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Pesticide Residues in Groundwater Samples in Bwari Communities, Abuja-Nigeria

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Abstract: Organochlorine pesticides' (OCPs) use has been a part of agricultural practices. These have found their way into waterbodies through percolation, leaching and runoffs. Potable water should be free from toxic substances. If therefore the presence of pesticide is discovered in water, it should be in concentrations that are less than the maximum residue limits, thereby safe for drinking and domestic use. This study analyzed OCPs in groundwater samples from selected communities in Bwari Area Council of the Federal Capital Territory (FCT). QuEChERS (Quick, Easy, Cheap, Efficient, Rugged and Safe) method was used for sample preparation and Gas Chromatography-Mass Spectrometry (GC-MS) method of analysis was used. Of the twenty OCPs analyzed, three pesticides were found to be above Maximum Residue Limit (MRL). These were beta-BHC, gamma-BHC, and gamma-Chlordane discovered in all water samples. beta-BHC had values ranging from 10.17 – 11.19 µg/L, gamma-BHC had between 13.94 – 19.64 µg/L and gamma-Chlordane 17.92 – 23.68 µg/L in Gaba borehole water (GBHW), Gaba Well Water (GWW), Zuma borehole water (ZBHW) and Zuma well water (ZWW) samples. Also, heptachlor, heptachlor epoxide and Endrin ketone were discovered to be slightly higher than the Adequate Daily Intake (ADI) but less than the MRL. These water sources could be a source of potential health risk, if consumed over time. The presence of these OCPs in the samples showed that these pesticides are still in use, despite their ban. Awareness must be raised of the dangers of using these pesticides as they leach into groundwater. Routine monitoring of pesticide residues in the study area is necessary to control environmental pollution and minimize health risks.

Keywords: *Pesticide Residues, Organochlorine, Groundwater, QuEChERS, Gas Chromatography-Mass Spectrometry, Health Risks.*

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I. INTRODUCTION

One of the most essential natural resources on earth is water. This is because everything that has life on the surface of the earth needs water to survive [1, 2]. Living almost gets impossible in the absence of water. Despite the earth's large banks of water collection as seas, lakes, rivers, streams, springs, wells, even aquifers, only a small portion is potable for drinking and daily use [3, 4].

The United Nation's sixth Sustainable Development Goals (SDGs) in part, declares the importance of achieving clean water and so, synthetic pesticides like lindane, endosulfan, aldrin, dieldrin, DDT and the likes, are potentially toxic to other non-target organisms, including humans [5, 6]. This underscores the need for the safe usage and proper disposal of pesticides as there is the continual increase in demand for water [3, 7].

In Nigeria, the impact of organochlorine pesticide residues has been found to affect different parts of the country, especially in communities which live around water bodies [8]. This therefore, poses a big threat to the public and the environment that use these pesticides legally or illegally on farmland soils, around the house, and on water bodies in such environments [9, 10].

The usage of pesticides is widely distributed in the world ranging from agricultural fields, homes, parks, schools, and so on. These pesticides often find their way further, into foods and indeed water, commonly consumed by man [6, 8, 11, 12]. For example, organochlorine pesticide (OCPs) residues get into aquatic environments through effluent release, discharges of domestic sewage and industrial wastewater, atmospheric depositions, run-off from agricultural fields, leaching, equipment washing, and disposal of empty containers and direct dumping of wastes into water systems [13]. They further breakdown into metabolites which become poisons when they reach specific concentrations in food and water. Caution must be exercised in handling and applications of pesticides, to avoid human exposure and contact, particularly through the food chain, so as to minimize health risks [13]. Organochlorine pesticides particularly have been linked to a wide range of health-related hazards like headaches, fatigue, malaria, typhoid, pruritus, dizziness, and nausea. Other chronic impact illnesses like

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cancer, reproductive issues, and endocrine disorders. Acute health impacts are noticed with the nerves, skin irritations, eye irritations and poisoning of the entire human body systems. This sometimes becomes critical, and even occasionally, fatal – leading to death. Prolonged and chronic health impacts may occur for years after even minimal exposure to these pesticide residues in the environment, ingested through food and water [14].

Pesticides are also used in public health to kill vectors of diseases, such as mosquitoes, hence, pesticides are classified according to their chemical class or intended use [15, 16]. The indiscriminate use of pesticides in Nigeria has resulted in the residues being found in biotic and abiotic compartments of the environment [9, 16, 17, 18, 19]. These pesticides could be washed into uncovered wells close to farms or around the homes of farmers where they are used.

In Ghana, Fosu-Mensah *et al.,* [20] carried out analysis of organochlorine pesticides in drinking water sources from cocoa farms. It was found out that the soil samples analyzed with GC-ECD showed the presence of four organochlorine pesticides lindane, beta-BHC, dieldrin and p,p'-DDT [20]. Dieldrin therefore had the most frequent recurrence. The water samples analyzed showed the presence of lindane, alpha-endosulfan, dieldrin, endosulfan-sulphate, p,p'-DDT and heptachlor. Also in Taraba State Nigeria, assessing organochlorine pesticide residues in water, [21] using the GC-MS, found that residual levels in water were generally below MRL (0.5 ppm or 500 µg/L) as compared with FAO/WHO [22]. Aldrin (420 µg/L) was detected in the water sample. Despite p,p'-DDD, p,p'-DDT, p,p'-DDE, heptachlor and methoxychlor were also detected; they were found to be below standards.

Modibbo *et al.,* [23] found that pesticide residues in water ranged from 150 to 920 µg/L from river Njuwa, Adamawa state. Tongo *et al.,* [24] reported very low concentrations of pesticide residues in water (0.6 to 1.0 µg/L) in water samples collected from Warri River. Akinnawo [25] in pesticide residue determination in water and sediment samples from selected areas of river Ilaje in Nigeria could not detect levels of pesticides in water.

