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Research Article

Analysis of Pesticide Residues in Sachet Water Vended in Birnin Kebbi and Environs, Kebbi State, Nigeria

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Abstract

The organochlorine and organophosphorus pesticide residues in sachet water sold in Birnin Kebbi and its environs were investigated to assess the level of contamination in this all important product. Samples of water were collected from the different sachet water producing plants, raw river water, which serves as a source for the manufacturers and borehole water samples were also collected. All the samples were subjected to liquid-liquid extraction process using methylene chloride and residue identification and quantification was done using GC-MS equipped with ^{63}Niselective electron capture detector. The results of the analysis revealed that DDE, one of the metabolites of DDT have the highest mean concentration of 0.008µg/L, found in 20 samples and has a percentage distribution of 25% of the detectable residues. DDT was the next abundant residues with a mean concentration of 0.007µg/L detected in 18 samples and has a percentage distribution of 21.88%.γ-HCH detected in 17 samples was the third highest with a mean concentration of 0.004µg/L and has a percentage distribution of 12.50%. Among the organophosphorus residues chlorpyrifos detected in 18 samples with a mean concentration of 0.007µg/Land having a percentage distribution of 28% was the highest. Malathion detected in 17 samples with a mean concentration of 0.004µg/L having a percentage distribution of 17% was the second most detected organophosphorus residue observed in the samples. The analysis also revealed that manufacturers who sourced their water from borehole showed the lowest concentration of residues than the river source. Generally, the concentrations of pesticide residues in the samples are higher than the maximum allowable limit of 0.001µg/L as stipulated by EU indicating a possible contamination of the products. To avoid the possible health hazards, the indiscriminate application of pesticides should be restricted and various substitute products like bio-pesticide should be introduced on a broad scale as soon as possible.

KEYWORDS: Sachet water, organochlorine, organophosphorus, borehole, methylene chloride.

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Introduction

Clean water is not only the basic need of human being but it has a great influence on the all aspects of human life (Ahmed, 2005; Dara, 1997; Snoeink and Tenkin, 1983; ASTM, 1981; Hawkins, 1976). Without water, it would not have been possible to sustain life on this planet. In 2000, the United Nations Declaration was adopted by about 180 member states. This led to the promulgation of the Millennium Development Goals (MDG). The MDG seeks to ensure environmental sustainability. According to the United Nations Mid-term Assessment Report (UNICEF and WHO, 2004), 80% of the world's population use an improved drinking water source in2004, up from 71% in 1990. Although these numbers indicate the world is on track to meet the goal, there will be challenges as population increases.

Water quality is important in our lives because it is essential to all life. We rely on water not only to sustain our lives, but to do the same for pets, livestock, yards and crops. If the quality of water is changed by the presence of pollutants, it is potentially harmful to these life forms, instead of sustaining those lives (Jerry *et al*., 2016).

Human kind has come to view pure water as a privilege of modern society. Technology makes it possible to expect to turn on the faucet and have clean, clear water readily available. However, the technology that makes this possible also creates stress on the very water resources that are now taken for granted (Jerry *et al*., 2016). Clean, quality water can be preserved through an understanding of the product and processes that endanger this valuable resource.

The introduction of sachet water into the market was to provide an alternative source of good quality water for consumption. The sachet water was supposed to be safe, hygienic, affordable and an instant source of water for consumers. With the flooding of the market with sachet water and vendors embarking on the best methods to sell their products, it is incumbent that the quality of water being offered for sale is ascertained. As one seeks to satisfy a natural requirement of the human body (drinking water when thirsty), the person needs to be able to make an informed choice on the type of water to be consumed.

Sachet water or packaged drinking water is everywhere. It is now available in homes, bottles and bulky transparent jars. It is sipped in clubs, malls and fitness centres;

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glugged after a walk, jog or trek; sold in motor parks and bus terminals, or pressed through car windows during traffic jams. Sachet water has made its way into offices, restaurants, hotels and stadia. It is practically true today that sachet water, the fastest growing segment in the beverage industry, actually contains deadly pesticide residues (Mathur *et al*., 2003).

In recent years, the growing awareness of the risks related to the intensive use of pesticides has led to a more critical attitude by the society toward the use of agrochemicals. At the same time, many national environmental agencies have been involved in the development of regulations to eliminate or severely restrict the use and production of a number of pesticides (Directive 91=414=EEC) (EEC, 1991). Despite these actions, pesticides continue to be present causing adverse effects on human and the environment. Monitoring of pesticides in different environmental compartments has been proved to be a useful tool to quantify the amount of pesticides entering the environment and to monitor ambient levels for trends and potential problems and different countries have undertaken, or currently undertaking, campaigns with various degrees of intensity and success (Wiersma, 2004;MacBean, 2015).

