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Study of Physicochemical Parameters and Organochlorine Pesticide Residues of Water from Gusau Dam and Water from Treatment Board in Gusau, Zamfara State, Nigeria

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Abstract- In this study, effect of conventional water treatment on the removal of organochlorine pesticide residues OCP was evaluated. Water samples were collected from Gusau Dam and Gusau water board. The two samples were analyzed for the present of OCP using QuECHERS and GC-ECD for samples preparation and analysis respectively. Twenty organochlorine pesticide standard were used and only five organochlorine pesticide residues were detected in the water samples from Dam namely; alpha lindane, endosulfan ether, isodrine, heptachlor epoxide and DDMU with concentration 0.0250 mg/L, 0.0270 mg/L, 0.0141 mg/L, 0.0003 mg/L, 0.0016 mg/L respectively. Only two OCP residues are detected in treated water samples namely; lindane and endosulfan with concentration 0.0001 mg/L and 0.0012 respectively. The entire organochlorine pesticide residue detected in dam water samples are within the maximum residual limit (MRL) except alpha lindane and endosulfan ether that are little higher than 0.02 mg/L of MRL while that of treated water are below MRL. Statistical analysis (t-test) of physicochemical shows that, there is no significance difference between the physicochemical parameters of water samples from Dam and water board. The presence of organochlorine pesticides residues in the dam shows that farmers are still using these banned organochlorine pesticides for pest control; therefore, there is need for routine monitoring and the use of effective absorbent for water treatment in order to minimize health risk to human.

Keywords: Organochlorine pesticide, physicochemical, Gusau Dam, Gusau Water Board

1. INTRODUCTION

The Gusau Dam is the main source of tap water that supplies the Gusau local government in the state of Zamfara. Vegetable farming and other agricultural activities take place on the riverside to provide water for irrigated agriculture. It's not new for farmers to use pesticides like organochlorine to protect their crops from pests and diseases in order to make good produce. This indiscriminate use of pesticides to ensure adequate crop protection can result in pesticide deposition in the soil and lingering in the environment for months or even years [14],[12].

The persistence of these pesticides can in turn enter the groundwater through runoff or through wind and erosion. The occurrence of these pesticides in surface and groundwater around the world has been confirmed by various researchers in varying concentrations, often above the maximum residual limit stipulated by the environmental ordinance. Even in traces amount they can form a complex mixture that can pose serious health risks [12],[16].

Commercial use of pesticides has the potential to contribute to significant symptomatic human disease,

both acute and toxic, with long-term carcinogenic potential. The U.S. Environmental Protection Agency and other international organizations set standards for the safe use of pesticides and the maximum amount of any pesticide that can be present in drinking water. This regulation seeks to minimize the harmful effects of pesticides and their breakdown by products on humans [5].[6],[7].

Physicochemical parameter that determine water quality

WHO 2006 guideline, defines safe (quality) drinking as water that does not pose a significant health risk throughout consumption, including differential sensitivities that may arise between life stages. Physicochemical parameters are the physical and chemical properties that determine the quality of water. These are pH, color, turbidity, chloride, nitrate/nitrite (NO_3/NO_2), electrical conductivity, sulfate and total hardness.

Traditional water treatment methods aim to remove 85-90 percent of the biochemical oxygen demand BOD and suspended solids, including the removal of coliform bacteria. Some water treatment plants use advanced techniques for filtration in order remove other pollutants and the use of chlorine, ozone and UV light. This conventional technique does not remove pesticides and their residues from the community's drinking water supply [8],[9].

With the increase in bandit activity in rural areas of Zamfara state, farmers are migrating to the cities for various agricultural practices. This has led to increase in agricultural activities and the use of pesticides and other agrochemicals on the banks of the Gusau Dam. The commercial pesticides such as organochlorine pesticides used by farmers enter and remain in the soil through direct application, which over time find their way into groundwater and drinking water supplies [2].

