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EVALUATION OF PESTICIDE RESIDUES IN BLOOD SAMPLES OF FARMERS AND NON-FARMERS IN SELECTED AGRICULTURAL COMMUNITIES IN SURU LOCAL GOVERNMENT AREA, KEBBI STATE, NIGERIA

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ABSTRACT: *Blood samples of 56 volunteers comprising of 35 farmers and 21 non-farmers were collected from seven major agricultural communities and evaluated for different pesticide residues level. Samples were extracted using n-hexane/diethyl ether (1:1) and clean-up following the standard procedure method specified by USEPA and the residues concentrations were determined using GC coupled with ^{63}Ni Selective Electron Capture Detector. The results obtained revealed that among the organochlorine residues detected in the farmers blood samples, DDE one of the metabolites of DDT is the most frequently detected with a mean concentration of 0.0338ng/g and a percentage distribution of 15.41% of the detectable residues. Chlorpyrifos showed the highest mean concentration of 0.0355ng/g among the organophosphorus residues detected. The results also revealed various residues contaminations in the blood samples of non-farmers indicating possible environmental contaminations resulting from indiscriminate use of agrochemicals in the catchment areas.*

KEYWORDS: Blood, Pesticide Residues, Farmers, Contamination, Agriculture

INTRODUCTION

Pesticide is a general term for substances which are used to poison pests (weeds, insects, molds, rodents etc.). The pesticides most acutely dangerous to humans are insecticides and rodenticides. Synthetic pesticides have been popular with farmers, because of their widespread availability, simplicity in application, efficacy and economic returns. But they also have huge environmental costs (Mathur *et al*., 2015).

The farm-workers during sprays on crops are directly exposed to pesticides while mixing, handling, spray, and through contaminated soil, air, drinking water, eating food and smoking at work places. Ultimately these are absorbed by inhalation, ingestion, and dermal contact (Vega, 2014). The residue concentrations of these compounds in the exposed farm-workers can lead to a variety of metabolic and systemic dysfunctions, and in some cases outright disease states. Therefore, the tremendous usage of pesticides has promoted monitoring studies in farming communities.

Common mode of action of the major pesticide products is to disrupt neurological function (Karalliede and Senanayake, 2015; Brown *et al*., 2015). In addition to being neurotoxic, these compounds are profoundly injurious to the immune and endocrine systems as well (Chambers and Levi, 2012; Arlien-Soberg, 2012; Luster and Rosenthal, 2013). Such ill health effects are

not limited only to those systems, but can cause a variety of dermatological, gastrointestinal, genitourinary, respiratory, musculoskeletal, and cardiological problems (Vial *et al*., 2016; Hueser, 2012).

Not many studies have been carried out to confirm that pesticides are responsible for various incidences of cancer and other diseases in Nigeria, but research worldwide has shown that pesticides do produce these effects. Biological monitoring provides the basis for estimating an internal chemical doze by measuring pesticides and their metabolite compounds concentrations in selected tissues, fluids, or bodily waste (feces and or urine) (Woollen, 2013).

Analysis of blood provides evidence of exposure of the body to pesticides and gives an indication of the body burden of the pesticide residues. Monitoring organochlorines (OCs) concentration in blood is most appropriate because these pesticides are lipophilic in nature. Similarly, monitoring organophosphorus (OP) concentrations in blood or blood products (serum, plasma) offers several advantages. The parent compounds can be monitored directly in blood products instead of their metabolites, which are usually measured in urine. Blood measurements provide an estimation of the dose available for the target site, allowing for prediction of dose-response relationships. Furthermore, because blood is a regulated fluid (the volume does not vary substantially with water intake or other factors), the blood concentrations of toxicants measured at a specific time interval after exposure will remain the same as long as the absorbed amounts are constant; therefore, no corrections for dilution are necessary (Wessels *et al.*, 2013)

Across the globe pesticides have been found in human blood, urine, breast milk, semen, adipose tissue, amniotic fluid, infant meconium and umbilical cord blood (Waliszewski *et al.*, 2015). Cumulative exposure to pesticides may come from food, water, air, dust, soil etc. Pesticides can be absorbed through skin contact, inhalation or accidental ingestion. Farm workers come into direct contact with pesticides at work and are also occupationally exposed to them. When a person is exposed to pesticides, body's detoxification mechanisms are activated. Some pesticides are metabolized into different chemicals and excreted and some are stored in fatty tissues in the body. Body burden data from analysis of blood provides evidence of exposure to chemicals stored in our body (Thrasher *et al.*, 2012).