The widespread use of pesticides for agricultural and nonagricultural purposes has resulted in the presence of their residues in surface and ground water resources. The physicochemical properties of pesticide compounds, particularly their solubility in water and organic solvents, characterized by their octanol-water partition coefficients, determine their character of leaching into surface and ground waters (MacBean, 2015). Depending on their chemical stability, these substances may undergo decomposition processes; therefore, not only active ingredients but their metabolites may also occur as contaminants (MacBean, 2015; Aizawa, 1989). Most pesticides released into the environment are regarded as toxic substances, and newly emerging toxicological interactions have also been identified (mutagenicity, carcinogenicity, hormone modulant effects of environmental Endocrine Disruptor Chemicals (EDCs), immunomodulant effects). Unfortunately not only pesticide residues but also other organic micropollutants (pharmaceuticals, personal care products, etc.) deteriorate water quality. Surfactants are common additives in agrochemical formulations to improve water solubility and uptake of the active ingredient and enhance its pesticide efficacy. Residues of surfactants are often detected in the environment; thus they can influence the effect of pesticide active ingredients. Recent studies indicate that

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combined toxicity of pesticide residues with other chemicals in agricultural use (e.g., adjuvants, detergents) has to be considered (Ali *et al*., 2014; Krieger, 2010).

Contamination occurs not only due to current use of agrochemicals but also due to leaching of persistent ingredients from soil. Pesticide contamination of surface water in a particular region depends on several factors, such as closeness of crop fields to surface water, characteristics of surrounding fields (soil, grassland, slope, and distance to water bodies), and climate conditions (temperature, humidity, wind, and precipitation). In consequence, pesticide residues are being reported as common organic contaminants worldwide in surface waters and other environmental matrices (Ali *et al*., 2014; Rathore and Nollet, 2012; Gilliom *et al*., 2007).

If the credits of pesticides include enhanced economic potential in terms of increased production of food and fiber, and amelioration of vector-borne diseases, then their debits have resulted in serious health implications to man and his environment. There is now overwhelming evidence that some of these chemicals do pose potential risk to humans and other life forms and unwanted side effects to the environment (Forget, 1993; Igbedioh, 1991). Ideally a pesticide must be lethal to the targeted pests, but not to non-target species, including man. Unfortunately, this is not so. The controversy of use and abuse of pesticides has surfaced. The rampant use of these chemicals, under the adage, "if little is good, a lot more will be better" has played havoc with human and other life forms (Karunakarani, 2008).

The organochlorine (OC) pesticides such as gamma hexachlorocyclohexane (γ-HCH), dichlorodiphenyltrichloroethane (DDT) and its metabolites dichlorodiphenyldichloroethylene (DDE),dichlorodiphenyldichloroethane (DDD), heptachlor, endosulfan, endrin, dieldrin and drins) are among the major types of pesticides, notorious for their high toxicity, their persistence in the physical environment and their ability to enter the food chain (Jiries *et al*. 2002). Although the production and use of many types of OCs and organophosphorus (OPs) have been severely limited in many countries, including Nigeria, they are, nevertheless, still being used unofficially in large quantities in many parts of Nigeria, and in other developing countries because of their effectiveness as pesticides and their relatively low cost (Ali et al., 2014; Ntow, *et al.,* 2006; Ntow, 2001).

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The OCs, unlike the OPs pesticides are much more resistant to microbial degradation and have a propensity to concentrate in lipid rich tissues of aquatic organisms and most mammals (Mathur *et al*., 2003). These properties lead directly to their most undesirable characteristics – the environmental persistence, bio-concentration, and bio-magnification through the food chain. Unlike the OPs which are readily deactivated and degraded by micro-organisms and therefore do not readily accumulate. The OCs residues are detectable in most surface water bodies and are bioconcentrated in shellfish and other biota in these ecosystems (Holland *et al*., 1995).

Like other parts of the country, pesticides are being used legally or illegally in considerable quantities in Birnin Kebbi for various purposes which can easily contaminate water sources for drinking. Sources of drinking water in Birnin Kebbi include raw river water, pond water, tap water and borehole water. As a result, these drinking water sources are at high risk of contamination. But little or no information is available about the level of pesticide residues in different water samples of Birnin Kebbi.

Moreover, there are no substantial works that have yet been done for the determination of pesticide residue levels in different types of water samples of Birnin Kebbi. Therefore, this area has been undertaken as the study area to identify and quantify the suspected pesticide residues in the water samples to demonstrate the present status of pesticides used in the area as well as to compare the present result with the result obtained from the past from researchers from Nigeria and globally.

Materials and Method

Description of the sampled site

Birnin Kebbi is a city in North Western Nigeria. It is the capital of Kebbi State and headquarters of the Gwandu Emirate. As of 2007 the city has an estimated population of 125,594. It lies on latitude 12.4660.78 and longitude 4.199524 and coordinate of $12^{0}27/57,8808$N and $4^{0}11/58,2864$E. The people of this area are predominately farmers and rely heavily on agrochemicals to enhance agricultural yield.