This study therefore, seeks to determine organochlorine pesticide (OCP) residues in groundwater samples in communities in Bwari Area Council of the Federal Capital Territory (FCT), Abuja – Nigeria. Twenty (20) Organochlorine pesticides including Aldrin, Heptachlor, Heptachlor-epoxide, Chlordane, Endosulfan, Endrin, Dieldrin, Hexachlorocyclohexanes (sometimes referred to as Benzene hexachlorides (BHC)), dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethane (DDD) and methoxychlor - specifically, the insecticidal class [26]. These compounds are known for their high toxicity, slow degradation and bioaccumulation [26] in living tissues. Furthermore, the lower Usman Dam is located in Bwari area council and is the main source of water supply for the FCT. It is therefore of utmost necessity that regular monitoring of the environment around the dam for pesticide residues be taken seriously. Also, the potential health risks that synthetic (organochlorine) pesticide residues pose to consumers of these sources of water in that environment was also assessed.

Lack of proper monitoring and control of the use of these pesticides could likely increase their presence and concentration levels in water around the area. Hence, the need to assess the presence and concentration levels of organochlorine pesticide residue in those environments to ascertain if they are within the limits that would not be injurious to the health of the inhabitants of those communities [11, 27] and also to provide baseline information on concentration of organochlorine pesticide residues in water samples.

II. MATERIALS AND METHODS

➢ *Sample and Study Area*

The area has its major source of water to be well water as well as borehole water, some of which are connected to storages. This study was conducted within communities in Bwari area council of the Federal Capital Territory, Abuja. They include Gaba 1, Gaba 2, Zuma 1 and Zuma 2; along Duste - Bwari road in the North- Eastern part of Abuja. It lies between Latitude 90 17' 05"N and Longitude 70 25' 23"E with sunrise at 07:16:48 and sunset at 19:54:52 [28]. It is sited at about 26 km from Abuja city and 10 km away from Bwari town [29]. The district has a tropical climate with characteristic dry and wet seasons. Dry season begins from November to February while the wet season lasts from March to October. It has its mean annual rainfall between 125 cm and 175 cm while the annual temperature is about 28 ^{o}C [29].

➢ *Sample Collection*

Water samples were collected from wells and boreholes within the communities. Water sampling bottles fitted with screw-caps were used for sample collections. Prior to sample collection, bottles were thoroughly washed, rinsed with distilled water and then with pure acetone (99.9 %). They were dried in an oven at a temperature of about 100 ^{o}C. Borehole water was collected from several locations in Gaba communities and composited to form a representative borehole water sample designated Gaba Borehole Water (GBHW). Also, well water was collected from several locations in Gaba communities and composited to form a representative well water sample for the community designated Gaba Well Water (GWW). Water samples were collected in Zuma communities as described for Gaba communities. Samples were collected in the pre-washed 2 L sample bottles, kept in ice-packed boxes and transported to the laboratory for analysis. Water samples for pesticide residue analysis were kept in the refrigerator prior to extraction and analysis. This is so as to inactivate microbes and also to preserve the integrity of the water samples.
Water samples collected are presented in table 1.

Table 1 showing sample descriptions and laboratory codes.

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Table 1 Water Samples Collected in the Study

Sample Description	Laboratory Code
Borehole Water samples from Gaba	GBHW
Well Water samples from Gaba	GWW
Borehole Water samples from Zuma	ZBHW
Well Water samples from Zuma	ZWW

- *Reagents for Analysis*

All chemicals and reagents that were used for the analysis were of analytical grade (AR). Anhydrous Magnesium sulfate (98 % Sigma-Aldrich, US), Acetonitrile (99.5 % Thermo-Scientific Chemicals, US), Glacial acetic acid (99.5% Welychem Co. Ltd, China), Anhydrous Sodium citrate (99 % Hawkins Inc., US), Sodium chloride (95 % Hawkins Inc., US), pure Acetone 99.5 % (Sigma-Aldrich, US).

- *Sample Extraction using QuEChERS Method*

Samples were extracted using multi-residue pesticide analysis technique which is QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method. QuEChERS AOAC 2007.01 [30] procedure with slight modification described by [31] was used to extract pesticide residues from water samples. 15 cm^3 of water sample was put in a 50 cm^3 centrifuge tube. 15 cm^3 of 1% acetic acid (HOAc) in acetonitrile (CH_3CN) was added. The centrifuge tube was capped and the mixture was vigorously vortexed for 1 minute. 6 g of anhydrous magnesium sulphate ($MgSO_4$) and 1.5 g of sodium acetate (NaOAc) was added. The mixture was shaken vigorously for 1 minute using a vortex mixer. This was then centrifuged at 1500 rcf for 1 minute. The supernatant (acetonitrile layer) was decanted to be used in the clean-up stage.

- *QuEChERS Clean-Up for Water Sample Extract*

Using the OAOC 2007.01 [30] procedure, 1 cm^3 aliquot of the extract from extraction and partitioning steps was transferred into a polypropylene centrifuge tube containing 100 mg anhydrous magnesium sulphate ($MgSO_4$), 75 mg graphite carbon black (C_{18}) sorbent (to remove plant pigment), and 20 mg Primary Secondary Amine (PSA) sorbent (to remove organic acids and excess water). The tube was again vortexed for 0.5 minute and centrifuged at 4500 rpm for 2 minutes. An aliquot of the supernatant was transferred into a glass test tube and acidified by adding 15 µL of 5% (v/v) formic acid in acetonitrile per cm^3 of extract for subsequent injection into the Gas Chromatography. The concentrated extract of the samples was then analyzed for twenty organochlorine pesticide residues.