Because of the hydrophilic and refractory nature of most pesticides, conventional water treatment techniques for municipal water supplies, such as coagulation, flocculation, sedimentation, and filtration, have been inefficient in removing these pesticides from drinking water. A trace level can pose a serious health risk with long-term carcinogenic potential [26].

2. MATERIALS AND METHODS

Chemicals, Reagents and pesticides standard used were of analytical grade. All glassware was cleaned with detergent raised with distilled water and acetone before use. Gas Chromatograph with Mass Spectrometer-Detector (GC-MS) pair are used for analysis. Gas Chromatograph with Mass Spectrometer-Detector (GC-MS) pair (Model 7890 Agilent instruments Technologies), oven (model: E028-280v), pH meter (Beckman model 72).

2.1 Sample Collection: water sample was collected from the Gusau Dam in October,2021, the period of collection will be monitor to Gusau water treatment board and collected water sample after treatments.

2.2 SAMPLES PREPARATION

Water samples from Dam and water board were filter using whatman No 5 filter paper to removed particulate matter. I% of HCL was added to each 1 liter of the samples in order to inhibit the biological activities and adjust the PH of the water samples.

2.3 Extraction of organochlorine pesticide residues from water samples

The Quick Easy Cheap Effective Rugged Safe (QuEChERS) method was used with a slight modification to extract organochlorine pesticide residues 10ml of water sample was measured into cleared 50 ml test tube; 2.5 cm^3 of acetonitrile was added and shaken vigorously for 30 minutes another 2.5 ml of acetonitrile was added and capped, then kept

In the freezer at about 18 oc for 15 minutes before 5 g of MgSO4 and Nacl was added for easy separation and increased the polarity. The mixtures were centrifuge at 4400 rmp for 5 minutes, this is to ensure, organic pesticides were dissolved in the solvent. The upper layer was removed into a cleared container containing MgSO4 to dried trace of water and further cleans up [3].

2.4 CLEAN UP

The extract was loaded onto the pesticide cartridge and washed with acetonile evaporated to dryness using a rotary evaporator and a nitrogen bleed this was re-evaporated before dilution with acetonile and saved for analysis [3.]

2.5 INSTRUMENTATION

The analysis was performed using an Agilent Technologies GC-MS model 7890 equipped with an auto sampler, a capillary column length of HP5 ms

with a length of 30 m and an internal diameter of 0.320 mm and 0.25 micron. The temperature was program 60°C held for 5 minutes at 8°C per minute to the final temperature of 300°C held for 0.5 minutes and the MSD transfer line was held at 300°C. A one micro liter split injection was performed at 300°C injector temperature with a purge flow of 3 ml/minute, the carrier gas used was helium at a flow rate of 2.17 ml/minute and the pressure was 150 kPa. The interface temperature was 300°C. The ionization mode of the Agilent Technologies Model 5975 mass spectrometer was electron impact with an ion source temperature of 230 °C and ranges from 45-500 M/Z in full scan mode.

The internal standard technique was used to analyze the samples extracts. The organochlorine standards used are Alpha-Lindane, Delta-Lindane, Endulfan I&II, Heptachlor, Aldrin, Isodrin, trans-Chlorine, DDMU, DDT, P,P-DDE, Dieldrin, Endrin, Mitotane, Endrin-Keto, Melhoxychlor and Delta -Pent.

The standards are prepared at various concentrations from 0.100ppm to 2.00ppm and were used to generate calibration curves for each compound. The efficiency of the method was validated with recoveries of reference material without pesticide residues and with four 0.1 ppm and 1.0 ppm spiked organochlorine pesticide residues.