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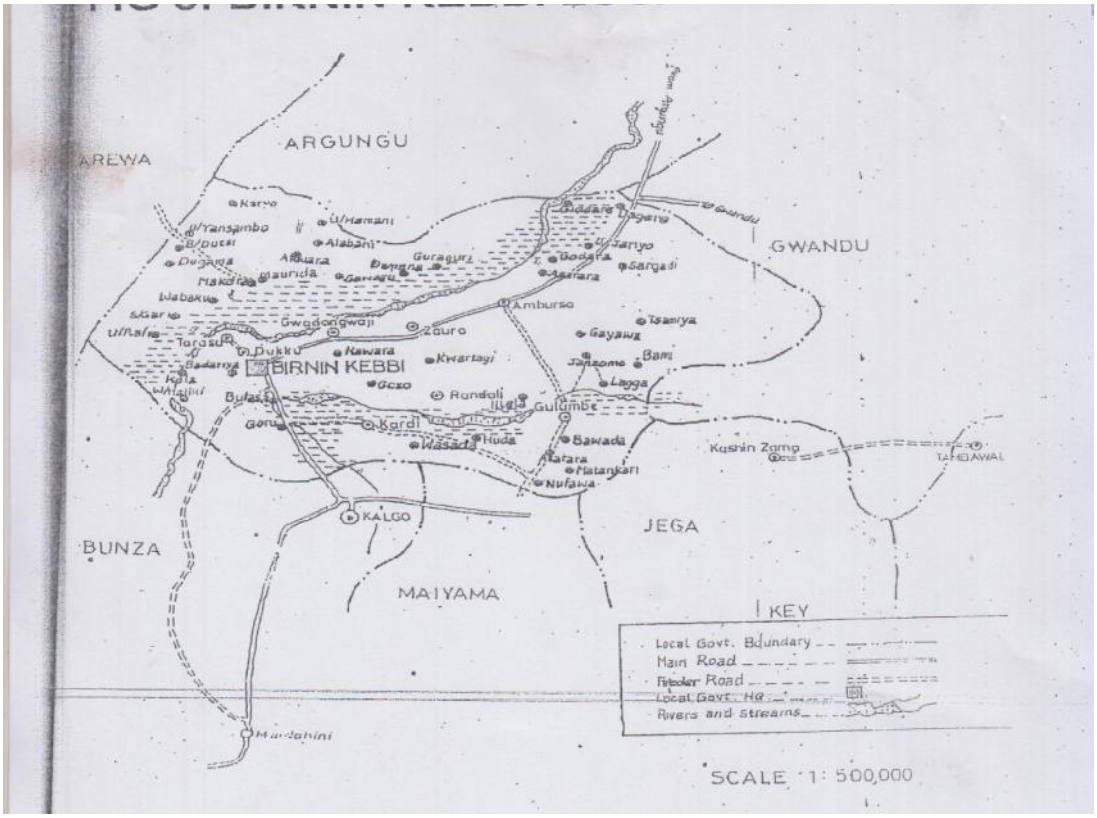

Figure 1: Map of Birnin Kebbi showing the surrounding towns where samples were collected

Sampling Location and Collection

Sachet water of top brands and other less popular brands which were being sold in Birnin Kebbi and nearby towns like Gwandu, Argungu, Jega, Ambursa and Kalgo were purchased randomly from the manufacturing plants. Details of the samples collected are given in Table 1.

Sampling period was between July 2016 to January 2017. Five sachets of each brand were randomly purchased from the manufacturing plant and homogenized to make an approximately 2.5L. All composite samples collected in prerinsed screw cap amber coloured water bottles were taken to the laboratory in ice packed containers and stored between 4^0C to 8^0C in a freezer prior to analysis.

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The method employed by EPA as reported by (Gregg, 2009) was adopted for the collection of raw water samples from Dukku River, which serves as a source of water supply to almost all the sachet water producing industries. Five (5) water samples on the river path were collected at different sites at an average interval of 500m – 700m. Each sample is a composite of three sub-samples. These were homogenized and stored in clean plastic bottles prerinsed with hexane and tightly capped. Borehole water was also collected directly from the tap. Water samples were analysed immediately after collection.

Table 1. Details of samples collected.

Sample Code	Name	Address	Water Source	Reg.No
SW1	Falke Table Water	Nasarawa Area	D R	Al-9584L
SW2	Ganki Table Water	Home Savings Qtrs	D R	B1-4207C
SW3	Shekara Table Water	Rima Basin Area	D R	01-1077L
SW4	Inganu Table Water	Area D	D R	Al-5470L
SW5	Makeraj Table Water	Bayan Tasha	B H	Bl-7668L
SW6	Beldo Table Water	Gesse 1	D R	Al-7665L
SW7	M/Gandu Table Water	Bye pass Rd	B H	Al-77281
SW8	Milke Table Water	Tsohon Tasha	D R	None
SW9	Kardel Table Water	Aziza Rd	D R	None
SW10	Rufaidah Table Water	M/Rafi Rd	D R	None
SW11	Al-kasim Table Water	Badariya Area	D R	None
SW12	Zafah Table Water	Mechanic Village	B H	None
SW13	Bani Arab Table Water	FilinSukuwa	D R	B1-8685L
SW14	Aboki Water	Gesse 11	D R	01-9391L
SW15	Daras Table Water	GwadangajiQts	B H	A1-0480L
SW16	Umi Table Water	GRA Area	D R	A1-1993L
SW17	SadamAma Water	Badariya Area	D R	None
SW18	Mutunchi Table Water	Gwadangaji Area	B H	B1-7666L
SW19	De-Lily Table Water	Patrick Aziza Rd	D R	A1-3512L
SW20	Mijinyawa Table Water	Behind VVF Hosp.	D R	None

Note: D R = Dukku River, B H = Borehole Water

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Equipment
A GC–MS, QP 5000 Shimadzu instrument equipped with the ^{63}Ni selective Electron-Capture Detectors with advanced software (Chromcard-32 bit Ver 1.06) was used for the identification and quantification of pesticide residues in the samples.