- *Instrumental Analysis*

GC-MS: Agilent HP-5-60 Gas Chromatography-Mass Spectrometry (GC-MS) was used to determine the concentration of organochlorine in the samples [32]. The instrument column was 30 m × 0.25 mm x 0.25 µm film thickness. It was operated at 250 ºC and attached to a Gas Chromatograph (6890N Agilent technologies) and Mass Selective Detector (Agilent 5975B). 1 µL samples was injected into the machine in a splitless mode with the initial oven temperature maintained at 100 ºC for 2 minutes. This temperature was later increased to 180 ºC at a rate of 15 ºC per minute. Thereafter it was ramped up to 250 ºC at a rate of 3 ºC per minute, where it was held for 9 minutes. Carrier gas used was helium, with a flow rate of 0.8 cm^3 per minute. The operation mode of the mass spectrometer was electron impact ionization with the use of automatic gain control. The storage window was programmed at full scan mode in the range of m/z 200 – 500, and Selected Ion Monitoring (SIM) mode was employed in acquiring data by Agilent ChemStation software.

- *Sample Analysis for Organochlorine Pesticide Residues*

Internal standard technique was used to analyze the food crop extracts [33]. The organochlorine standards containing a mixture of 14 organochlorine compounds of high purity (alpha BHC, beta-BHC, Lindane, delta-BHC, Heptachlor, Aldrin, Heptachlor – epoxide, Endosulfan I, p,p'-DDE, Dieldrin, Endrin, Endosulfan II, p,p'-DDT, and Endosulfan sulphate) were prepared at concentrations ranging from 0.100 to 2.000 ppm, with Anthracene, PCB-153, and PF-38 added as Internal Standards. The modern Shimadzu GC-MS QP 2010 was used to analyze the standards. Also, calibration curve for each compound was prepared automatically [34]. Food crop sample extracts from the clean-up were then analyzed under the same conditions as for the standards, while Selective Ion Mode (SIM) had m/z values ranging from 65 to 274.

- *Limit of Quantification (LOQ)*

Limit of Quantification (LOQ) is the concentration at which the analyte can be quantified with linear response. The Limit of Quantification of each pesticide in this study was estimated using the concentration that gives a signal response equal to 10 times the standard deviation of the background signal. Equation (1) was used to determine the LOQ:

$$LOQ = 10 \times \frac{\delta}{S} \qquad (1)$$

Where δ is the standard deviation and S is the slope from calibration curves.

- *Recovery Studies*

The efficiency of the method was validated with recovery studies. Fortification of reference materials without pesticide residues with four organochlorine compounds at two concentration levels 100 µg/L and 1000 µg/L were carried out in triplicate and the same method of extraction and clean-up was followed. Other quality assurance measures applied in the laboratory included rigorous contamination control procedures (washing and cleaning procedures), monitoring of blank levels of solvents and analysis of procedural blanks. The samples were then analyzed with GC-MS with percentage recovery [35] calculated using equation (2):

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$$\text{Percentage Recovery} = \text{Residue concentration} / \text{fortification concentration} * 100 \quad (2)$$

Where fortification concentration is the same as spike concentration.

➤ *Quality Assurance*

Glass wares and tools that were used during laboratory analysis were thoroughly washed with detergent and running water. This was followed by rinsing with distilled water and then proper drying. These were further rinsed with acetone before they were used in the laboratory. Chemicals and reagents used were all of analytical grade and obtained from BDH and Sigma and Co. They were all used in accordance to given instructions. Instruments were calibrated and test-run before they were used.

➤ *Statistical Analysis*

The results obtained from this study were analyzed using Microsoft Excel. Correlation of determination associated with the estimated linear regression was also used to test the linearity of the response of the calibration curves to the gas chromatograph to concentrations. The concentrations of organochlorine pesticide residues in soil, water and food crop samples from the study area were then compared to the Maximum Residue Limits (MRLs) by European Union 2011 [36].

III. RESULTS AND DISCUSSION

Organochlorine pesticide (OCP) residues for GC-MS standard chromatograms for all water samples from the communities were very clear, distinct and sharp. This shows that samples were properly prepared, extracted and cleaned up prior to the analysis. Mean concentration values for all water samples were calculated and designated appropriately. The percentage distribution of various OCP residues were calculated, as well as retention time and Q-values.

➤ *Organochlorine Pesticide Residue Concentrations as Observed in Gaba Groundwater Samples*

Gaba Water Samples: The mean concentration value of organochlorine pesticide residue in Gaba borehole water (GBHW) sample ranged from 0.01 ± 0.00 µg/L to 23.68 ± 5.13 µg/L while that of Gaba well water (GWW) sample, ranged from 0.03 ± 0.00 µg/L to 18.70 ± 15.63 µg/L. Mean concentration value for GBHW gamma-Chlordane (23.68 ± 5.13 µg/L) was the most abundant OCP residue with percentage distribution of 23.60 %, followed by p,p'-DDE (21.17 ± 8.46 µg/L), gamma-BHC (19.64 ± 4.36 µg/L) and beta-BHC (11.19 ± 5.79 µg/L), respectively. This was followed by p,p'-DDE (21.17 %) and gamma-BHC (19.64 %). The percentage distribution of the other organochlorine residues was relatively small compared to those aforementioned (gamma-chlordane, p,p'-DDE and gamma-BHC).

Fig. 1, shows the chart of mean concentrations of OCPs analyzed in Gaba groundwater samples.

