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Assessment of Organophosphorus and Pyrethroid Pesticide Residues in Watermelon (*Citrulus lanatus*) and Soil Samples from Gashua, Bade Local Government Area Yobe State, Nigeria

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Abstract Watermelon (*Citrulus lanatus*) samples were freshly harvested from the Mashangwari, Katakam and Krigasawa agricultural locations in Gashua, Bade Local Government Area, Yobe State Nigeria. The watermelon samples were divided into peel, pulp, seed, leaf, root and stem for the determination of some organophosphate pesticide residues (dichlorvos, diazinon, chlorpyrifos, fenthion, malathion and fenitrothion) and pyrethroid pesticide residues (cypermethrin, bifenthrin, permethrin and deltamethrin). Soil samples were also collected at different depths for the determination of the above pesticides. Sample collection and preparation was conducted using standard procedures. The concentrations of all the pesticides in the soil and watermelon samples were determined using GC/MS SHIMADZU (GC-17A) equipped with electron capture detector (ECD). The highest concentrations of organophosphorous and pyrethroid pesticides from the three agricultural locations were observed in the peel, while the lowest concentrations were detected in the root. The concentrations of all the pesticides detected in the soil samples were observed to be higher at a depth of 21-30 cm, while the lowest concentrations were observed at a depth of 0-10 cm. The concentrations of dichlorvos, diazinon, chlorpyrifos, fenthion, malathion, fenitrothion, bifenthrin, permethrin and deltamethrin in the watermelon and soil samples were much higher than the maximum residue limits (MRLs) set for vegetables and soil. The results also showed that there is an existence of a variety of organophosphorus and pyrethroid pesticides in the watermelon and soil from the three agricultural locations. The observed concentrations of the studied pesticides from the agricultural locations could explain either their persistence in the environment or continued use in the study area. Hence, routine monitoring of pesticide residues in these study locations is necessary for the prevention, control and reduction of environmental pollution, so as to minimize health risks.

Keywords: *organophosphorus, pyrethroid, pesticide, residues, watermelon*

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1. Introduction

Pesticide is any substance or mixture of substances intended for preventing, destroying, repelling or mitigating any pest (insects, mice and other animals, unwanted plants, fungi, microorganisms such as bacteria and viruses, and prions) [10], Considering their chemical structure, the pesticides are organophosphorus, carbamates, organochlorines and pyrethroid [10]. Pesticides are of environmental concern in streams in both the water column and sediment. Those pesticides that are more hydrophobic tend to be detected more frequently in sediment; thus, measuring pesticides in sediment is important for tracking their fate in the environment and evaluating for potential toxicity [8].

Gashua is located in Yobe State, intense watermelon agricultural activities take place in the area, and is 10 km along the Lake Chad Basin area. The people in the areas are 98% predominantly farmers out of this, merely 85% are crop cultivating farmers. Watermelon (*Citrulus lanatus*), a member of the Cucurbitaceae family, is related to the cantaloupe, squash, pumpkin and other plants that also grow on vines on the ground. The watermelon production farmers in the study area use pesticides to control pests, diseases, weeds and other plant pathogens in an effort to reduce or eliminate yield losses and preserve high production quality. Lack of knowledge of the uses and effect of these pesticides among small and large scale farmers has resulted in contamination of the crops and soil with pesticide. Such contamination might be absorbed by the plant or vegetable while others leached to the underground water. Such accumulation by plants may affect humans and other species that depend on such watermelon and plants as food. Gashua in Bade Local Government Area (L.G.A), is primarily an agricultural area with intense pesticide usage for cultivating watermelon. Watermelon constitutes an important source of vitamin and mineral for the inhabitants in the area and around the country. Agricultural activities have impacted negatively on the soil. Bioaccumulation and bio-concentration of pesticides in the watermelon is capable of reaching toxic levels in the watermelon even when exposure is low. The study of the levels of pesticide residue in watermelon is very limited in the country. Therefore, the contamination status of watermelon by pesticide residues is unknown. This calls for an extensive study of the pesticide residues status of watermelon in Gashua, Bade Local Government Area.

2. Material and Methods

2.1. Sample Collection

Fresh mature watermelon samples of uniform colour and size were collected from three different agricultural locations namely Mashangwari, Katakam and Krigasawa in Gashua, Bade Local Government Area Yobe State, Nigeria. The leaf, stem and root of watermelon samples were also collected and transported to the laboratory, stored at 25°C for a period of six month. Soil samples were collected from ten plots. In each plot, soil was collected at three depths (0-10 cm, 10-20 cm and 20-30 cm), by using a spiral auger of 2.5 cm diameter. Soil was randomly sampled and bulked together to form a composite sample, collected in clean plastic bags and transported to the laboratory.

2.2. Sample Preparation

The watermelon was thoroughly washed with distilled water to remove dirt, dust, pesticide residues and then washed with pure ethanol to remove micro flora on the surface of the fruit prior to extraction. All glassware and knives were autoclaved at 121 °C for 45 min and all other equipments were sanitized with hypochlorite prior to usage. Each unit sample of watermelon was cut into 6 vertical pieces and then divided into peel, pulp and seed portions. Each prepared sample was maintained frozen at −20°C until when needed for analysis and was individually homogenized using a blender (BLIXER-5Plus) immediately before analysis.

2.3. Extraction of Watermelon Samples

Each homogenized (20 g of pulp and 10 g each of peel, seed, leaf, stem and root watermelon respectively) was weighed into an Erlenmeyer flask and extracted using 100 ml of acetonitrile by shaking for 30 min using a reciprocal shaker. The mixture was then filtered by vacuum suction and the residual cake was washed using 50 ml acetonitrile. The filtrates were combined and made up to 200 ml using acetonitrile.

2.4. Clean-up of Sample Extracts

A 2 ml aliquot of the acetonitrile extract was cleaned using solid-phase extraction with a styrene-divinylbenzene cartridge. Eight-ml of water was added to the acetonitrile extract and the mixture was loaded onto the cartridge. The cartridge was washed using 10 ml acetonitrile: water (1: 4, $^{V}/v$) and 15 ml tetrahydrofuran was passed through the cartridge; the eluate was evaporated to dryness using a rotary evaporator and nitrogen blow down apparatus. The residue was dissolved and diluted using 10 ml of acetonitrile: toluene (3: 1, $^{V}/v$) and loaded onto a graphite carbon black cartridge (500 mg/6 ml, (Supelclean ENVI-Carb; Sigma- Aldrich, MO, USA;) conditioned with the acetonitrile: toluene mixture). An additional 20 ml of the acetonitrile: toluene mixture was passed twice through the cartridge. All of the eluate was collected in a round-bottom flask and evaporated to dryness using a rotary evaporator and nitrogen blow down apparatus, after which the residue was dissolved and diluted using a suitable volume of acetonitrile: water (4 : 1, $^{V}/v$) mixture.