Solvents
All the solvents used — methylene chloride, methyl- tertiary - butyl- ether (HPLC) grade — for the analysis was purchased from E-Merck.

Chemicals
All the chemicals (sodium chloride, sodium sulfate) were purchased from s. d.Fine Chem Ltd, India. The standards of organochlorine pesticides like aldrin, HCH mixed isomers, DDD, DDE, DDT, heptachlor, dieldrin, α and β- endosulfan and organophosphorus pesticides like methyl parathion, dimethoate, malathion, phosphamidon, profenofos, chlorpyrifos, parathion and diazinon chosen for this study were obtained from RDH Laborchemikalien GmbH & Co., KG D-30918 Seelze and Sigma Aldrich chemicals, Germany.

Sample Extraction and Clean- up
Extraction: Water samples were shaken well and filtered through Whatman filter paper no.1. pH of the samples was checked and it was found that pH of all the samples was neutral. After filtration, 1 litre water sample was taken in a 2 litre capacity separatory funnel and 20-30 mL of saturated sodium chloride solution was added. The water sample was partitioned with 100 mL of methylene chloride (thrice) by shaking the separatory funnel vigorously for 2-3 minutes and releasing the pressure intermittently. The layers were allowed to separate. The three extracts of methylene chloride layers were combined and passed through anhydrous sodium sulphate and concentrated to about 1-2 mL using a rotary vacuum evaporator. Again 10 mL methylene chloride was added for adsorption chromatography

Clean up*:* Cleanup was done by column chromatography packed with activated silica gel 10g (2h at 130°C) packed between two layers of sodium sulphate (5g each) and the column was eluted with 150 ml methylene chloride. Eluent was collected and concentrated to dryness. Final samples were prepared in methyl tertiary butyl ether (HPLC grade) and analyzed by Gas Chromatograph

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Sample Analysis
2 µl of the sample was injected and analyzed for the presence of pesticides, by GC–MS, QP 5000 Shimadzu instrument equipped with ^{63}Ni selective Electron-Capture Detectors. This detector allows the detection of contaminants at trace level concentrations in the lower ppb range in the presence of a multitude of compounds extracted from the matrix to which the detector does not respond.

The capillary column used was DB-5 coated with 5% diphenyl and 95%dimethylpolysiloxane. The carrier gas and the makeup gas was nitrogen with a 0.4 ml/min and 60-ml/min-flow rate respectively employing the split less mode. The oven temperature was kept at 60°C to 300°C with a ramp of 4°C/min. The detector and injector were maintained at 320°C and 250°C, respectively. The samples were calibrated (retention time, area count) against standard mixture of known concentration of all the organochlorine and organophosphorous pesticides analysed. Each peak was characterized by comparing relative retention time with those of standards. Identifications were confirmed by spiking with known standard and by performing thin layer chromatography of the pooled extract. Solvent systems used were 2% acetone in heptane and 10%chloroform in hexane. The spots corresponding to the position of standards were scraped, extracted and analysed by GLC.

The identifications were crosschecked with another GLC capillary column – DB-17-coated with 50% phenyl, 50% methyl polysiloxane (length 30m, ID 0.25 mm and film0.25 µm).

Recovery Test
Percentage recovery of the pesticides was studied by spiking each pesticide in distilled water that contains no pesticides at two concentration levels (250 and 500 µg/L).

The spiked samples were extracted using the same procedure followed in the extraction of other water samples and analyzed using the same method. The mean percentage recoveries for the various pesticides were calculated using the following equation:

$$P_i = (S_i/T_i) \times 100$$

where P_i is the percent recovery,
S_i is the analytical results from the laboratory control standard and
T_i is the known concentration of the spike.

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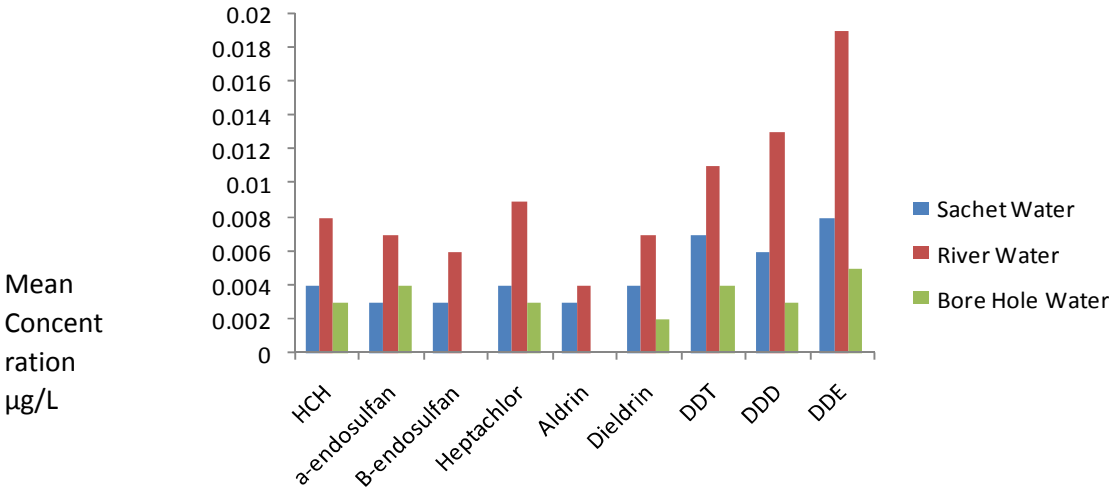
Recovery was in the range of 80-90 per cent for organochlorines and 70-80 per cent for organophosphorous pesticides indicating that the analytical procedure was satisfactory.