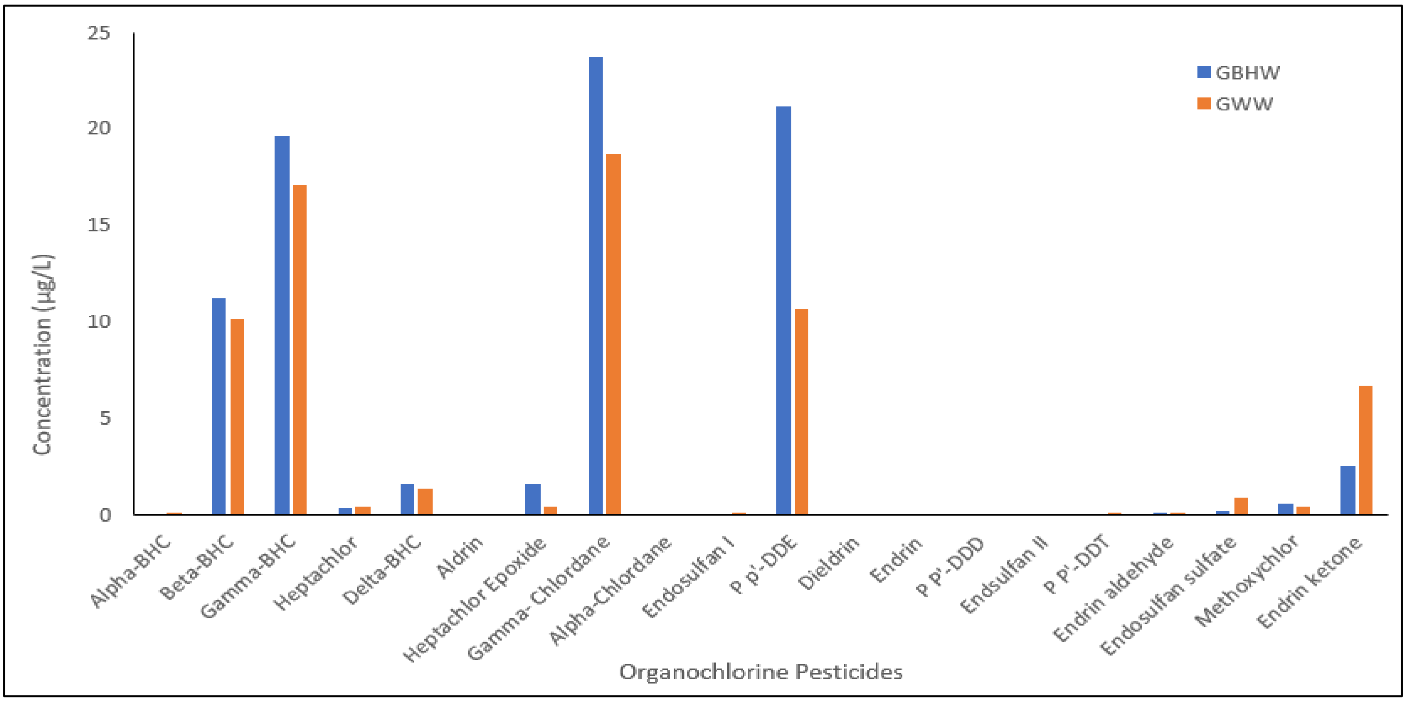

Fig 1 Graphical Representation of OCPs in Gaba Water Samples

Water samples obtained from Gaba communities were contaminated with all 20 organochlorine pesticides examined at various levels of contamination. Metabolite products of dichlorodiphenyltrichloroethane (DDT) were also found in water samples such that, in Gaba borehole water (GBHW): p,p'-DDE (21.17 µg/L), p,p'-DDD (0.02 µg/L), p,p'-DDT (0.05 µg/L) and methoxychlor (0.61 µg/L) were detected.

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Mean Concentrations of DDT and its metabolites reported in the study were found to be higher than those by [20] reported for drinking water from cocoa farms in Ghana (0.01–0.04 µg/L), and that reported by [18] for water samples of Lagos Lagoon (0.012 to 0.910 µg/L). William [16] also reported DDT of concentration range of 8.79 ± 0.58 ng/L to 10.34 ± 1.22 ng/L for water samples from Agboyi Creek, Lagos [16].

Isomers of 1, 2, 3, 4, 5, 6-hexachlorohexane (HCH or Benzene hexachloride (BHC)) were also detected in the water samples at various concentration levels. This includes alpha-BHC (0.04 µg/L), beta-BHC (11.19 µg/L), gamma-BHC (lindane) (19.61 µg/L) and delta-BHC (1.60 µg/L) in Gaba borehole water (GBHW). Also, in Gaba well water sample, alpha-BHC (0.10 µg/L), beta-BHC (10.17 µg/L), gamma-BHC (lindane) (17.11 µg/L) and delta-BHC (1.36 µg/L) were detected.

In a similar manner, in Gaba well water (GWW): p,p'-DDE (10.65 µg/L), p,p'-DDD (0.03 µg/L), p,p'-DDT (0.15 µg/L) and methoxychlor (0.47 µg/L) were detected. In GWW, gamma-Chlordane was most abundant (18.70 ± 15.63 µg/L) followed by gamma-BHC (17.11 ± 16.36 µg/L), p,p'-DDE (10.65 ± 3.17 µg/L) and beta-BHC (10.17 ± 9.56 µg/L). The percentage distribution of other organochlorine residues was relatively low compared to the three mentioned earlier. Concentrations of pesticide residues varied in water samples and were generally less than MRLs while a few were slightly above the Average Daily Intake (ADI). These low values in other OCPs analyzed in this study corresponds with the study by [37] who detected low mean concentrations of organochlorine pesticide residues in well water in Lagos. Also, Okechukwu and Onwukeme [38] detected low mean concentrations of OCPs in groundwater in Imo State. In a groundwater study by [39] in Ile-Ife, Osun State, heptachlor and methoxychlor was reported to be higher than maximum residue levels recommended by the European Union while dieldrin and heptachlor epoxide in this study was found to be far below MRLs but slightly higher ADI. Research carried out by Alani *et al.*, [40] detected the presence of dieldrin and heptachlor epoxide OCP concentrations in groundwater samples exceeding MRLs, showing that most of these banned OCPs are in use and are present in our water. The presence of degradation or metabolite products of the parent compound DDT in the water samples indicates that either DDT have been used for agricultural purposes or for vector pest control in the community [8].