Presently, pesticide spray is global concern due to their potential risks to the health of the community (Rothlein *et al*., 2016; Latif *et al*., 2014). Because of successive pesticide application and their high toxicity, numerous cases of fatal poisoning by accidental ingestion and suicidal ingestion or homicidal rationales were reported. Indications of acute poisoning may develop during or after the period of exposure, depending on the type of pesticides and the manner of contact. Pesticides usually disturb the physiological and biochemical activities of lymphocytes and erythrocytes (Bamerjee *et al*., 2012). Also, it has been reported that such residues persist in adipose tissues for long periods up to many decades, found to be endocrine disrupters; inhibit many enzymes, cause immune suppression and go ahead to higher susceptibility to beginning of cancer (Iscan *et al*., 2012; Wolff *et al*., 2013; Safi, 2012).

In Nigeria, about 70% of the population involved in agriculture sector directly or indirectly are domiciled in the villages. To protect the crops from pests' attack, farmers use synthetic pesticides and their tendency is increasing day by day (Azmi, 2016). In Nigeria, utilization of pesticides is not well controlled as compared to the developed countries due to ineffective legislation, deficient in awareness about the dangerous outcomes and technical know-how

along with the agricultural community, pesticide administration is not being appropriately regulated (Latif *et al*., 2011; Latif *et al*., 2013). Thus, due to mishandling and malpractices as the farm workers do not follow the necessary precautions, dangerous consequences may occur in their own health and causing various troubles such as pesticide contamination to the food chain and pesticide residue accumulation in the consumer's body. The direction of tolerances including maximum residue level (MRL), acceptable daily intake (ADI) and no observable adverse effect level (NOAEL) for different pesticides in foodstuffs are reported by Codex Alimentarius Commission (CODEX, 2014). In Nigeria, limited studies have been carried out on pesticide residues in human blood, and urine (Azmi *et al*., 2015). The aim of the present study was to evaluate pesticide residues in blood samples of some volunteers of selected rural areas that were either directly or indirectly exposed to pesticide applications in farming activities in Srur Local Government Area, Kebbi state.

MATERIALS AND METHODS

Selection and Description of Sampling Population

Selection of areas was based on the higher pesticide consumption and extensive agriculture activities. Before taking the blood samples from the volunteers, interviews were conducted with reference to their occupational histories to get knowledge about their years of involvement to pesticide exposure, age, sex and clinical history.

This study was carried out on the agriculture farmers that were involved in intensive use of agrochemicals to enhance crop yields and are inhabitants to 7 towns and villages; Dakingari, Suru, Aljannare, Barbarejo, Bandam, Kwaifa and Giro of Suru Local Government Area in Kebbi State, Nigeria. These towns and villages were selected based on their intensive and repeated sprays of pesticides on crops of fruits and vegetables and especially rice during the year 2018 harvest season (7^{th} -9^{th} September, 2018). Blood samples were taken from 56 farmers including 35 workers involved in sprays i.e. subjects (average age 35.6 years) and 21 controls (average age 34.8 years) who belonged to farmers' community but never spray pesticides on crops or anywhere else.

Sample Collection

Venous blood (5ml) of 105 people comprising of 70 farmers (subject) and 35 non-farmers (control) from 7 different towns/villages of Suru Local Government in Kebbi State were collected from the veins in the inner forearms of each volunteer in the month of September, 2018. Blood samples were collected in residue free heparinised 20 ml glass vials containing 200 USP units of heparin in 0.2 ml solution with the help of sterilized syringe. Whole blood samples were transported in dry ice to the laboratory and stored at - 8^0C until analysed.