2.5. Extraction of Soil Sample

Soil samples were extracted using a soil-packed bulb column. Each sample (25 g) was weighed into a glass jar, the soil got fortified at this step, before adding pre-cleaned sand (25 g) and granular sodium sulphate (50 g). The sample mixture was manually shaken for 30 sec, placed on a roller for 30s and then allowed to stand for 20 min to provide time for the sodium sulphate to adsorb any residual moisture from the soil. The sample mixture was transferred to a 250 ml bulb column and the sample jar was triple rinsed with small amounts of 5 ml hexane and transferred to the bulb column. The soil contents were extracted with acetone: hexane (1:1 $^{V}/v$, 250 ml mixture) and the eluate collected and concentrated to 100 ml using a rotary evaporator. The soil extract was then subjected to additional clean-up.

2.6. Clean-up of Soil Extracts

The concentrated soil eluate was washed by liquid-liquid partitioning with saturated sodium sulphate (25 ml) and distilled water (300 ml) in a separatory funnel (500 ml). After shaking, the aqueous layer was drained into a beaker and the hexane was transferred to a separatory funnel (250 ml). The aqueous layer was returned to the 500 ml separatory funnel and re-extracted with 15 % dichloromethane in hexane (40 ml). The organic layers were combined in the 250 ml separatory funnel and gently washed with distilled water (100 ml) for about 30 sec. After discarding the aqueous layer, the organic layer was filtered through sodium sulphate, evaporated to near dryness on a rotary evaporator; the sides of the flask were rinsed down with hexane (20 ml), and evaporated to about 1 ml. The sample extract was quantitatively transferred to a centrifuge tube, concentrated on a nitrogen evaporator to 0.5 ml, and diluted to 2.0 ml final volume in hexane prior to Gas-Chromatographic (GC) analysis.

2.7. Determination of Pesticide Residues

The SHIMADZU GC/MS (GC – 17A), equipped with electron capture detector was used for the chromatographic separation and was achieved using a

35% diphenyl/65% dimethyl polysiloxane column. The oven was programmed as follows: initial temperature 40°C, 1.5 mins; to 150°C, 0.0 min. 5°C/min. to 200°C, 7.5 mins; 25°C/mins; to 290°C with a final hold time of 12 mins. and a constant column flow rate of 1mL/min. The detection of pesticides were performed using the GC-ion trap MS with optional MSn mode. The scanning mode offered enhances selectivity over either full scaned or selected ion monitoring (SIM). In SIM, at the elution time of each pesticide, the ratio of the intensity of matrix ions increase exponentially versus that of the pesticide ions as the concentration of the pesticide approach the detection limit, decreasing the accuracy at lower levels. The GC-ion trap MS was operated in MSn mode and performed tandem MS function by injecting ions into the ion trap and destabilizing matrix ions, isolating only the pesticide ions. The retention time, peak area and peak height of the samples were compared with those of the standards for quantization.

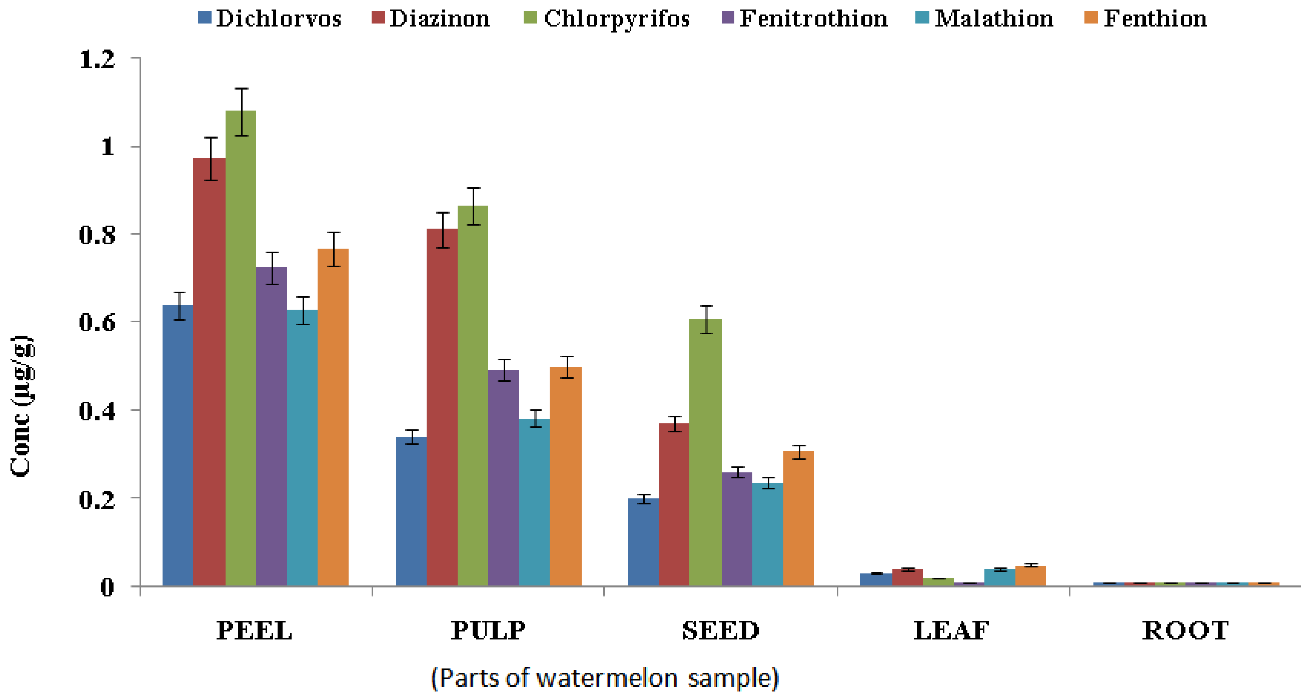

Figure 1. Mean concentrations of Organophosphorus Pesticide Residues in Different Parts of Watermelon Samples from Mashangwari Gashua, BadeLocal Governemnt Araea, Yobe State