➢ *Organochlorine Pesticide Residue Concentrations as Observed in Zuma Groundwater Samples*

Zuma Water Samples: Mean concentration value of organochlorine pesticide residue in Zuma borehole water was found to be between 0.03 ± 0.01 µg/L to 13.40 ± 1.07 µg/L. The most abundant OCP from mean concentration of ZBHW was p,p'-DDE (13.40 ± 1.07 µg/L) followed by gamma-Chlordane (12.36 ± 1.66 µg/L). The percentage distribution (%D) of pesticide residues in the water samples indicated that, Zuma borehole water (ZBHW) samples had p,p'-DDE (13.40 %) and is the most abundant organochlorine pesticide residue in borehole water in study area. This was followed by gamma-chlordane (12.36 %) and gamma-BHC (8.29 %). The percentage distribution of other organochlorine pesticide residues was minute as compared to the three mentioned earlier.

Similarly, mean concentration values of Zuma well water was between 0.03 ± 0.00 µg/L to 19.69 ± 1.56 µg/L. For ZWW, the most abundant OCP residue was p,p'-DDE (19.69 ± 1.56 µg/L), followed by gamma-Chlordane (17.92 ± 1.28 µg/L) and gamma-BHC (13.94 ± 1.42 µg/L). Some other pesticide residues showed values slightly above ADI but were generally, less than MRLs.

Fig. 2 shows the chart of mean concentrations of OCPs analyzed in Zuma groundwater samples.

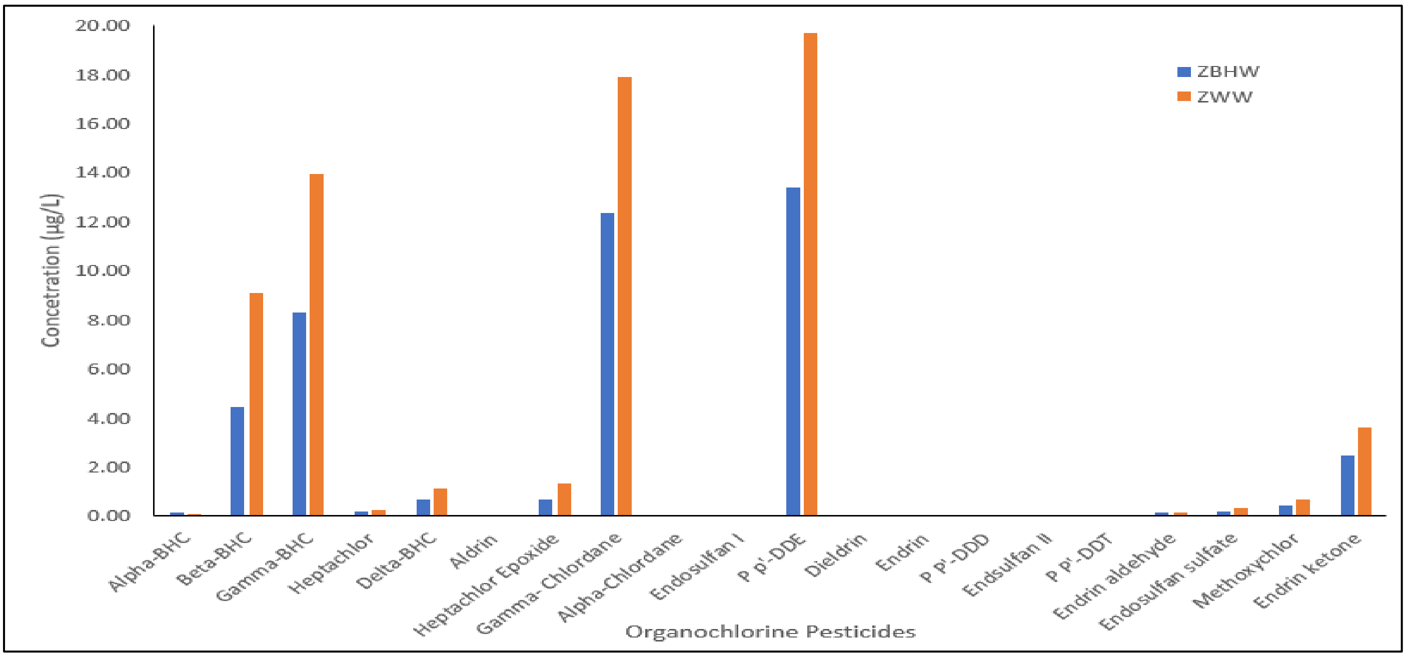

Fig 2 Graphical Representation of OCPs in Zuma Water Samples

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Zuma communities water samples were also contaminated with all 20 organochlorine pesticides investigated, in the study. DDT and its metabolite products were found in water samples such that in Zuma borehole water (ZBHW) sample: p,p'-DDE (13.40 µg/L), p,p'-DDD (0.05 µg/L), p,p'-DDT (0.07 µg/L) and methoxychlor (0.45 µg/L) were detected. In a similar manner, in Zuma well water (ZWW) sample: p,p'-DDE (19.69 µg/L), p,p'-DDD (0.03 µg/L), p,p'-DDT (0.06 µg/L) and methoxychlor (0.45 µg/L) were all detected.

Despite being present in the water samples, their values were within, and some, below the EU/CODEX/FAO Acceptable Daily Intake (ADI) 20 µg/L and Maximum Residue Limits (MRLs) 50 µg/L for p,p'-DDE; p,p'-DDD and p,p'-DDT. This corresponds with the study by [41], detecting OCPs in water samples far below MRLs and also below the background levels detected in other parts of the country. Also, Mutiyar *et al.*, [42] in a drinking water well-field in Delhi region of India, found out in his study that boreholes or borewells produced better water quality compared to water from wells. The study also showed the presence of OCP residues but at concentrations lower than standards.