..Comparison of Organochlorine pesticide residues in the Sachet Water, River Water and Borehole Water Samples.

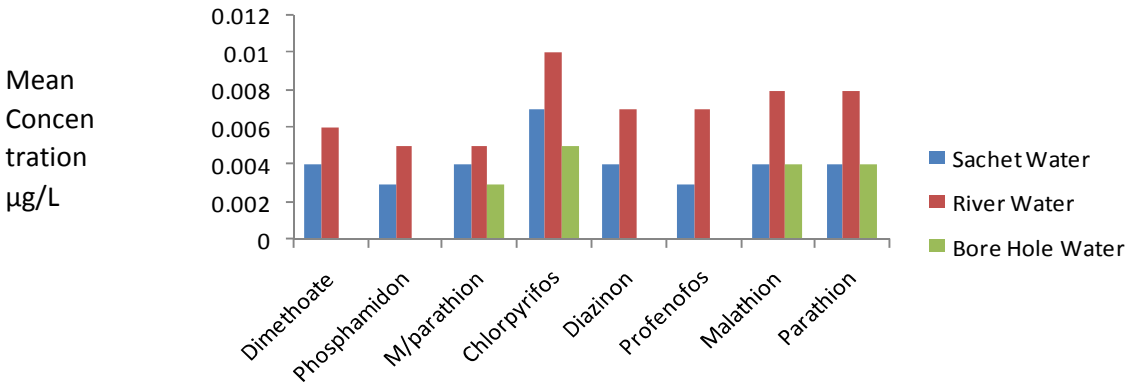


Fig. 2: Comparison of Organophosphorous pesticide residues in the Sachet Water, River Water and Borehole Water Samples.

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Table 2: Organochlorine Pesticide Residues in Sachet Water Collected from Different Stations (Conc. in µg/L).

S.Code	γ-HCH	α-endosulfan	β-endosulfan	Heptachlor	Aldrin	Dieldrin	DDT	DDD	DDE	Total
SW1	0.004±0.002	0.003±0.001	ND	0.007±0.002	0.003±0.001	0.005±0.002	0.009±0.003	0.007±0.002	0.009±0.003	0.047
SW2	0.002±0.002	ND	ND	0.005±0.001	ND	ND	0.006±0.001	0.007±0.001	0.009±0.002	0.029
SW3	ND	0.002±0.001	0.002±0.001	ND	ND	ND	0.008±0.004	0.008±0.002	0.008±0.002	0.028
SW4	0.005±0.001	0.003±0.002	0.002±0.001	0.003±0.001	0.003±0.001	0.004±0.001	0.008±0.002	0.009±0.004	0.005±0.003	0.042
SW5	0.005±0.003	0.003±0.001	ND	ND	ND	0.005±0.002	0.006±0.003	0.009±0.004	0.009±0.004	0.037
SW6	0.003±0.001	0.002±0.001	0.002±0.01	0.005±0.003	0.003±0.001	0.006±0.003	0.008±0.002	0.005±0.002	0.008±0.004	0.042
SW7	0.004±0.002	ND	0.003±0.001	ND	ND	ND	0.005±0.001	ND	0.007±0.002	0.019
SW8	0.005±0.002	0.005±0.003	ND	0.005±0.002	ND	0.003±0.001	0.007±0.001	0.006±0.003	0.009±0.001	0.040
SW9	ND	0.003±0.002	ND	0.005±0.001	0.002±0.001	0.005±0.002	0.007±0.004	0.007±0.002	0.005±0.003	0.034
SW10	0.003±0.001	0.004±0.001	0.004±0.002	0.003±0.001	ND	0.002±0.001	0.004±0.001	0.003±0.001	0.005±0.001	0.028
SW11	0.004±0.002	0.004±0.002	0.002±0.001	0.003±0.001	0.002±0.001	0.002±0.001	0.006±0.003	0.003±0.002	0.006±0.002	0.029
SW12	ND	ND	ND	0.003±0.001	ND	ND	0.005±0.002	ND	0.006±0.001	0.014
SW13	0.004±0.002	0.003±0.001	ND	0.004±0.003	0.003±0.002	0.006±0.004	0.006±0.003	0.005±0.003	0.009±0.004	0.040
SW14	0.004±0.003	0.004±0.002	ND	0.004±0.001	0.003±0.002	0.005±0.002	0.006±0.003	0.006±0.004	0.007±0.002	0.039
SW15	0.003±0.002	0.003±0.001	0.002±0.001	ND	ND	ND	ND	ND	0.006±0.003	0.014
SW16	0.005±0.003	0.004±0.002	0.003±0.001	0.004±0.002	0.003±0.001	0.005±0.003	0.006±0.003	0.006±0.004	0.008±0.003	0.044
SW17	0.005±0.002	0.005±0.003	0.003±0.001	0.003±0.001	0.003±0.001	0.004±0.002	0.007±0.004	0.006±0.003	0.009±0.004	0.045
SW18	0.004±0.001	0.004±0.001	ND	ND	ND	ND	0.006±0.002	0.006±0.003	0.007±0.002	0.027
SW19	0.005±0.003	ND	ND	0.003±0.002	ND	0.003±0.001	ND	ND	0.006±0.003	0.017
SW20	0.004±0.002	0.003±0.002	0.002±0.001	0.004±0.001	0.003±0.002	0.005±0.002	0.007±0.003	0.007±0.002	0.009±0.004	0.044
Mean Value	0.004	0.003	0.003	0.004	0.003	0.004	0.007	0.006	0.008	0.032
No of Samples Pesticide were Identified 17	16	10	15	10	14	18	16	20	20	
Min. Value	0.002	0.002	0.002	0.003	0.002	0.002	0.004	0.003	0.005	0.014
Max. Value	0.005	0.005	0.004	0.005	0.003	0.006	0.009	0.009	0.009	0.047
River water	0.008±0.003	0.007±0.004	0.006±0.003	0.009±0.004	0.004±0.002	0.007±0.003	0.011±0.005	0.013±0.005	0.019±0.004	0.084
Bore hole water	0.003±0.001	0.004±0.002	ND	0.003±0.002	ND	0.002±0.001	0.004±0.002	0.003±0.001	0.005±0.002	0.024