Table 1: Measurement and Condition of GC-MS

Parameter	Optimized conditions
Colum temperature	250^{oc}
Detector temperature	300^{oC}
Injection system	Split mode
Injection temperature	300^{OC}
Injection volume	1.0µL
Carrier gas	Helium
Colum length	300 mm
Rate of carrier gas	2.17/min

3. RESULTS AND DISCUSSION

Table 2 Results of physicochemical analysis water from Dam and water board presented in mean, standard deviation and standard error

Parameters	**DAM water**	**Treated water**	**WHO STD**
Temperature	28.9967±0.00701 (±0.02%)	28.5667 ±0.0533 (±0.19%)	--
pH	7.86±0.0489 (±0.62%)	7.76 ±0.0789 (±1.02%)	6.5-8.5
Turbidity (µTU)	13.48 ±0.0244 (±0.18%)	6.83 ±0.048 (±0.70%)	5
TDS (mg/L)	184.08 ±0.00924 (±0.01%	166.2 ±0 (±0.00%)	500
Alkalinty mg/L	45.97 ±0.0562 (±0.04%)	77.2667 ±0.0896 (±0.12%)	-
Total hardness	248.625±170.013 (±68.38%)	115.5667±0.0533 (±0.05%)	150
Sulphate mg/L	24.18 ±0.257 (±1.06%)	10.2667 ±0.0533 (±0.52%	100
Nitrate mg/L	19.6333 ±0.0533 (±0.27%	8.2633 ±0.00533 (±0.06%)	0.2
Chloride mg/L	14.43 ±0.0562 (±0.39%)	46.3433 ±0.0107 (±0.02%)	250
Fluoride mg/L	1.65 ± 0.00924 (±0.56%)	2.0867 ±0.00533 (±0.26%	1.5
Conductivity µs/cm	106.60 ± 00621	412.00 ± 0.0032	1000

STATISTICAL ANALYSIS

Using statistical tool (t test) to compared physicochemical parameter of data obtained from Dam and water board (treated water). The two tailed P value is 0.7447 and conventional criteria shows that the two data are not statistically s significant.

a. Temperature: the temperature of water sample from Dam is 28.99 ± 0.007 and that of sample from treated water sample from water board is 28.56 ± 0.005. The temperature of water sample from Dam is little higher that treated water. The reason may not far, that water from Dam is exposed to direct sunlight and other sources of heat.

Temperature of water is used in calculation of various form of alkalinity and identification of source of water supply.

The value of temperature of water sample from dam is higher than the value of temperature (19.10) reported by [20] in water sample from gold mining area in northern Nigeria. [13]also reported the value of temperature (26.05) in well water samples from Gusau metropolis. The result of present study shows a higher value of temperature than the value reported by [20]. The variant in the results maybe result of period or the season when samples were collected.

The pH of water sample from Dan is 7.86±0.0489 which is higher than Ph of water from water board (7.76 ±0.0789) both the pH are with the range standard pH set by WHO ranges from 6.5 – 8.5. it worthy to known that pH value, refers to a measure of how acidic or basic the water is. One of the main goals in controlling pH is to minimize corrosion and scale in the distribution system.

b. Alkalinity of water from Dam is 45.97 ±0.0562 which is lower than the alkalinity of water from water board77.2667 ±0.0896.Alkalinity of water is mainly caused by the presence of hydroxide ions (OH^-), bicarbonate ions ($HCO3^-$), and carbonate ions ($CO32^-$), or a mixture of two of these ions in water. The alkalinity of the present research is lower that the value of alkalinity reported by [21] from drinking water obtained drinking water in Abuja, Nigeria.

c. Chloride: the chloride level of treated water from the board is 46.34mg/L which is higher than 14.43 mg
/L of chloride obtained from Gusau Dam, the higher value of chloride in the treated water may be as result of addition of chlorine as a disinfectant for killing of germs. It worthy to known that chlorine gives Salty taste and the concentration varies depending on the chemical composition of the water. Chlorine above 250 mg/liter of chlorine can have a noticeable salty taste.

d. Total hardness: the total hardness of water sample from Dam is 248.645 mg/l which is higher than the value of total hardness obtained after treatment (115.566 mg/L). Total hardness revealed the total concentration of metal ions, expressed in mg/L equivalent CaCO3 and the primary ions are Ca^{2+} and Mg^{2+} and ions like Fe^{2+} and Mn^{2+} make up the total hardness. The present value is lower than the result of [21] that reported 136.72 mg/L in drinking water from Abuja, Nigeria. The result is also lower than the value reported by Rabiu *et al*, 2018, from water sample obtained from matari Dam.