The presence of DDT metabolites in the samples indicates that it could have been used severally for many years and had accumulated and leached into the water. Also, its use for agricultural purposes or for vector pest control in the community [8] could be suspected. The mean concentrations of DDT metabolites reported in the study were found to be higher than the values reported by [20], for drinking water from cocoa farms in Ghana (0.01–0.04 µg/L). Also, Adeyemi *et al.*, [18] reported DDT concentration range of 0.012 µg/L to 0.910 µg/L for water samples of Lagos Lagoon. DDT and its derivatives were reported to be an endocrine disruptor, human carcinogen and androgen receptor antagonist [43].

Benzene hexachloride (BHC) isomers were also detected in the water samples at various concentrations. These included alpha-BHC (0.17 µg/L), beta-BHC (4.43 µg/L), gamma-BHC (lindane) (8.29 µg/L) and delta-BHC (0.71 µg/L) in Zuma borehole water (ZBHW). Also, in Zuma well water sample alpha-BHC (0.08 µg/L), beta-BHC (9.09 µg/L), gamma-BHC (lindane) (13.94 µg/L) and delta-BHC (1.16 µg/L) were detected.

Though the use of these classes of organochlorine has been banned in Nigeria, their presence detected in this study may be due to many factors including that of poor pesticide education, leading to extensive mis-use in such areas and in Nigeria [44, 45]. Concentration of heptachlor, aldrin, alpha-chlordane, dieldrin, endrin and endrin aldehyde present in the study's water samples were similar to those reported by [46] for borehole and well water samples from Adamawa State, Nigeria. Its concentrations were less than 1 µg/L value set by FEPA and EU as permissible limit. Thus, they pose no significant health issues at the moment. However, high concentrations of beta-BHC, gamma-BHC, gamma-chlordane, p,p'-DDE and endrin ketone detected in the samples are certainly of great concern.

Comparing Gaba borehole and Zuma borehole water samples, it was observed that GBHW water samples showed higher concentration of OCPs. This was most observed in beta-BHC, gamma-BHC and gamma-Chlordane; which were higher than MRLs, as shown in fig. 3. Despite their presence, p,p'-DDE (in GBHW) and Endrin ketone were found to be above ADI for humans but below MRLs [47, 48].

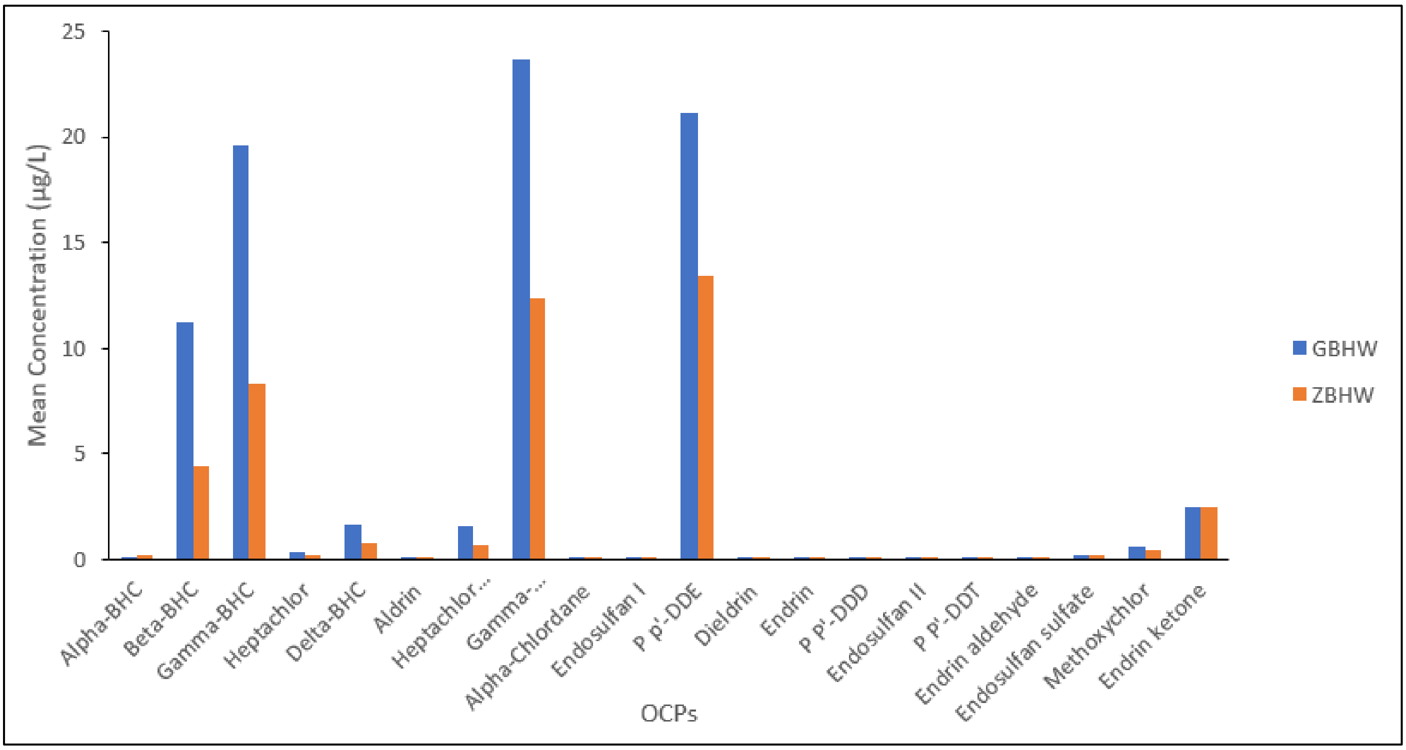

Fig 3 Graphical Comparison of OCPs in Gaba and Zuma Borehole Water Samples

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Similarly, comparing Gaba well water and Zuma well water samples of the study area, it was also discovered that Gaba well water had more concentrations of OCPs. This is shown in beta-BHC, gamma-BHC, gamma-Chlordane and endrin ketone [48, 49]. For p,p'-DDE, ZWW was seen to be more in OCP concentration as shown in fig. 4.