Reagents

Reference standards of pesticides were purchased from Sigma-Aldrich (Germany) with purity between 98% - 99%. Methanol, diethyl ether, n-hexane and acetone were obtained from Sharlau (Barcelona, Spain) and anhydrous sodium sulfate was acquired from Merck (Germany). Stock solutions of each pesticide standard with concentration of 100 mg/kg were prepared in n-hexane and stored in a freezer at –8^0C. A mixture from stock solution of all

pesticide standards was prepared by transferring 1 ml of each stock solution to a 100 ml volumetric flask and diluted up to the mark with n-hexane.

Sample Extraction and Clean-up

Aliquot of 2.0 ml of serum was equilibrated to room temperature and 1.0 ml of methanol was added; the sample was agitated for 1 min, 5ml n-hexane: diethyl ether (1:1 v/v) mixture was added and again agitated for 2 min. Further, sample was centrifuged for 5 min at 2500rpm. The organic phase was collected, and the aqueous phase was extracted twice with 5 ml of n-hexane: diethyl ether (1:1 v/v) mixture. Collected organic phases were combined and evaporated to 1 ml. Clean-up of the sample was done by USEPA method 3620B using florisil as adsorbent in column chromatography and diethyl ether and hexane as eluent, final reconstitution was done with n-hexane: acetone (1:1 v/v) with final volume of 2 ml and analysed by GC-ECD (Moreno *et al*., 2016).

Instrumental

Estimation of pesticide residues was undertaken using Gas chromatograph (GC) equipped with ^{63}Ni Electron Capture Detector (ECD) and Flame Thermionic Detector (Shimadzu 2010 Plus). The GC oven temperature for electron capture detector was programmed for an initial temperature of 170°C withhold time of 13 min, and then increased to 270°C at a rate of 3°C/min withhold time of 20 min. Whereas for flame thermionic detector oven temperature was programmed for an initial temperature of 180°C withhold time for 2 min, then increased to 270°C at a rate of 10°C/min withhold time of 3 min and finally to 280°C at a rate of 5°C/min withhold time of 5 min. The injection port temperature was kept at 280°C and the detectors temperature at 310°C. The concentrations of target pesticide residues in blood samples were quantified by comparing the peak area and retention time of the particular compound in sample extracts to that of the corresponding external standard of pesticide run under the same operating conditions separately. The trueness of the method used was estimated by calculating the recovery from spiked samples with known concentrations. The mean recovery values were ranged from 85.4% to 95.5%. The calculated concentrations of residues in samples were not corrected for recovery. The limit of detection was established as 1ng/g for OCPs and 2ng/g for OPs. The confirmation of pesticide residues detected by GC was done on Gas chromatography-Mass spectrometry (Shimadzu GCMS QP 2010 plus). The mass spectrometer was operated in electron impact mode. The emission current for the ionization filament was set at 80μA generating electrons with energy of 70eV. Helium (99.99%) at a flow rate of 0.94 ml/min was used as carrier and collision gas. Selective ion monitoring (SIM) mode in GCMS for OCPs, and OPs was used considering retention time windows and base peak ion.

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RESULTS AND DISCUSSION

Table 1: Pesticide Residues in Whole Blood Samples of Farmers (Conc. ng/g)