e. Turbidity: the result of turbidity of water sample from Dam is higher (110) than water sample from water board (5). The higher value of turbidity obtained from Dam water maybe as result of particles present in the open Dam. Also after treatment the turbidity reduced significantly, this maybe as result of filtration and sedimentation process. This present result is higher than the value of turbidity reported in the work of [21] from drinking water source from Abuja, Nigeria. Turbidity Suspended matter and organic particles can cloud the water and make it cloudier. This sediment can carry pathogenic pollutants harmful to humans. When the turbidity is above 15 Nephlometric Turbidity Units (NTU) it considers harmful [1].

F. Sulphate level in the dam water sample is 24.18 mg/L, this is higher than water sample from treatment board. If the sulphate level in the water exceeds 250mg/L, it will make the water uncomfortable to drink [23]. This shows that the treatment process might had reduced the sulphate level in the water. While the nitrate in the Dam water 12.8 mg/l and reduced to 4.1 mg/l after it undergoes treatment process. The concentration of nitrates in water is normally low, but can reach high levels due to leaching from agricultural land or contamination from human or animal waste. The maximum permissible guideline value of the WHO for nitrate is 50 mg/liter and for nitrite 3 mg/liter[23

Table 3 GC-MS Result of Organochlorine Pesticide Residues in Water Samples

Organochlorine residues	RT ofstd (min)	RT of sample (min)	Area of std	Area of sample	Conc. of OCP residues DAM mg/L	CONC. of OCP residues in WB Mg/L
.delta.-Pentachlorocyclohexene	10.028	0	353817	ND	ND	ND
.alpha.-Lindane	11.738	11.761	129752	327	0.0250	0.0001
.delta.-Lindane	14.29	ND	1142875	ND	ND	ND
Endosulfan ether	14.519	14.514	276180	739	0. 0270	0.0012
Heptachlor	15.229	ND	2515872	ND	ND	ND
Aldrin	16.047	ND	1901251	ND	ND	ND
Isodrin	16.654	16.671	86294	122	0.0141	ND
Heptachlor epoxide	17.128	17.569	2447491	72	0.0003	ND
trans-Chlordane	17.769	ND	3529360	ND	ND	ND
DDMU	18.055	18.004	357696	58	0.0016	ND
trans-Nonachlor	18.422	ND	2710779	ND	ND	ND
p,p'-DDE	18.622	ND	6311	ND	ND	ND
Dieldrin	18.879	18.874	1473560	ND	ND	ND
p,p'-DDE	19.057	ND	3154273	ND	ND	ND
Endrin	19.48	ND	598174	ND	ND	ND
Endosulfan	19.892	19.852	745763	ND	ND	ND
Mitotane	20.482	ND	4536	ND	ND	ND
Endosulfan sulfate	21.191	ND	579813	ND	ND	ND
Endrinketone	22.564	ND	777102	ND	ND	ND
Methoxychlor	23.405	ND	5700249	ND	ND	ND

KEY; RT = retention time, OCP = organochlorine pesticide, ND = not detected

Tables 2 shows the GC- MS result of organochlorine standard and water samples from Dam and water board, twenty organochlorine pesticide standards were used for the analysis. The area of chromatogram peaks of standards and sample as well as retention time of both samples and standard were reported in the table 1 above.

Five organochlorine pesticide residues were detected from water sample from Dam namely; alpha lindane, endosulfan ether, isodrine, heptachlor epoxide and DDMU with concentration 0.0253 mg/ L, 0.0270 mg/L, 0.0141 mg/L, 0.0003 mg/L and 0.0016 mg/L respectively. Alpha lindane and endosulfan ether are detected in the treated water from water board.

The concentration of endosulfan ether (0.0270 mg/L) is the highest in water sample from the Dam, follow by alpha lindane (0.0250 mg/L), isodrine (0.0141 mg/L), DDMU is (0.0016 mg/L), and the lowest concentration of organochlorine pesticide residues detected is heptachlor (0.0003 mg/L) in the water from DAM.