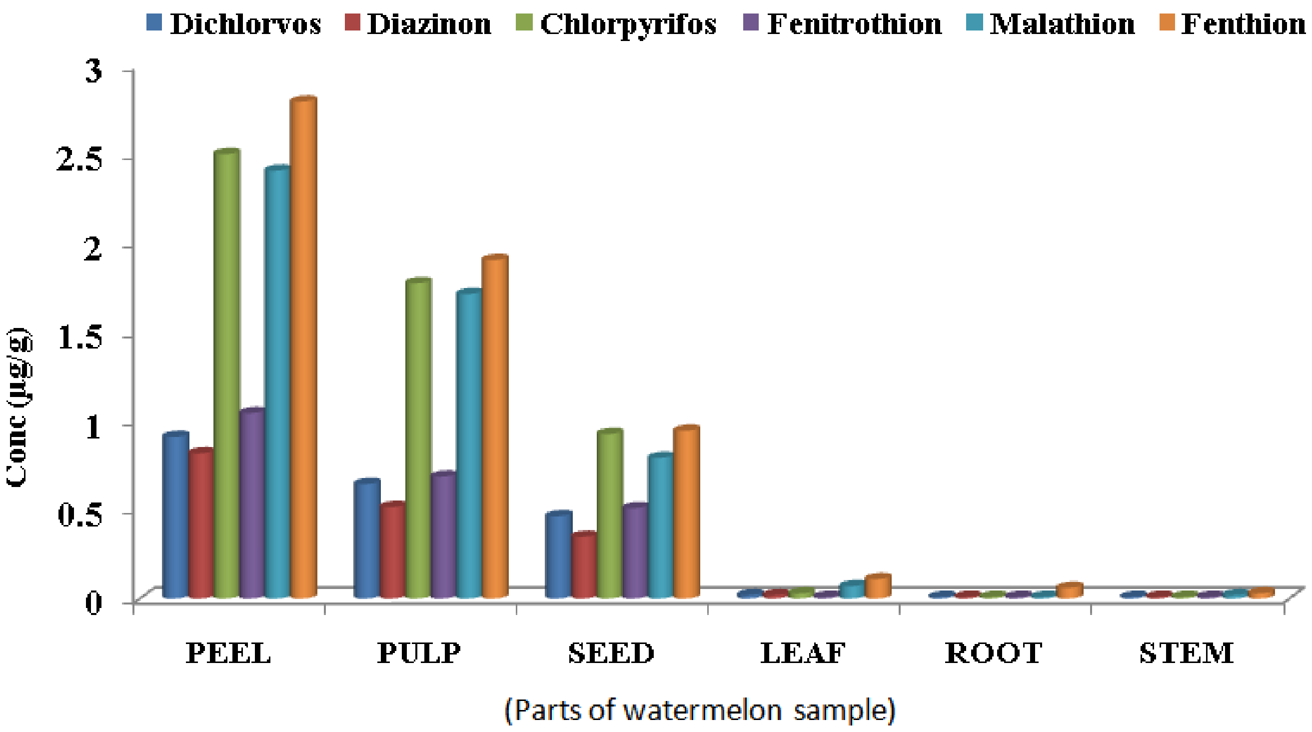

Figure 2. Mean concentrations of Some Organophosphorus Pesticide Residues in Different Parts of Watermelon Samples from Katakam, Gashua, Bade Local Governemnt Araea, Yobe State

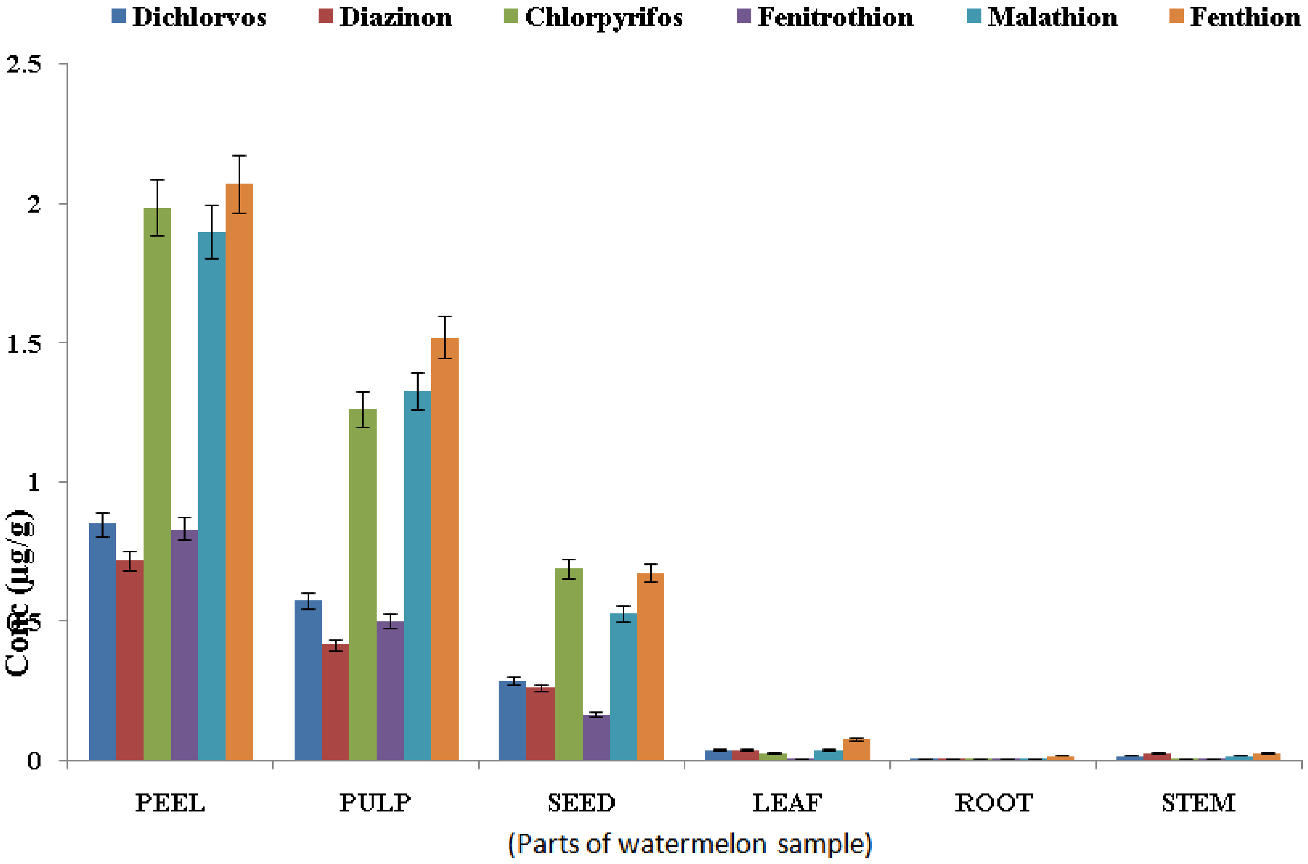

Figure 3. Mean concentrations of Organophosphorus Pesticide Residues in Different Parts of Watermelon Samples from Krigasawa, Gashua, Bade Local Governemnt Araea, Yobe State