Samples	Code	γ-HCH	DDT	DDD	DDE	Endosulfan	Chlorpyrifos	Parathion	Monocrotofos	Malathion	Phosphamidon
Dakingari	BS1	0.0327±0.021	0.0412±0.013	0.0541±0.004	0.0513±0.006	0.0162±0.009	0.0563±0.007	0.0276±0.005	0.0000	0.0111±0.001	0.0051±0001
	BS2	0.0247±0.006	0.0401±0.006	0.0552±0.007	0.0314±0.002	0.0081±0.005	0.0479±0.005	0.0152±0.002	0.0064±0.008	0.0000	0.0000
	BS3	0.0338±0.011	0.0189±0.006	0.0361±0.006	0.0360±0.005	0.0304±0.007	0.0415±0.002	0.0000	0.0034±0.004	0.0000	0.0000
	BS4	0.0098±0.003	0.0067±0.002	0.0371±0.009	0.0290±0.002	0.0000	0.0376±0.006	0.0095±0.003	0.0107±0.007	0.0058±0.004	0.0052±0.001
	BS5	0.0303±0.002	0.0055±0.001	0.0404±0.005	0.0430±0.005	0.0076±0.001	0.0363±0.004	0.0000	0.0044±0.001	0.0023±0.001	0.0022±0.001
Aljannare	BS1	0.0000	0.0391±0.004	0.0419±0.009	0.0453±0.003	0.0000	0.0447±0.008	0.0115±0.007	0.0125±0.006	0.0112±0.004	0.0000
	BS2	0.0311±0.007	0.0327±0.006	0.0341±0.006	0.0444±0.008	0.0116±0.002	0.0448±0.006	0.0089±0.001	0.0000	0.0171±0.007	0.0000
	BS3	0.0501±0.010	0.0333±0.008	0.0337±0.003	0.0437±0.006	0.0177±0.005	0.0511±0.011	0.0113±0.007	0.0091±0.003	0.0000	0.0000
	BS4	0.0366±0.009	0.0211±0.007	0.0388±0.004	0.0491±0.005	0.0211±0.002	0.0443±0.005	0.0000	0.0101±0.003	0.0000	0.0000
	BS5	0.0321±0.007	0.0000	0.0227±0.007	0.0271±0.004	0.0000	0.0480±0.009	0.0000	0.0000	0.0000	0.0000
Barbarejo	BS1	0.0339±0.010	0.0371±0.009	0.0377±0.009	0.0379±0.007	0.0214±0.007	0.0344±0.003	0.0098±0.002	0.0116±0.008	0.0077±0.001	0.0075±0.003
	BS2	0.0000	0.0237±0.002	0.0251±0.002	0.0263±0.003	0.0081±0.002	0.0321±0.002	0.0100±0.002	0.0111±0.002	0.0084±0.002	0.0112±0.002
	BS3	0.0334±0.003	0.0310±0.001	0.0335±0.007	0.0411±0.009	0.0300±0.006	0.0481±0.009	0.0000	0.0113±0.003	0.0000	0.0000
	BS4	0.0233±0.002	0.0238±0.007	0.0255±0.005	0.0313±0.004	0.0371±0.005	0.0380±0.011	0.0112±0.002	0.0121±0.005	0.0117±0.007	0.0066±0.006
	BS5	0.0000	0.0000	0.0201±0.002	0.0279±0.003	0.0214±0.003	0.0332±0.002	0.0114±0.001	0.0000	0.0111±0.001	0.0000
Bandam	BS1	0.0228±0.001	0.0254±0.002	0.0266±0.006	0.0286±0.008	0.0116±0.001	0.0347±0.003	0.0112±0.001	0.0144±0.004	0.0044±0.002	0.0000
	BS2	0.0317±0.003	0.0311±0.003	0.0332±0.002	0.0346±0.004	0.0113±0.003	0.0343±0.004	0.0000	0.0142±0.002	0.0000	0.0000