The alpha lindane detected with concentration of (0.0250 mg/L) is higher than 0.02 mg/L maximum residual limit accepted in drinking water byWHO. The reduction of concentration (0.0001 mg/L) after water treatment may be as result of filtration and sedimentation process of water treatment, some might have be trapped by the filter material [18].

Alpha lindane is an isomer of hexachlorocyclohexane (HCH), which has been banned for agricultural insecticide because of its neurotoxin effect in human [24].

The presence of lindane in the water samples from Dam might has come from the indiscriminate used by farmer along the river bank, because farmers consider this pesticide very active, cheap and readily available despite banned by regulatory agents[19.]

The concentration is lower that the concentration of alpha lindane reported by [12] in the water samples from coco farm land in Ghana.

Endosulfan ether was determined with concentration of (0.027 mg/L) and (0.0012 mg.L**)** in water from Dam and water board respectively. The concentration from dam is higher than the concentration after the dam water undergoes treatment. Both concentrations are below the maximum residual limit (MRL) of 0.5 mg/L accepted by WHO. It was reported that endosulfan ether persists in the soil more than other organochlorine pesticide residues [14] reported high endosulfan (1.924 mg/L) in cocoa producing area in Ondo state. The result of [12] is also higher than the present concentration of endosulfan from Gusau Dam.

2,2-bis(chlorophenyl)-1-chloroethane DDMU was detected in water from Dam with concentration 0.0016 mg/. But not detected in treated water sample. This might have trapped by the filter material that reduced the concentration beyond the limit of detection of the instrument.

The presence of DDMU indicated the use of DDT by the farmer for pest control, because DDMU is one of the degradation products of DDT. Dichlorodiphenyltrichloroethane has been banned worldwide for agricultural application because of its health hazard and unfavorable environmental effect [25].

Nonetheless, DDT and its metabolites such as DDD, DDE and DDMU have been identified as contributors to public health concern, and have been linked to cancer, asthma and growth disorder in children WHO, (2011)

However, the isodrin detected in water from Dam (0.0141 mg/L) is a little higher than MRL set by WHO/FAO, (0.01 mg/L). Isodrin organochlorine pesticide was developed after the banned of DDT worldwide as an alternative pesticide. It was later banned by FAO/WHO because of its persistent and slow degradation in soil and health hazard [24].

Heptachlor epoxide was present only in dam water sample at a concentration of 0.0016mg/L. but reduced beyond limit of detection after water treatment. Heptachlor has been banned by the WHO/FAO because the insecticide causes liver disease in animal and is also suspected to be carcinogenic in human [8] the presence of heptachlor that the pesticide is still in used for agricultural purposes despite been banned because of potential health hazard. Indiscriminate use of this banned pesticide and lack of good agricultural practice (GAP) may result to the present heptachlor in the water sample from Dam sample. Environmental Protection Agency (EPA) classified heptachlor as possible human carcinogenic and it has long half life [5

4. Conclusion

The results obtained from the present research shows that a number of organochlorine pesticide residues are present in water samples from Gusau Dam in Zamfara State. They include alpha lindane (0.0250 mg/L), endosulfan ether (0.0012 mg/L), Isodrin (0.0141 mg/L), heptachlor epoxide (0.0030 mg/L), and DMMU (0.0016mg/L). These concentrations reduced after the water undergoes conventional treatment where only alpha lindane (0.0001 mg/L) and endosulfan ether (0.0012 mg/L) are detected in the treated water. The entire organochlorine pesticide residue detected in dam water sample are within the maximum residual limit (MRL) except alpha lindane and endosulfan ether that are little higher than 0.02 mg/L of MRL while that of treated water are below MRL. There is need to research more on the suitable absorbents to replace the present filtration that would removed all the pesticide residues and other organic pollutants from the drinking water.

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CONFLICT OF INTEREST

None conflict of interest declared

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