3. Results

3.1. Organophosphorous Pesticide Residues in Different Parts of Watermelon Samples from the Three Agricultural Location

The concentrations of some organophosphorous pesticide residues in the peel, pulp, seed, leaf, root and stem of watermelon samples from Mashangwari location are as presented in Figure 1. The concentration of dichlorvos ranged from 0.01 to 0.63 µg/g; 0.02 to 0.97 µg/g diazinon; 0.03 to 1.0 µg/g chlorpyrifos; 0.01 to 0.72 µg/g fenitrothion. For malathion, the concentration ranged from 0.01 to 0.62 µg/g, while that of fenthion ranged from 0.01 to 0.67 µg/g. For Katakam agricultural location, the concentration of organophosphorous pesticide residues in peel, pulp, seed, seed, leaf, root and stem of watermelon samples is as presented in Figure 2. The concentrations of dichlorvos ranged from 0.02 to 0.91 µg/g; 0.01 to 0.81 µg/g diazinon; 0.03 to 1.77 µg/g chlorpyrifos; 0.01 to 1.04 µg/g fenitrothion. For malathion, the concentration ranged from 0.03 to 2.40 µg/g, while the concentration of fenthion ranged from 0.11 to 2.80 µg/g. Similarly, for Krigasawa agricultural location; the concentration of dichlorvos ranged from 0.01 to 0.85 µg/g; 0.02 to 0.71 µg/g diazinon; 0.01 to 1.99 µg/g chlorpyrifos; 0.02 to 0.83 µg/g fenitrothion. For malathion, the concentration ranged from 0.03 to 1.90 µg/g, while the concentration of fenthion ranged from 0.02 to 2.07 µg/g Figure 3. The highest concentration of dichlorvos in the watermelon samples from Mashangwari agricultural location was found in the peel with a value of 0.64 µg/g, while the lowest concentration of 0.01 µg/g was in the root. For diazinon, the highest concentration of 0.09 µg/g was detected in the peel, while the lowest concentration of 0.01 µg/g was also in the root. Similarly, for chlorpyrifos, fenitrothion, malathion and fenthion the highest concentrations were observed in the peel with values ranging from 0.06 to 1.08 µg/g, while the lowest concentration of 0.01 µg/g was observed in the root. A similar trend was observed at the Katakam and krigasawa agricultural locations.

3.2. Pyrethroid Pesticide Residues in Different Parts of Watermelon Samples from Mashangwari Agricultural Location

The concentrations of some pyrethroid pesticide residues in the peel, pulp, seed, leaf, root and stem of watermelon samples from Mashangwari agricultural location are as presented in Figure 4. The concentration of cypermenthrin ranged from 0.13 to 0.4 3 µg/g; 0.07 to 0.24 µg/g bifenthrin, 0.05 to 0.29 µg/g permethrin, while the concentration of deltamethrin ranged from 0.07 to 0.24 µg/g. The highest concentration of cypermethrin in the watermelon samples from the Mashangwari Agricultural location was observed in the peel with a value of 0.43 µg/g, while the lowest concentration of 0.13 µg/g was observed in the root. For bifenthrin, the highest concentration of 0.24 µg/g was observed in the peel, while the lowest concentration of 0.07 µg/g was also observed in the root. Similarly, the highest concentrations of permethrin and deltamethrin were observed in the peel with values ranging from 0.24 to 0.29 µg/g, while the lowest concentrations were observed in the roots with values ranging from 0.05 to 0.07 µg/g. For Katakam agricultural location, the concentrations of some pyrethroid pesticide residues in the peel, pulp, seed, leaf, root and stem of watermelon samples is as presented in Figure 5. The concentration of cypermenthrin ranged from 0.04 to 0.47 µg/g; 0.02 to 0.28 µg/g bifenthrin; 0.05 to 0.34 µg/g permethrin; and the concentration of deltamethrin ranged from 0.07 to 0.27 µg/g. The highest concentration of cypermethrin in the watermelon samples from the Katakam agricultural location was observed in the peel with a value of 0.47 µg/g, while the lowest concentration of 0.04 µg/g was observed in the root. For bifenthrin, the highest concentration of 0.28 µg/g was observed in the peel, while the lowest concentration of 0.02 µg/g was also observed in the root. Similarly, for permethrin and deltamethrin the highest concentrations were observed in the peels with values ranging from 0.27 to 0.34 µg/g, while the lowest concentrations were observed in the roots with the values of 0.05 and 0.07 µg/g.

Similarly, the concentration of some pyrethroid pesticide residues in peel, pulp, seed, leaf, root and stem of watermelon samples from Krigasawa is as presented in Figure 6. The concentration of cypermenthrin ranged from 0.04 to 0.38 µg/g; 0.01 to 0.18 µg/g bifenthrin; 0.05 to 0.27 µg/g permethrin; and the concentration of deltamethrin ranged from 0.03 to 0.20 µg/g. The highest concentration of cypermethrin in the watermelon samples from the Krigasawa agricultural location was observed in the peel with a value of 0.38 µg/g, while the lowest concentration of 0.04 µg/g was observed in the root. For bifenthrin, the highest concentration of 0.18 µg/g was observed in the peel, while the lowest concentration of 0.07 µg/g was also observed in the root. For permethrin and deltamethrin, the highest concentrations were observed in the leaf and peel with values ranging from 0.20 and 0.27 µg/g, while the lowest concentrations were observed in the root and seed with values of 0.05 and 0.03 µg/g from the Krigasawa agricultural location.

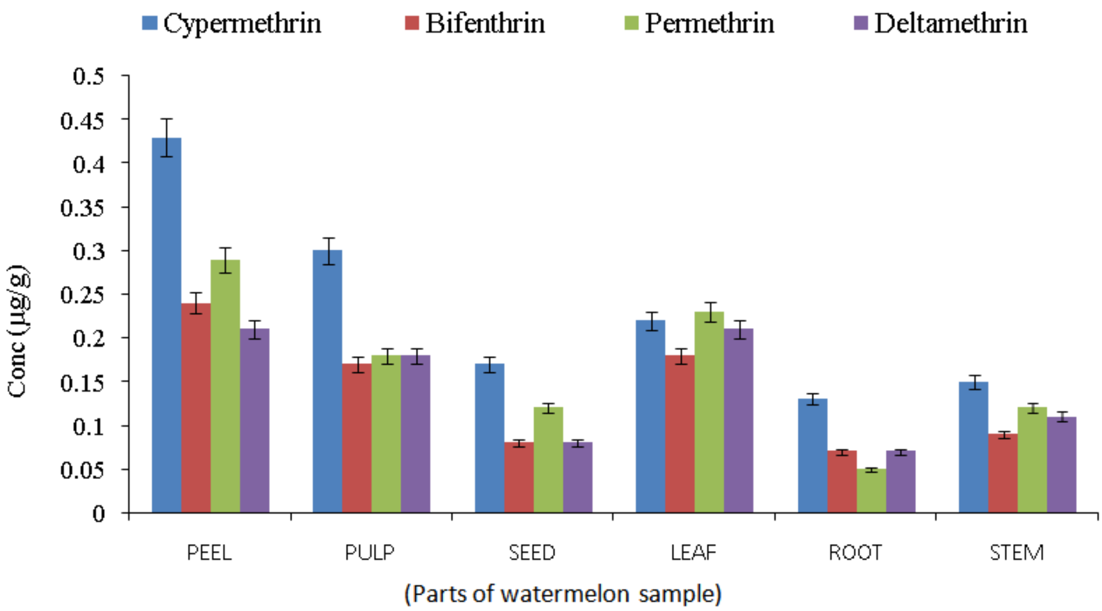

Figure 4. Mean concentrations of Some Pyrethroid Pesticide Residues in Different Parts of Watermelon Samples from Mashangwari, Gashua, Bade Local Governemnt Araea, Yobe State