NOTE: Mean ± SD of Triplicate; ND= Not Detected;

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Table 3: Organophosphorus Pesticide Residues in Sachet Water Collected From Different Plants (Conc. in µg/L)

S.Cde	Dimethoate	Phosphamidon	M/parathion	Chlorpyrifos	Diazinon	Profenofos	Malathion	Parathion	Total	Total OC + OP
SW1	0.003±0.001	ND	0.005±0.001	0.007±0.004	0.005±0.002	ND	0.005±0.003	0.004±0.002	0.029	0.076
SW2	ND	ND	0.003±0.001	0.008±0.002	0.003±0.001	0.002±0.001	0.005±0.002	0.005±0.001	0.026	0.055
SW3	0.005±0.003	0.002±0.001	0.003±0.002	0.006±0.003	ND	ND	0.003±0.001	0.004±0.002	0.023	0.051
SW4	0.005±0.002	0.002±0.001	0.004±0.003	0.007±0.002	0.004±0.002	0.003±0.002	ND	0.004±0.002	0.029	0.071
SW5	0.002±0.001	ND	ND	0.005±0.002	ND	ND	0.003±0.002	0.003±0.001	0.013	0.050
SW6	0.003±0.002	ND	ND	0.005±0.004	0.003±0.001	0.003±0.002	0.004±0.002	0.004±0.003	0.022	0.064
SW7	ND	ND	ND	ND	ND	0.002±0.001	0.003±0.001	0.003±0.002	0.008	0.027
SW8	0.005±0.003	0.004±0.002	0.006±0.004	0.009±0.007	0.006±0.003	0.004±0.002	0.005±0.001	0.005±0.003	0.044	0.084
SW9	0.003±0.001	0.004±0.003	0.004±0.002	0.007±0.005	0.004±0.002	0.005±0.003	ND	ND	0.027	0.061
SW10	ND	ND	0.006±0.003	0.008±0.004	ND	ND	0.005±0.002	0.004±0.001	0.023	0.051
SW11	0.003±0.001	0.003±0.001	0.004±0.002	ND	0.002±0.001	ND	0.004±0.001	0.003±0.001	0.019	0.048
SW12	ND	ND	ND	0.006±0.001	ND	ND	0.003±0.001	ND	0.009	0.023
SW13	0.005±0.003	ND	0.005±0.001	0.009±0.001	0.005±0.003	0.003±0.001	0.004±0.002	0.005±0.003	0.036	0.076
SW14	0.006±0.001	0.004±0.002	0.004±0.001	0.007±0.003	0.004±0.002	0.003±0.001	0.005±0.003	0.005±0.001	0.038	0.077
SW15	ND	ND	0.003±0.001	0.006±0.001	ND	ND	ND	0.003±0.001	0.012	0.026
SW16	0.004±0.001	ND	0.004±0.001	0.008±0.002	0.004±0.001	ND	0.004±0.001	0.004±0.002	0.028	0.072
SW17	0.005±0.002	ND	ND	0.009±0.003	0.005±0.003	ND	0.005±0.004	0.006±0.002	0.030	0.075
SW18	ND	ND	0.003±0.001	0.005±0.001	ND	ND	0.003±0.001	ND	0.011	0.038
SW19	0.004±0.003	0.003±0.001	0.005±0.003	0.009±0.005	0.006±0.003	0.003±0.002	0.006±0.003	0.007±0.004	0.043	0.060
SW20	0.005±0.002	0.005±0.003	ND	0.007±0.003	ND	0.004±0.001	0.005±0.002	0.005±0.001	0.031	0.075
Mean Value	0.004	0.003	0.004	0.007	0.004	0.003	0.004	0.004	0.025	0.057
No of Samples Pesticides were Identified	14	8	14	18	12	10	17	17	20	20
Min Value	0.002	0.002	0.003	0.005	0.002	0.002	0.003	0.003	0.008	0.023
Max. Value	0.006	0.005	0.006	0.009	0.006	0.005	0.006	0.007	0.044	0.077
River Water	0.006±0.001	0.005±0.003	0.005±0.003	0.010±0.005	0.007±0.003	0.007±0.002	0.008±0.004	0.008±0.001	0.053	0.137
Bore Hole Water	ND	ND	0.003±0.001	0.005±0.003	ND	ND	0.004±0.001	0.004±0.002	0.014	0.038

NOTE: Mean ± SD of Triplicate. ND = Not Detected.