	BS3	0.0241±0.002	0.0322±0.007	0.0331±0.004	0.0337±0.007	0.0229±0.003	0.0339±0.009	0.0212±0.002	0.0115±0.004	0.0112±0.001	0.0000
	BS4	0.0000	0.0331±0.004	0.0344±0.003	0.0371±0.004	0.0000	0.0344±0.005	0.0117±0.003	0.0107±0.003	0.0111±0.002	0.0075±0.003
	BS5	0.0229±0.007	0.0311±0.009	0.0451±0.005	0.0449±0.007	0.0337±0.006	0.0337±0.007	0.0209±0.002	0.0119±0.004	0.0177±0.004	0.0115±0.005
Suru	BS1	0.0300±0.005	0.0377±0.009	0.0000	0.0000	0.0115±0.002	0.0307±0.004	0.0220±0.005	0.0000	0.0000	0.0000
	BS2	0.0000	0.0312±0.006	0.0337±0.007	0.0343±0.006	0.0225±0.005	0.0331±0.009	0.0116±0.003	0.0077±0.001	0.0081±0.001	0.0066±0.001
	BS3	0.0227±0.004	0.0331±0.002	0.0323±0.003	0.0377±0.007	0.0221±0.001	0.0299±0.005	0.0000	0.0225±0.007	0.0000	0.0000
	BS4	0.0211±0.007	0.0320±0.005	0.0341±0.004	0.0338±0.009	0.0117±0.007	0.0342±0.005	0.0229±0.004	0.0209±0.003	0.0114±0.002	0.0112±0.002
	BS5	0.0287±0.007	0.0226±0.007	0.0288±0.003	0.0259±0.004	0.0211±0.002	0.0279±0.003	0.0212±0.003	0.0223±0.003	0.0117±0.002	0.0121±0.003
Kwaifa	BS1	0.0244±0.002	0.0236±0.003	0.0000	0.0000	0.0000	0.0228±0.007	0.0000	0.0000	0.0000	0.0000
	BS2	0.0251±0.003	0.0223±0.008	0.0215±0.003	0.0238±0.003	0.0000	0.0311±0.005	0.0000	0.0000	0.0000	0.0000
	BS3	0.0000	0.0214±0.006	0.0226±0.005	0.0219±0.006	0.0000	0.0309±0.003	0.0065±0.001	0.0044±0.004	0.0057±0.003	0.0000
	BS4	0.0179±0.002	0.0211±0.001	0.0228±0.003	0.0289±0.004	0.0118±0.007	0.0221±0.005	0.0110±0.002	0.0127±0.007	0.0114±0.005	0.0000
	BS5	0.0119±0.007	0.0277±0.003	0.0213±0.008	0.0225±0.005	0.0124±0.005	0.0231±0.002	0.0108±0.004	0.0116±0.001	0.0000	0.0000
Giro	BS1	0.0312±0.003	0.0331±0.005	0.0311±0.007	0.0335±0.003	0.0113±0.009	0.0354±0.005	0.0344±0.007	0.0113±0.004	0.0102±0.004	0.0091±0.007
	BS2	0.0000	0.0277±0.005	0.0000	0.0000	0.0230±0.003	0.0300±0.005	0.0000	0.0217±0.004	0.0000	0.0000
	BS3	0.0000	0.0224±0.002	0.0235±0.005	0.0266±0.003	0.0000	0.0288±0.006	0.0000	0.0000	0.0055±0.001	0.0000
	BS4	0.0223±0.003	0.0215±0.005	0.0265±0.003	0.0208±0.004	0.0117±0.006	0.0311±0.009	0.0115±0.003	0.0221±0.002	0.0104±0.003	0.0042±0.002
	BS5	0.0227±0.005	0.0221±0.002	0.0251±0.007	0.0271±0.003	0.0000	0.0209±0.009	0.0000	0.0115±0.006	0.0000	0.0000
No of Samples Pesticides was Identified		27	33	32	32	26	35	23	27	21	13
	Mean	0.0262	0.0275	0.0322	0.0338	0.0180	0.0355	0.0149	0.0139	0.0098	0.0076