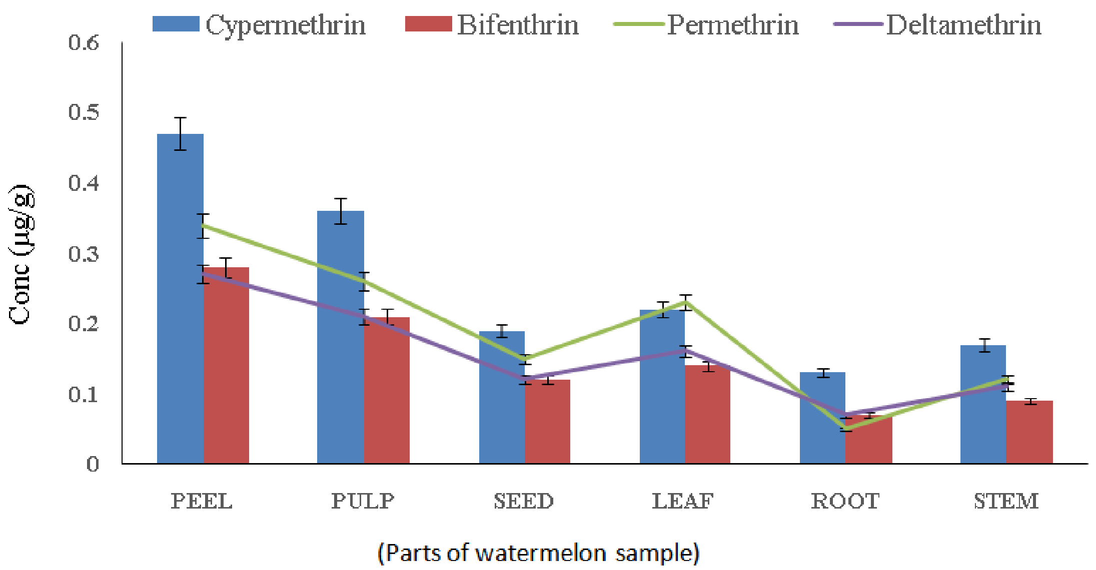

Figure 5. Mean concentrations of Some Pyrethroid Pesticide Residues in Different Parts of Watermelon Samples from Katakam, Gashua, Bade Local Governemnt Araea, Gashua, Yobe State

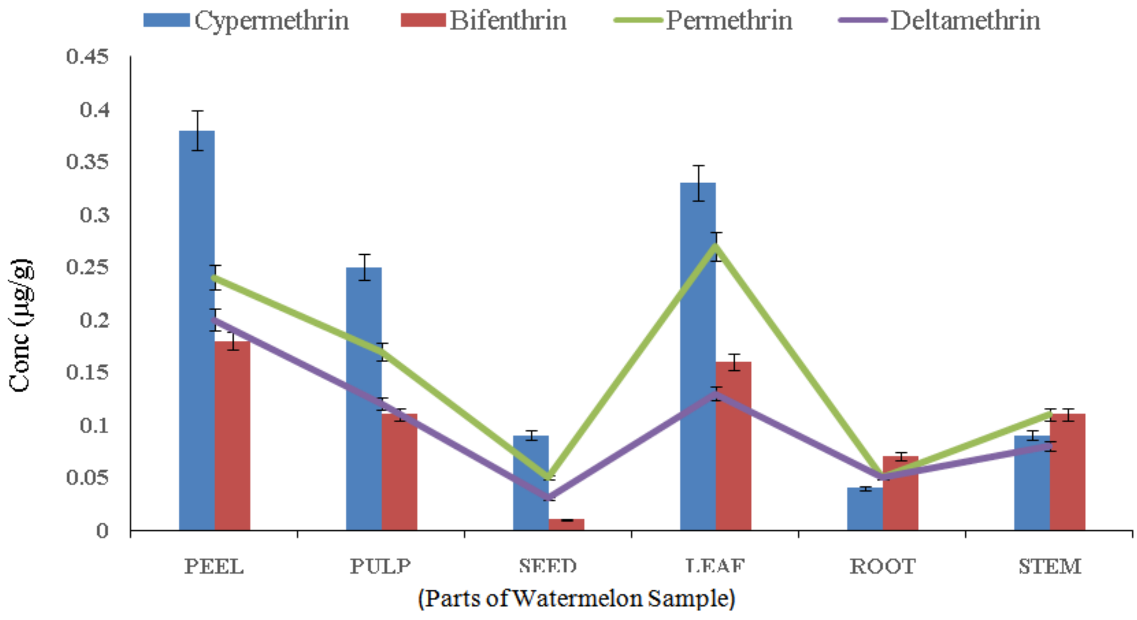

Figure 6. Mean concentrations of Some Pyrethroid Pesticide Residues in Different Parts of Watermelon Samples from Krigasawa, Gashua, Bade Local Governemnt Araea, Yobe State