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Discussion

The analysis of sachet water samples collected from Birnin Kebbi metropolis andits environs showed the frequent presence of organochlorine and organophosphorus pesticide residues. Among the organochlorines DDE detected in 20 samples has the highest mean concentration of 0.008µg/L with a percentage distribution of 25.0%. DDT was detected in 18 samples with a mean concentration of 0.007µg/L and a percentage distribution of 21.88% of the total detectable residues. DDD was the third most detectable residues found in 16 samples with a mean concentration of 0.006µg/L and a percentage distribution of 18.75%.The existence of DDT along with its metabolite, DDD and DDE is an indication of both past and present usage of this pesticide within the catchment areas. γ-HCH was detected in 17 samples with a mean concentration of 0.004µg/L and a percentage distribution of 12.5%.HCH is used against sucking and biting pest and as smoke for control of pests in grain sores. HCH, previously called BHC (benzene hexachloride), is a mixture of eight isomers of which five are found in the crude product (α, β, γ, δ, ε). Only the γ-isomer or lindane has powerful insecticidal properties. It is very effective against a wide variety of insects, including domestic insects and mosquitoes. γ-HCH (lindane) appears in the list of pesticides for restricted use. Only γ-isomer of HCH was detected in the water samples analysed, which might be because γ-HCH is more resistant to biological and chemical degradation under aerobic conditions (El beit *et al*., 2011) and is most commonly used.

The presence of lindane, which is still a popular pesticide for seed dressing in the region, in various compartments in this sub-catchment, is an indicator of its potential source of contamination in Dukku River as it had been reported earlier (Osesua *et al*., 2017a).

Among the organophosphorus pesticide residues chlorpyrifos showed the highest mean concentration of 0.007µg/L detected in 18 samples having a percentage distribution of 28%. The high level of Chlorpyriphos observed in this work could be attributed to high initial usage and frequency of application as this substance forms a major component of several pesticide formulations. Parathion, malathion, dimethoate, methylparathion and diazinon each showed a mean concentration of 0.004µg/L and a percentage distribution of 17%, 17%, 14%, 14% and 12% respectively.

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Substantial residue levels of organochlorine insecticides including γ-HCH, heptachlor, aldrin, DDT and its metabolite and dieldrin in water could indicate possible illegal usage in the study area (Wandiga 2001) and/or their persistence from previous application before they were banned in 1997.

Comparing the total residues concentrations in the samples showed that brands which source their water from boreholes (SW7, SW12, and SW15) have relatively low levels of pesticide contamination as shown in Tables 2and 3. The soil acts as a sink to many pesticide residues. They are strongly adsorbed to the soil system and particulate matter. This interaction greatly affects the mobility of pesticide residues in the soil as a result many of the residues are retained in the top few layers of the soil especially the OCs and consequently their leaching into the ground water is minimized (Osesua *et al*., 2017b).This is in agreement with studies of organochlorine pesticide residues in surface and ground water samples, which have shown that the concentrations of organochlorine pesticide residues in surface water are generally higher than their corresponding concentrations in the water column (Osesua *et al*., 2017b).

The variation in concentrations between the sachet water and the source water (river and borehole are shown in Figures 1 and 2. This result reveals that the concentration of residues (organochlorine and organophosphorus) were highest in the river water than the borehole water and the sachet water. This is understandable because the Dukku River which supply over 70% of the raw water is surrounded by farmlands where intensive agrochemicals are being used to enhance agricultural productivities. These chemicals are easily washed into the river during runoffs from rains or irrigation processes. In general, the concentrations of the residues in water in this study were higher than the EU drinking water limits of 0.001 µg/L for individual pesticide and 1.0 µg/L for total pesticide concentration and corresponding levels reported in other agricultural sub-catchment sites in other tropical ecosystems such as in a banana plantation system in Jamaica (Mansingh and Wilson, 2015;USEPA, 2012),showing that Dukku River water was contaminated with various pesticide residues, including HCH, dieldrin, DDT and its metabolites (DDE and DDD), chlorpyrifos, diazinon and parathion.

Higher amounts of pesticide residues present in the river samples (Table 2 and 3) suggest that large quantities of pesticides had been applied in the surrounding agricultural fields. Although the usage of the banned organochlorine pesticides such as aldrin, dieldrin, DDT, and endosulfan in the study area was not established during the

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sampling period, their presence in the water was assumed to be due to previous application, high residual retention during the slow and gradual phase of dissipation from the water following previous application, and/or illegal recent usage. Mean concentrations of aldrin and dieldrin,which is an epoxide of aldrin, in sachet water were 0.003 and 0.004 µg/L, respectively (Table 2). Aldrin in water is changed by photolysis and microbial action to dieldrin which then degrades very slowly in soil, water, and sediment (Crawford, 2004).