Note: BS = Blood Sample. Each value is an average of triplicate.

Table 2: Pesticide Residues in Whole Blood Samples of Non-farmers (Conc. ng/g).

Samples	Code	γ-HCH	DDT	DDD	DDE	Endosulfan	Chlorpyrifos	Parathion	Monocrotofos	Malathion	Phosphamidon
Dakingari	BS1	0.0000	0.0021±0.001	0.0022±0.001	0.0022±0.001	0.0000	0.0021±0.001	0.0000	0.0000	0.0000	0.0000
	BS2	0.0000	0.0000	0.0024±0.001	0.0022±0.001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	BS3	0.0000	0.0000	0.0000	0.0000	0.0000	0.0024±0.001	0.0000	0.0000	0.0000	0.0000
Aljannare	BS1	0.0022±0.001	0.0024±0.001	0.0031±0.002	0.0033±0.002	0.0020±0.001	0.0033±0.001	0.0000	0.0000	0.0000	0.0000
	BS2	0.0000	0.0033±0.001	0.0000	0.0000	0.0000	0.0025±0.001	0.0000	0.0000	0.0000	0.0000
	BS3	0.0024±0.001	0.0032±0.002	0.0000	0.0000	0.0022±0.001	0.0031±0.002	0.0000	0.0022±0.001	0.0000	0.0000
Barbarejo	BS1	0.0000	0.0033±0.002	0.0035±0.001	0.0031±0.002	0.0000	0.0038±0.002	0.0000	0.0000	0.0022±0.001	0.0000
	BS2	0.0033±0.001	0.0000	0.0033±0.001	0.0037±0.001	0.0000	0.0044±0.002	0.0000	0.0000	0.0000	0.0000
	BS3	0.0031±0.002	0.0000	0.0036±0.002	0.0035±0.002	0.0027±0.001	0.0041±0.002	0.0000	0.0023±0.001	0.0025±0.001	0.0000
Bandam	BS1	0.0000	0.0031±0.001	0.0040±0.002	0.0043±0.002	0.0000	0.0042±0.002	0.0000	0.0000	0.0000	0.0000
	BS2	0.0033±0.001	0.0037±0.002	0.0037±0.002	0.0039±0.002	0.0000	0.0043±0.001	0.0000	0.0027±0.002	0.0000	0.0000
	BS3	0.0000	0.0000	0.0000	0.0000	0.0000	0.0033±0.002	0.0000	0.0000	0.0000	0.0000
Suru	BS1	0.0031±0.002	0.0033±0.001	0.0036±0.001	0.0039±0.002	0.0000	0.0046±0.002	0.0023±0.001	0.0025±0.001	0.0022±0.001	0.0000
	BS2	0.0000	0.0000	0.0033±0.002	0.0031±0.001	0.0027±0.001	0.0049±0.001	0.0000	0.0022±0.001	0.0000	0.0000
	BS3	0.0036±0.001	0.0032±0.001	0.0035±0.001	0.0039±0.002	0.0000	0.0034±0.001	0.0000	0.0000	0.0000	0.0000
Kwaifa	BS1	0.0031±0.001	0.0033±0.001	0.0034±0.002	0.0032±0.002	0.0000	0.0044±0.002	0.0027±0.002	0.0021±0.001	0.0022±0.001	0.0000
	BS2	0.0033±0.002	0.0033±0.002	0.0036±0.001	0.0035±0.002	0.0000	0.0046±0.001	0.0000	0.0000	0.0000	0.0000
	BS3	0.0000	0.0000	0.0033±0.001	0.0037±0.001	0.0000	0.0000	0.0000	0.0023±0.001	0.0000	0.0000
Giro	BS1	0.0000	0.0037±0.001	0.0036±0.002	0.0040±0.002	0.0000	0.0041±0.002	0.0000	0.0031±0.002	0.0000	0.0000
	BS2	0.0033±0.001	0.0033±0.002	0.0035±0.001	0.0035±0.002	0.0000	0.0037±0.001	0.0000	0.0000	0.0000	0.0000
	BS3	0.0031±0.002	0.0000	0.0031±0.001	0.0037±0.001	0.0000	0.0044±0.001	0.0000	0.0000	0.0000	0.0000
No of Samples Pesticide was Detected.		11	13	17	17	4	19	2	8	4	0
Mean		0.0031	0.0032	0.0032	0.0033	0.0024	0.0038	0.0025	0.0024	0.0023	0.0000

Note: BS = Blood Sample. Each value is an average of triplicate.