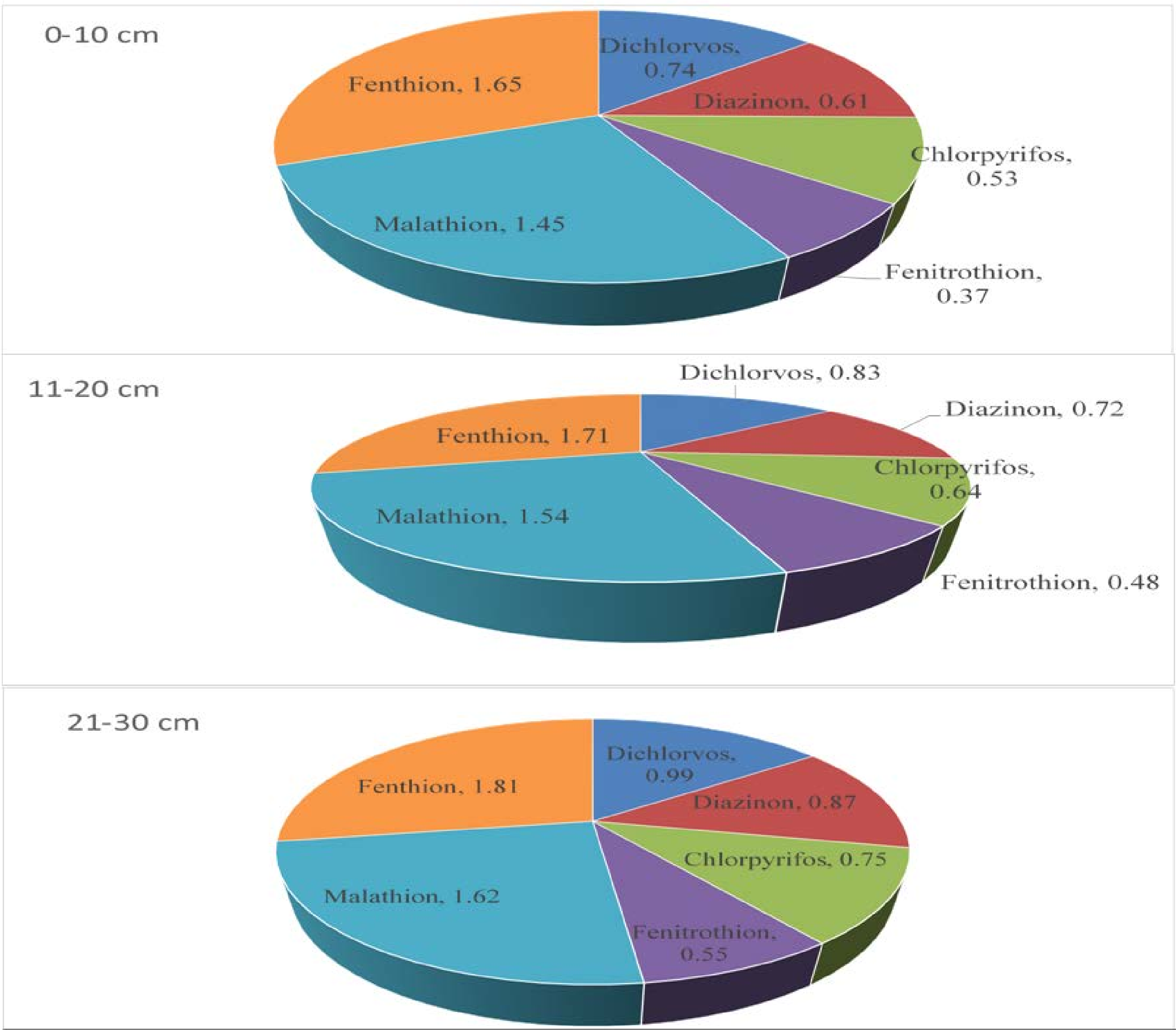

Figure 7. Mean concentrations of Organophosphorus Pesticide Residues in Soil Samples from Different Depth in Mashangwari Agricultural Local, Gashual Local Government Araea, Gashua, Yobe State

3.3. Organophosphorus Pesticide Residues in Soil Samples at Different Depths from the Three Agricultural Location

The concentration of some organophosphorous pesticide residues in soil samples at a depth of (0-10, 11-12 and 21-30 cm) from the Mashangwari agricultural location is as presented in Figure 7. The concentration of dichlorvos ranged from 0.74 to 0.99 µg/g; 0.61 to 0.87 µg/g diazinon; 0.53 to 0.75 µg/g chlorpyrifos and 0.37 to 0.55 µg/g fenitrothion. For malathion, the concentration ranged from 1.45 to 1.62 µg/g, while that of fenthion ranged from 1.65 to 1.81 µg/g. The highest concentration of dichlorvos in the soil sample was observed at a depth of 21-30 cm with a value of 0.99 µg/g, while the lowest concentration of 0.74 µg/g was observed at a depth of 0-10 cm. For diazinon, the highest concentration of 0.87 µg/g was also observed at 21-30 cm depth, while the lowest concentration of 0.61 µg/g was also observed at 0-10cm depth. The highest concentrations of chlorpyrifos, fnitrothion, malathion and fenthion were observed at a depth of 21-30 cm with values ranging from 0.55 to 1.81 µg/g, while the lowest concentrations were also observed at a depth of 0-10 cm with the values ranging from 0.37 to 1.65 µg/g. At the Katakam agricultural location Figure 8, the concentration of dichlorvos ranged from 0.81 to 1.54 µg/g; 0.78 to 1.08 µg/g diazinon; 0.66 to 0.83 µg/g chlorpyrifos and 0.52 to 0.76 µg/g fenitrothion. For malathion, the concentration ranged from 1.43 to 1.63 µg/g, while that of fenthion ranged from 1.53 to 1.71 µg/g. The highest concentration of dichlorvos in the soil sample was observed at a depth of 21-30 cm with a value of 1.54 µg/g, while the lowest concentration of 0.81 µg/g was observed at a depth of 0-10 cm. For diazinon, chlorpyrifos, fnitrothion, malathion and fenthion, the highest concentrations were also observed at a depth of 21-30 cm with values ranging from 0.76 to 1.71 µg/g, while the lowest concentrations were also observed at a depth of 0-10 cm with values ranging from 0.52 to 1.53 µg/g. Similar trend were also observed at the Krigasawa agricultural location Figure 4.9, where the concentration of dichlorvos in the soil sample ranged from 0.94 to 1.55 µg/g; 0.76 to 1.26 µg/g diazinon; 0.58 to 0.97 µg/g chlorpyrifos; 0.34 to 0.65 µg/g and 1.25 to 1.42 µg/g malathion, while the concentration of fenthion ranged from 1.33 to 1.53 µg/g. The highest concentrations of dichlorvos, diazinon, chlorpyrifos, fenitrothion, malathion and fenthion in the soil sample were observed at a depth of 21-30 cm with values ranging from 0.65 to 1.55 µg/g, while the lowest concentration ranged from 0.34 to 1.33 µg/g were observed at a depth of 0-10 cm.