Lindane detected at 0.004µg/L, 0.008µg/L and 0.003µg/L concentration in sachet water, river water and borehole water respectively in the present study may be photolyzed to β-BHC or to tetra- or penta-chlorinated cyclohexanes on exposure to sunlight (Diaz *et al*.,1995). These chemical changes could influence the concentrations in water with time.

The concentration of chlorpyrifos was the highest of all the OP pesticides detected with a mean concentration of0.007 µg/L, 0.010µg/L and 0.005µg/L in sachet, river and borehole water respectively (Table 3). This high concentration suggests that higher amounts of chlorpyrifos may have been applied in agricultural activities in the area as chlorpyrifos forms a major component of most pesticide formulations.

Although pesticides are perceived to dissipate faster in the tropics due to adverse environmental factors (Lalah *et al*., 2001; Wandiga, 2001; Bereket, 2000; Diaz *et al*., 1995; Matsumura, 1985), other factors such as intensive initial applications, bound residue formation with time and water cover by weeds, preventing loss due to photodegradation, volatilization, and leaching, may have contributed to the persistence of these high residue levels in the water. Since leaching and runoff are major pathways of contamination of Dukku River, given the topology and slope of the land toward the river, it is reasonable to correlate high residual levels detected in the water to concentrations of residues leaching from the several agricultural fields. More residues could also have come into the river through leaching and surface runoffs.

Due to their high water solubilities, organophosphorus pesticides such as dimethoate (water solubility: 242 mg/L), diazinon (42 mg/L), parathion (33 mg/L), and profenofos (33,000 mg/L), which are used in the study site, therefore, would pose a threat to aquatic organisms including fish in Dukku River (Osesua*et al*., 2017a).

DDT and its metabolites, HCH, dieldrin and endosulfan are among the nonleachers residues found in high concentration in borehole water (Table 2). These compound

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show high Kow values and small leaching potentials and consequently their residues are adsorbed strongly enough in soil system (Barlas, 2002). Their presence in this compartment could be attributed to their high usage in the catchment areas around Dukku River (Osesua *et al*., 2017a).

Organochlorine pesticide residues and their metabolites are very stable with long half lives in the environment (El-Mekkawi *et al*. 2009) and have a potentiality for bioaccumulation in the food chain posing a great threat to human health and the environment worldwide due to their low polarity, low aqueous solubility and high lipophilicity, unlike organophosphorus which are readily deactivated and degraded by micro-organisms and therefore do not readily accumulate (Afful *et al*., 2010).

The results obtained from this study were higher than those reported by Mathur *et al*. (2003) in bottled water in India. The mean concentration of OCPs obtained for the water samples were however lower than those reported by Ogunfowokan *et al*., (2012); the results obtained were also lower than those reported for other rivers in Nigeria (Okoya *et al*., 2013; Ize-Iyamu *et al*., 2007). The results showed that the mean concentration level of pesticide residues detected in the water samples were above the maximum acceptable concentration of 0.001µg/L value set by the European Union for the protection of the aquatic environment and drinking water, whilst the levels were very low when compared to the FEPA allowable level of 10µg/L. According to National Food and Drug Administration and Control (NAFDAC) pesticide residues covered under the relevant rule of the Prevention of Food Adulteration Act, 2001, should be "below detectable limits" when tested in accordance with the relevant methods.

Conclusion

Sachet water has become a necessity in people's lives due to the poor quality of municipal water supply. However, from the results obtained from this study, we can conclude that even the so called pure water (sachet water) contains much of the poisonous agrochemicals frequently used to enhance agricultural yields. However, out of 5 top brands and other less popular brands tested for 9 organochlorine pesticides and 8 organophosphorus pesticides, most of the sachet water samples were contaminated with pesticide residues. The levels, however, were lower than the raw water.

The concentration of organochlorine and organophosphorus pesticide residues was higher in the raw water samples than detected in the sachet water samples manufactured at these plants, which suggests that the treatment given at various plants

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reduces the concentration of pesticides residues but does not completely remove them. Even the top brands, which claim to use treatment methods like purification filtration, activated carbon filtration, and demineralization and reverse osmosis, were found to contain pesticides.

Residues of pesticides were detected even in the finished water samples of different brands of packaged drinking water, which means that treatment methods (like microfiltration, ultra filtration, reverse osmosis) followed by various manufacturers are either not effective in complete removal of pesticides, or the treatment is given to a part of the source water and not the entire water

The concentration levels of individual pesticide residues including γ-HCH, dieldrin, DDT and its metabolite (DDE and DDD), chlorpyrifos, malathion and parathion detected in the sachet water exceeded the EU drinking water limit requirement of 0.001µg/L. This indicates potential health risks to the local community who depend on sachet water for drinking and other domestic needs. An immediate mitigation would be needed to abate human exposure to these chemicals. Since these chemicals get into the water sources through agricultural practices and household application, the need to educate farmers mostly and the general public on proper handling of pesticides and avoid indiscriminate use becomes very imperative. It is also important to note that if measures are not taken to reduce the indiscriminate use of agrochemicals in this area or totaling substituting persistent organic pollutants with bio-pesticides, the concentration of these pollutants will accumulate higher and bio-magnify in the food chain.

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