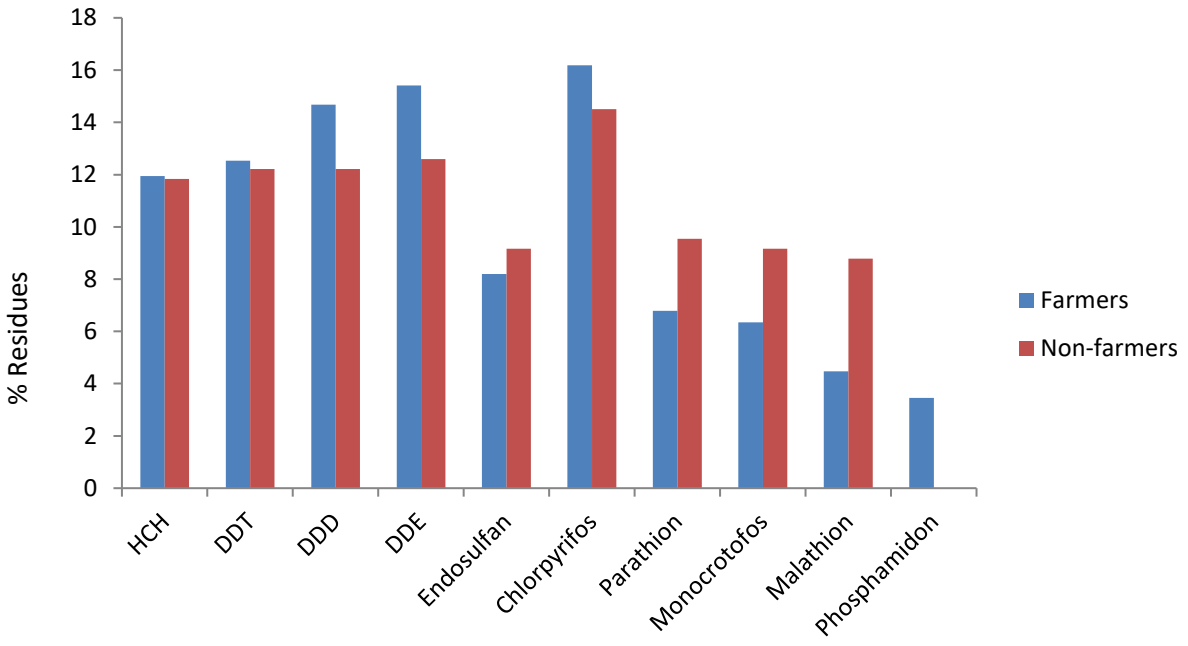

Figure 1: Percentage Distribution of Residues in Whole Blood of Farmers and Non-Farmers

DISCUSSION

Fifty-six (56) blood samples of farmers (35) and non-farmers (21) collected from seven (7) different villages of Dakingari, Aljannare, Barbarejo, Bandam, Suru, Kwaifa and Giro in Suru Local Government Area of Kebbi State were analysed for 5 organochlorines and 5 organophosphorus pesticides following methodology based on USEPA protocols and the results are shown in Tables 1 and 2.

Table 1 showed the residues concentration in whole blood samples of farmers who are actively involved in pesticide formulations, dilution, spraying etc at least in the last three years. Among the organochlorine's pesticides in Table 1, γ-HCH was detected in 27 samples with a mean level of 0.0262ng/g and a percentage distribution of 11.94% Figure 1. The detection of γ-HCH a powerful insecticide in whole blood samples might be due to its resistance to biological and chemical degradation under aerobic conditions (El Beit *et al.*, 2016).

Dichlorodiphenyltrichloroethane (DDT) is a potent non-systemic insecticide. It was detected in 33 of the whole blood samples analysed at mean levels of 0.0275ng/g with a percentage distribution of 12.53%. A major metabolite of DDT is 2,2-bis (*p*-chlorophenyl)-1,1-dichloroethylene (pp' DDE) was detected in 32 samples at mean levels of 0. 0338ng/g and have 15.41% distribution in the whole blood samples analysed. DDE is more persistent than DDT. 2,2-bis(p-chlorophenyl)-1,1-dichloroethane (DDD) another metabolite of DDT was detected in 32 samples at mean levels 0.0322ng/g in 14.68% (Figure 1) of the detectable residues. DDT was detected in blood samples perhaps due to its persistent nature. Since DDT is known to undergo metabolic conversion and dehydrochlorination, presence of metabolites of DDT i.e. DDD and DDE encountered in this study might be due to such metabolic processes. The

observed concentration levels for ∑-DDT (DDD+DDE+DDT) are comparatively lower than that reported in blood samples from similar catchment areas (Dua, *et al., 2014;* Bhatnagar, *et al.*, 2016). The existence of DDT and its metabolites (DDD and DDE) encountered in this study could be an indication of both past and present applications. Though the uses of DDT in agriculture and household activities have been banned in many countries, their uses in some countries still continue due to lack of suitable alternative (WHO, 2016). Furthermore, residues of DDT were observed to be lower than those recorded in Romania (2420 ng/ml), Spain (4895.8 ng/ml) and Sweden (836.1 ng/ml) (Glynn *et al*., 2015; Dirtu *et al* 2016; Porta *et al*., 2016).