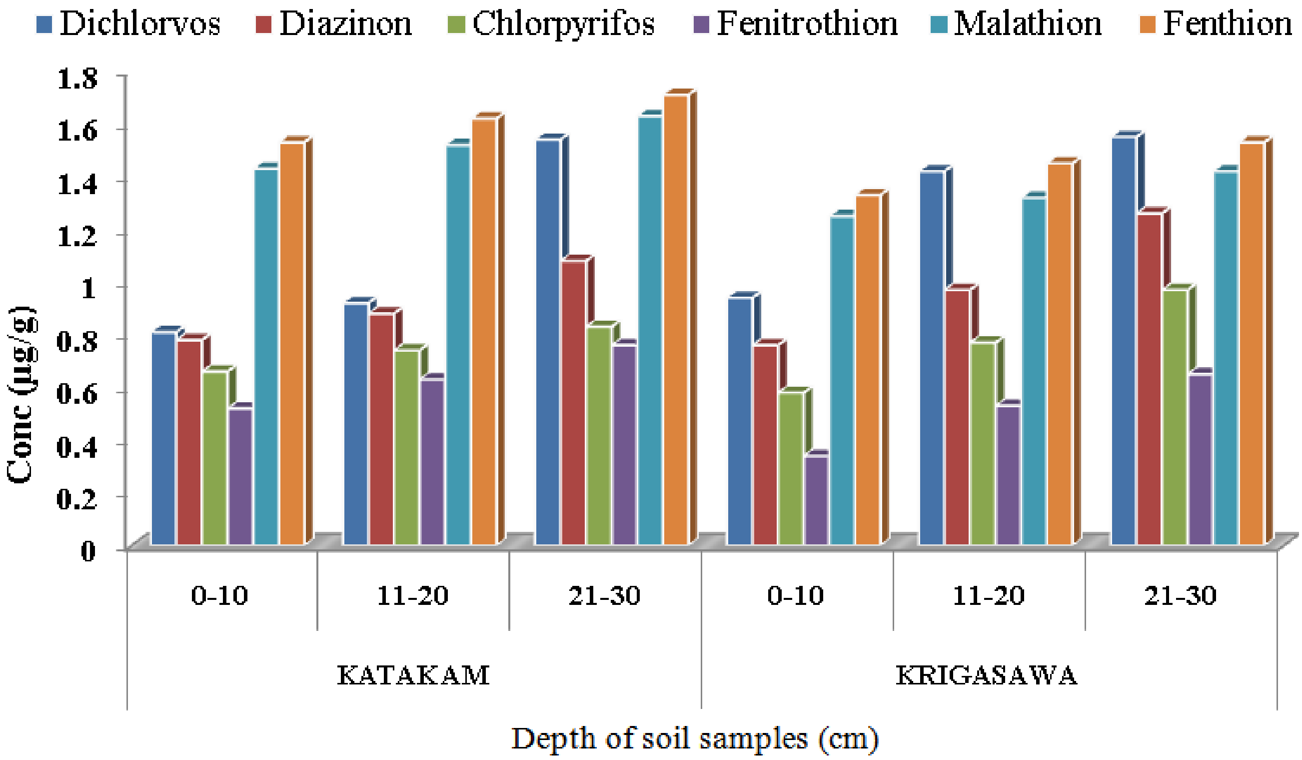

Figure 8. Mean Concentrations of Some Organophosphorus Pesticide Residues in Different Depths of Soil Samples from Different Katakam and Krigasawa Agricultural location, Gashua, Bade Local Government Area, Yobe State

3.4. Pyrethroid Pesticide Residues in Soil Samples at Different Depths from the Three Agricultural Locations

The concentration of pyrethroid pesticide residues at a depth of 0-10, 11-20 and 21-30 cm depth of soil samples from Mashangwari location is as presented in Figure 9. The concentrations of cypermethrin ranged from 0.44 to 0.71 µg/g; 0.43 to 0.64 µg/g bifenthrin. For permethrin, the concentration ranged from 0.33 to 0.53 µg/g, while the concentration of deltamethrin ranges from 0.21 to 0.33 µg/g. The highest concentration of cypermethrin in the soil sample was observed at a depth of 21-30 cm with a value of 0.71 µg/g, while the lowest concentration of 0.44 µg/g was observed at a depth of 0-10 cm. For bifenthrin, permethrin and deltamethrin, the highest concentrations of 0.64, 0.53 and 0.33 µg/g were observed at a depth of 21-

30 cm, while the lowest concentrations of 0.43, 0.33 and 0.21 µg/g were also observed at a depth of 0-10 cm. For Katakam agricultural location, the concentrations of some pyrethroid pesticide residues at a depth of 0-10, 11-20 and 21-30 cm is as presented in Figure 9. The concentrations of cypermethrin ranged from 0.61 to 0.92 µg/g; 0.69 to 0.83 µg/g. For permthrin, the concentration ranged from 0.44 to 0.63 µg/g, while the concentration of deltamethrin ranged from 0.21 to 0.33 µg/g. The highest concentration of cypermethrin in the soil sample was observed at 21-30 cm depth with a value of 0.92 µg/g, while the lowest concentration of 0.61 µg/g was observed at 0-10 cm depth. For bifenthrin, the highest concentration of 0.83 µg/g was also observed at 21-30 cm depth, while the lowest concentration of 0.69 µg/g was also observed at 0-10 cm depth. The highest concentrations of permethrin and deltamethrin were observed at 21-30 cm depth with values of 0.63 and 0.43 µg/g, while the lowest concentrations were also observed at a depth 0-10 cm with the values of 0.44 and 0.26 µg/g. Similarly, for Krigasawa agricultural location Figure 4.10, the concentration of cypermethrin ranged from 0.66 to 0.83 µg/g; 0.42 to 0.63 µg/g bifenthrin. For permethrin, the concentration ranged from 0.22 to 0.31 µg/g, while the concentration of deltamethrin ranged from 0.11 to 0.22 µg/g. The highest concentration of cypermethrin in the soil sample was observed at a depth of 21-30cm with a value of 0.83 µg/g, while the lowest concentration of 0.66 µg/g was observed at 0-10cm depth. For bifenthrin, the highest concentration of 0.63 µg/g was also observed at 21-30cm depth, while the lowest concentration of 0.42 µg/g was also observed at 0-10cm depth. The highest concentrations of permethrin and deltamethrin were observed at a depth of 21-30cm with values of 0.31 µg/g and 0.22 µg/g, while the lowest concentrations were also observed at 0-10cm depth with values of 0.22 µg/g and 0.11 µg/g respectively.

