official Analytical Chemists (AOAC) 2000. Official methods of analysis,

Vol. 25, 18th edn. Washington DC, pp. 1864- 1871.

Bouwman H & Kylin H 2009. Malaria control insecticide residues in breast milk: The need to consider infant health risks. *Environ. Health Perspect.,* 117(10): 1477-1480 doi:10.1289/ehp.0900606

Damien AD, Georges M, Puy L, Jean-Luc P & Eric P 2005. Multi-residues analysis of pre-emergence herbicides in fluvial sediments:application to the mid-Garonne River Ecole Nationale Supe´rieure Agronomique de Toulouse, Institut National Polytechnique, Laboratoire Agronomie Environnement Ecotoxicologie (AEE), Avenue de l'Agrobiopole, BP 32607, Auzeville tolosane, 31326 Castanet-Tolosan.

Hernández AF, Parrón T, Tsatsakis AM, Requena M, Alarcón R & López-Guarnido O 2013. Toxic effects of pesticide mixtures at a molecular level: their relevance to human health. *Toxicol*., 307: 136-145. Doi:10.1016/j.tox.2012.06.009

Johnen BG 1999. Herbicides and food quality a misfit. In: *Proceedings of Brighton Conference, Weeds*,Vol. 3, British Crop Protection Council, UK, pp. 875–882.

Manahan SE 2000. Environmental Chemistry, 7th edn. CRC Press: Boca Raton, FL, doi:10.1201/9781420056716

Ogah CO & Coker HB 2012. Quantification of organophosphorus and carbamate pesticides residues in maize. *J. Appl. Pharm. Sci.,* 2(9): 093-097.

Rowley A 2001. Evaluating uncertainty for laboratories:apractical guide and handbook. Vol. 1, Allan Rowley Associates.

Sereda BH, Bouwman H & Kylin H 2009. Water, bovine milk and indoor residual spraying as contributing sources of DDT and pyrethroid residues in human milk from Northern KwaZulu-Natal, South Africa. *J. Toxicol. Environ. Health Part A*,72: 842-851.

Shinggu DY, Maitera ON & Barminas JT 2015. Levels of organochlorine pesticides in fish, water and sediments in Biu Dam (Reservoir) Borno State Nigeria. *Int. Res. J. Pure Appl. Chem.,* 5(2): 150-159.

Sudi IY 2017. Assessment of herbicides and pesticides residues in Gella surface water, *Asian J. Adv. Agri. Res.,* 3(1): 1-3. DOI: 10.9734/AJAAR/2017/36785

Sudi IY, Buba FA, Ahmed MU, Gideon HB & Zaruwa MZ 2017. Quality evaluation of earth dam and pond water in Gella, Mubi South local government area. *Asian J. Environ. Ecol.,* 4(2): 1-10. http://www.sciencedomain.org/issue/3003

USEPA 2016. United States Environmental Protection Agency. National Primary Drinking Water Regulations.

WHO 2004. World Health Organization, Guideline for Drinking Water Quality, 3rd Edition.