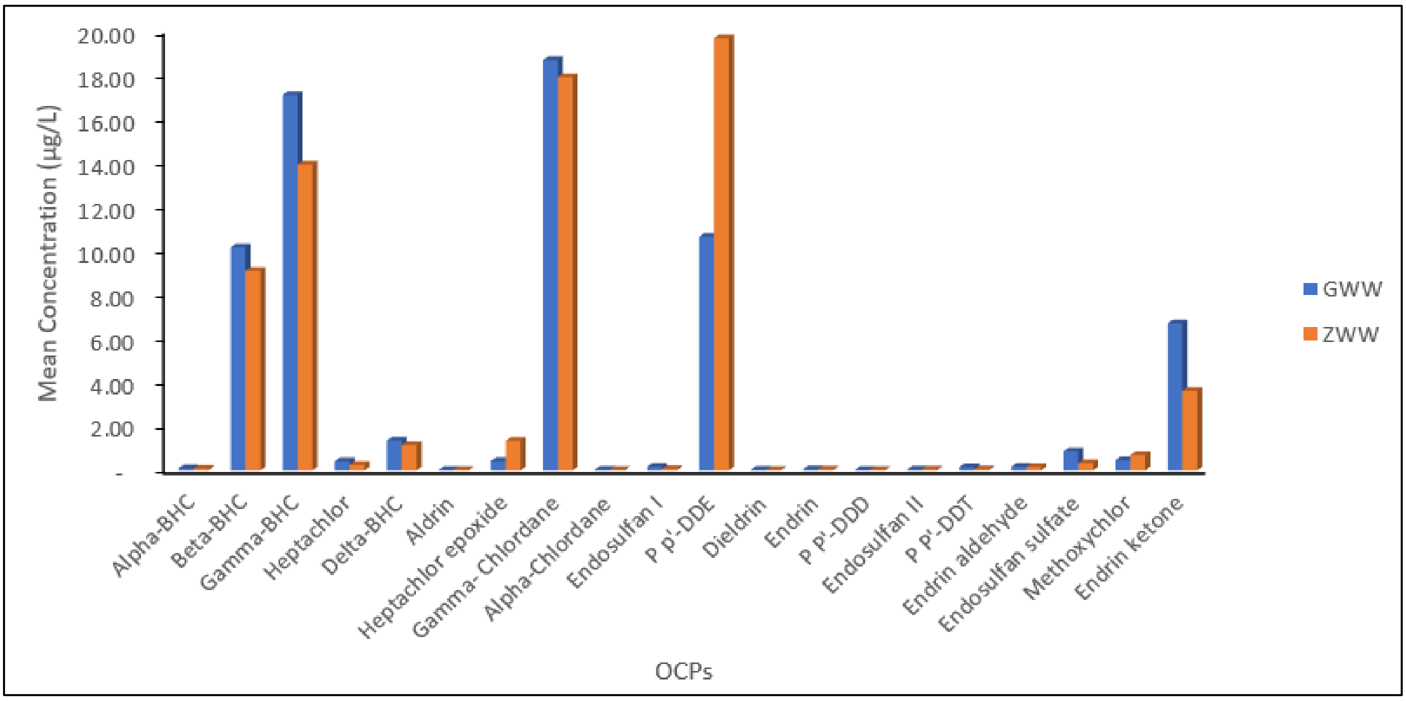

Fig 4 Graphical Comparison of OCPs in Gaba Well and Zuma Well Water Samples

Comparing the concentration of all water samples, OCP residues followed the trend; GBHW > GWW > ZWW > ZBHW thereby, making Gaba borehole water highest in OCP residues as shown in fig. 5.