Endosulfan was detected in the 26 whole blood samples of farmers with a mean concentration of 0.0180ng/g. The presence of endosulfan residues in blood samples in the present study may reflect either environmental exposure during spraying or consumption of food containing excessive levels of this pesticide. The concentration levels observed in this study is however lower than the 1.39ng/g reported by Pathak *et al*., (2016) in maternal blood samples in India, and Torres *et al*., (2016) reported endosulfan residues at a level of 76.38 ng/ml in pregnant women blood samples from Spain.

Among the organophosphorus residues, chlorpyrifos one of the most widely used insecticides in homes and agriculture was detected in 100% of the whole blood samples analysed with a mean concentration of 0.0355ng/g and a percentage distribution of 16.18% Figure 1. Monocrotophos, a

non-specific, systemic insecticide and acaricide is shown to cause delayed neuropathy. It is included in the PIC (Prior Informed Consent) procedure, an international convention that recognizes certain acutely hazardous pesticides as a human health risk. It was detected in 27 of the whole blood samples analysed at mean levels of 0.0139ng/g with percentage distribution of 6.34%. Higher levels of monocrotophos in blood samples could be due to higher repeated exposure of test samples to this pesticide during applications in fields.

Phosphamidon was detected in 13 of the samples at mean levels 0.0076ng/g and a distribution of 3.46% of the whole blood samples analysed. The low levels of phosphamidon observed in this study could be attributed to its low usage in the studied areas.

Table 2 showed the distribution and concentration of pesticide residues in whole blood samples of non-farmers. Chlorpyrifos detected in 19 of the 21 samples analsed has the highest mean concentration of 0.0038ng/g and a distribution of 14.5%. The existence of chlorpyrifos and any other pesticide residues in the blood samples of non-farmers could be attributed to environmental factors such as proximity to agricultural fields where intensive pesticide applications are carried out and also from contaminations of foods as a result of residues deposit.

The pesticides detected in the blood samples of volunteers (farmers/non-farmers) selected for this study are classified as insecticides, generally used by the farm workers to control different kinds of pests to protect their crops. The pattern of contamination showed by the seven villages sampled was found to be almost similar as there is no significant difference in residues contamination amongst the villages. This may be due to the same climatic conditions and farming activities. But there is a significant difference between residues concentrations observed in farmers and non-farmers whole blood samples analysed.

Due to deficiencies in schooling, knowledge and broad information regarding the application of pesticides from government associations/activities in these regions, farmers are susceptible to diseases and various kinds of illness due to inappropriate usage, storage, discarding and especially as they are not sheltered with special protecting equipment (gloves, rubber boots, safety goggles, masks, overalls with long sleeves etc.). The presence of pesticide residues in the blood of non-farmers is also very alarming and indicative of environmental exposure. After studying various other factors, it is assumed that the presence of chlorpyrifos, DDT and its metabolites in the blood of non-farmers may be due to the massive use of these pesticides since last couple of decades, or may be other potential sources involved such as impurity of other pesticides or the direct use of these pesticides in the catchment areas.

In conclusion, this work has shown that the population monitored (farmers and non-farmers) have been occupationally and environmentally exposed due to the excessive use of pesticides for pest control in their catchment areas. It can therefore be inferred from this study that human pesticide residue is a biological index of pesticide exposure and studies on blood can be used for assessing the total body burden data of pesticides in the occupationally exposed and unexposed population. There is a need to revitalize the pesticide regulation in view of the types of pesticides commonly used and the residues detected in the blood. From this study, it is also concluded that the existence of DDT and its metabolites and chlorpyrifos with higher frequencies are predisposing the entire population towards numerous health hazards, so for now, the global restrictions for the use of these pesticides should be observed in the areas. As the health consequences of pesticide residues levels in human blood are uncertain, the need for future monitoring studies are required to assess the relationship between residues levels and their deleterious effects particularly cancer on human health and environment.

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