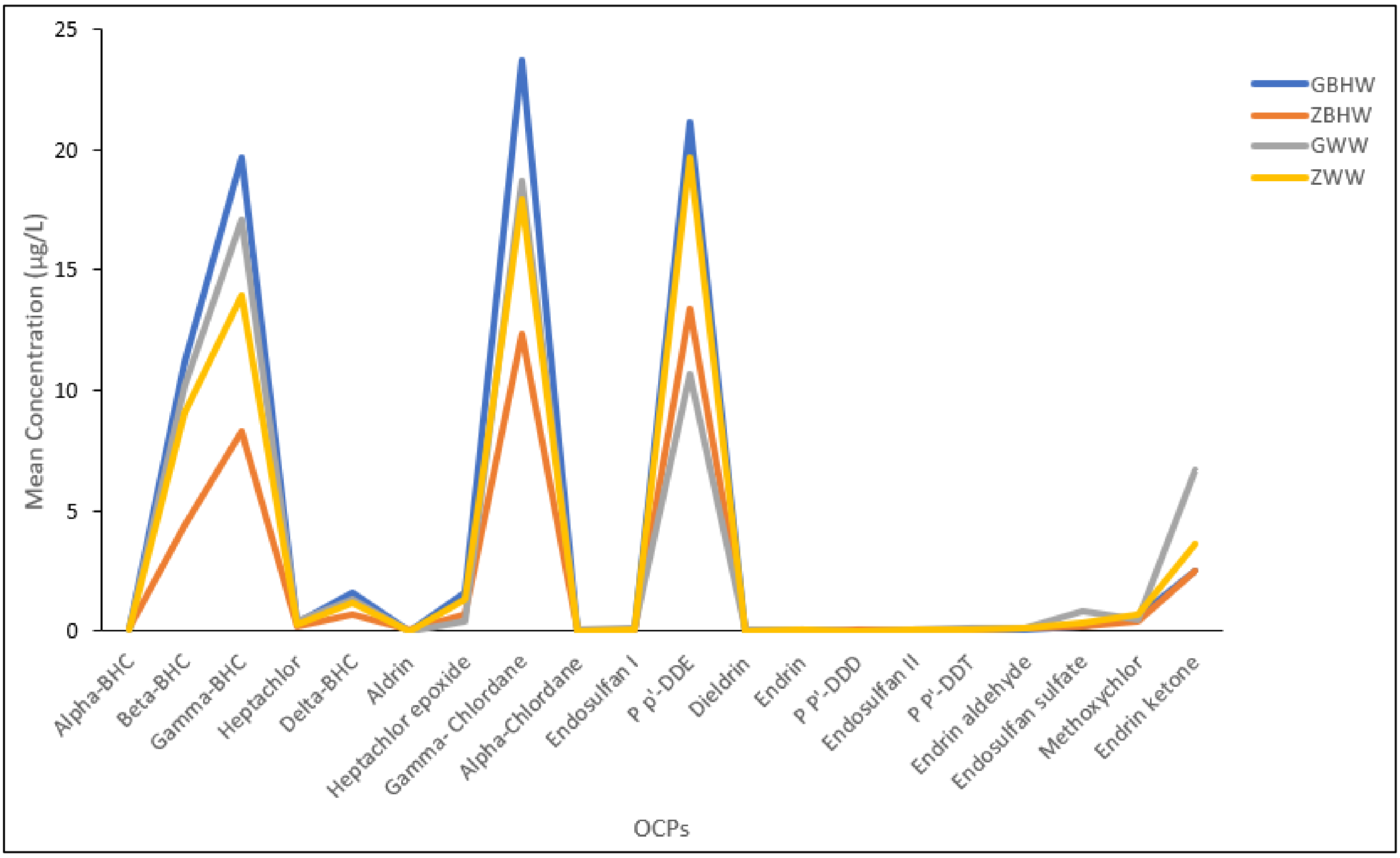

Fig 5 Graphical Representation of all water Samples

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Key:

GBHW – Gaba borehole water

GWW – Gaba well water

ZWW – Zuma well water

ZBHW – Zuma borehole water

IV. HEALTH RISK INDEX FOR WATER SAMPLES

Health Risk Index is a tool used to assess the potential health risks associated with exposure to chemicals. This is often used in environmental safety concerns. This is carried out by comparing actual exposure levels to safe limits of those chemicals. It helps in the determination of negative health impact from exposure to chemicals; either through dermal contact, ingestion or inhalation.

Health Risk Index is calculated with the ratio of actual exposure level to a reference dose or tolerable intake level for a particular chemical. It can be applied to food safety, environmental risk assessment or even workplace health.

The health risks associated with BHC include dizziness, headaches, nausea, and vomiting. Prolonged exposure may lead to more serious health problems such as liver damage, skin irritation, and nerve damage. Ingesting BHC can also be toxic, causing stomach pain, diarrhea, or even death. It has been reported that lindane accumulates in the food chain and high levels of exposure could result in nervous system dysfunction, and liver damage. High concentrations of beta-BHC and gamma-BHC recorded in this study is similar to that reported by [50], with (0.217-0.391 µg/g) in River Ilaje water, and [16] (8.73 ± 0.60 µg/g), in Agboyi Creek water samples [16, 50]. Gamma-chlordane, has been reported as one of the most bioactive cyclodienes due to the harmful effects it poses on the human health and also the environment [16]. It would hardly degrade in the environment and in humans and animals and would readily accumulate in lipids (fatty tissues). Excessive exposure to chlordane/heptachlor and/or its metabolites (oxychlordane, heptachlor epoxide) could give rise to type-2 diabetes, lymphoma, prostate cancer, obesity, testicular cancer and breast cancer [51, 52, 53, 54].

The summary of the health risk index for water samples is therefore shown in table 2.

Table 2 Health Risk Index

Compound	Gaba Water	Zuma Water
Alpha-BHC	2.7948	3.1236
Beta-BHC	70.418	3.288
Gamma-BHC	1117.92	16.44
Heptachlor	57.54	608.28
Delta-BHC	6.7404	1.4796
Aldrin	41.1	32.88
Heptachlor epoxide	476.76	3074.28
Gamma- Chlordane	1813.332	554.028
Alpha-Chlordane	13.152	6.576
Endosulfan I	1.4796	1.3152
P,p'-DDE	59.4306	369.8589
Dieldrin	65.76	221.94
Endrin	16.44	24.66
P,p'-DDD	0.5343	0.2877
Endosulfan II	0.6165	0.411
P,p'-DDT	0.3288	0.1233
Endrin aldehyde	24.66	41.1
Endosulfan sulfate	1.918	2.466
Methoxychlor	4.932	8.5488
Endrin ketone	3957.93	986.4

Values on the above table which are 100 and above, would pose a significantly negative health impact on its consumers as they have high contaminant levels. Whereas, values less than 100 are still safe for human consumption, but would pose a risk to consumers over time, if it increases.

Health Risk Index (HRI = [EDI/ADI] *100) for Water Samples (3)

Where,

HRI = Health Risk Index

EDI = Estimated Daily Intake

ADI = Adequate Daily Intake

But, $EDI = \frac{Cr}{bw} * FIR$ (4)

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(Where Cr is the Concentration of OCPs in sample, FRI is the Food Injection Rate and bw is the body weight).

V. CONCLUSION

This study discovered the presence of organochlorine pesticides in varying concentrations in water samples under investigation. Although most of them were below MRLs, their presence in the water samples showed they are still in use in the study area. Of the twenty OCPs analyzed, three pesticides were found to be above Maximum Residue Limit (MRL): beta-BHC, gamma-BHC, and gamma-Chlordane. These water sources could be a source of potential health risk, if consumed over time. The presence of these OCPs in the samples showed that these pesticides are still in use, despite their ban. Awareness must be raised of the dangers of using these pesticides as they leach into groundwater with time. Routine monitoring of pesticide residues in the study area is necessary to control environmental pollution and minimize health risks. QuEChERS method ha proven to be an effective sample preparation method not only for food but also for water with fast analyte recoveries. Further research should also be carried out in areas where the use of organochlorine pesticides is prevalent.

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