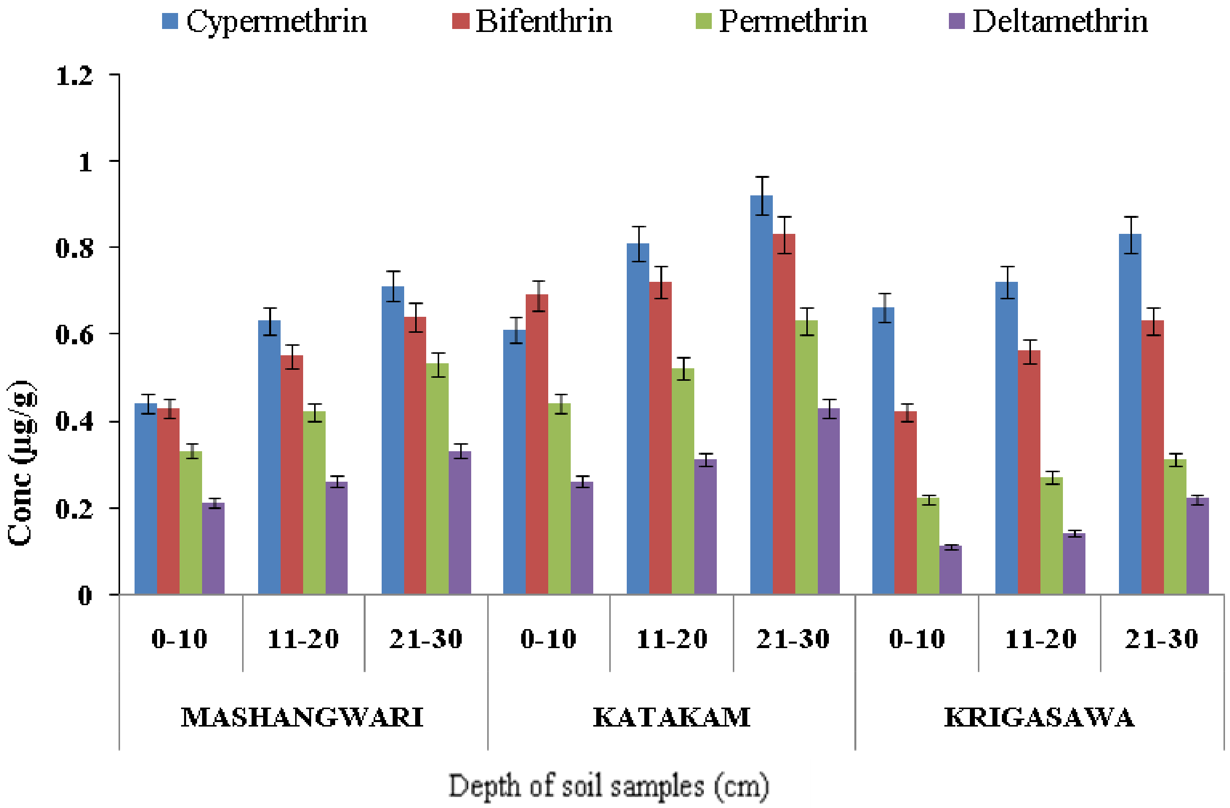

Figure 9. Mean Concentrations of Some Pyrethroid Pesticide Residues in Different Depth of Soil Samples from Different Mashangwari, Katakam and Krigasawa Agricultural location, Gashua, Bade Local Government Area, Yobe State

4. Discussion

The highest concentration of dichlorvos in the watermelon samples from Mashangwari agricultural location was significantly observed in the peel with a value of 0.64 µg/g, while the lowest concentration of 0.01 µg/g was observed in the root. For diazinon, the highest concentration of 0.09µg/g was observed in the peel, while the lowest concentration of 0.01µg/g was also observed in the root. Similarly, the highest concentrations of chlorpyrifos, fenitrothion, malathion and fenthion were observed in the peel with values of 1.08, 0.72, 0.63 and 0.77 µg/g, while the lowest concentration of 0.01 µg/g was observed in the roots. Similar trend were observed in the Katakam and Krigasawa agricultural locations. The levels of diazinon, chlorpyrifos, fenitrothion detected in the peel, pulp, seed, leaf and stem of watermelon samples from the three agricultural locations were above the EU set maximum residue limit (MRL) of 0.04 µg/kg for diazinon, 0.30 µg/kg for chlorpyrifos and 0.01 µg/kg for fenitrothion, with exception of the root which was lower than the above limits. The Acceptable Daily Intake values (ADIs) of diazinon, chlorpyrifos and fenitrothion for watermelon are 0.0002 µg/kg, 0.01µg/kg and 0.005 µg/kg respectively [3]. Results from the present study exceeded these acceptable daily intake values and this may indicate that these pesticides are present in the environment even after some of them had been banned.

The highest concentrations of dichlorvos, diazinon, chlorpyrifos, fenitrothion, malathion and fenthion in the soil sample were significantly observed at a depth of 21-

30cm with values ranging from 0.65 to 1.55 µg/g, while the lowest concentrations of 0.34 µg/g to 1.33 µg/g were observed at a depth of 0-10cm. The most serious concern relating to the organophosphate is that they are still suspected to have serious toxicological impact upon terrestrial wildlife and man [1]. A similar observation was also reported by Gitau [4] in another study in Lake Naivasha catchment, which indicated that most of the pesticides being used are harmful to the environment. The implications of high pesticide residues include muscle cell degeneration, which involves the respiratory muscles. Chronic exposure to organophosphates might damage the peripheral nervous system, and the patient's behavioral abilities and/or personality, chronic fatigue syndrome and effects on the heart. Sheep dip farmers have been identified to report exhaustion, long term fatigue, memory loss and confusion. However, the concentrations of all the organophosphate pesticide residues in the soil samples from the three agricultural locations were above the EU set maximum residue limits (MRLs) of 0.04 µg/g for diazinon, 0.30 µg/g for chlorpyrifos, 0.02 µg/g for malathion, 0.04 µg/g for fenthion and 0.01 µg/g for fenithrothion [3] and this may indicate that these pesticides are present in the environment even after some of them have been banned.

4.1. Pyrethroid Pesticide Residues in Different Parts of Watermelon and Soil Samples from Mashangwari, Katakam and Krigasawa Agricultural Locations

The highest concentration of cypermethrin in the watermelon samples from the Mashangwari agricultural location was observed in the peel with a value of 0.43 µg/g, while the lowest concentration of 0.13 µg/g was observed in the root. For bifenthrin, permethrin and deltamethrin, the highest concentration of 0.24, 0.29 and 0.24 µg/g were observed in the peel, while the lowest concentrations of 0.05 and 0.07 µg/g were also observed in the root. For Katakam agricultural location, the highest concentrations of cypermethrin, bifenthrin, permethrin and deltamethrin were observed in the peel with values ranging 0.28 to 0.34 µg/g, while the lowest concentrations of 0.04 to 0.07 µg/g were observed in the root. Also, the highest concentrations of cypermethrin, bifenthrin, permethrin and deltamethrin in the watermelon samples from the krigasawa agricultural location were observed in the peel with values ranging from 0.18 to 0.38 µg/g, while the lowest concentration of 0.03 to 0.05 µg/g were observed in the root. The highest concentration of cypermethrin, bifenthrin, permethrin and deltamethrin in the soil sample were observed at a depth of 21-30cm with values ranging from of 0.33 to 0.92 µg/g while the lowest concentrations ranged from 0.11 to 0.44 µg/g were observed at a depth of 0-10cm.

Cypermethrin may become an air pollutant and its toxic effects in humans include abnormal facial sensations, coughing, dizziness, tingling, burning, itching, headache, nausea, anorexia and fatigue, vomiting and increased stomach secretion. It is also a skin and eye irritant [5,9]. Patients with severe exposure to cypermethrin may suffer from muscular twitching, coma and convulsive attacks. Mice on exposure to cypermethrin display symptoms including writhing, convolutions and salivation, [6]. Chronic symptoms after exposure to cypermethrin include brain and locomotory disorders, polyneuropathy and immuno-suppression which resemble the multiple chemical sensitivity syndromes [7]. Cypermethrin has also been seen to induce liver injury. Exposure to cypermethrin damages the normal architecture of the liver lobules. The number of the hepatocytes was found to be reduced with distorted polygonal shapes and widened sinusoids. Cypermethrin also induces liver fibrosis and necrosis. The minimum concentrations of cypermethrin (0.13 µg/g) in the different parts of watermelon samples from the three agricultural locations were lower than the Codex 2009, EU set maximum residue limits (MRLs) 0.7 µg/g [3]. Bifenthrin is hardly soluble in water, so nearly all bifenthrin will stay in the soil, but it is very harmful for the aquatic life. Even in small concentrations, the plant is affected by bifenthrin. The concentration of bifenthrin in the different parts of watermelon samples were higher than the Codex 2009, EU set maximum residue limit (MRLs) of 0.01 µg/g. In mammals, permethrin has complex effects on the nervous system. As in insects, it causes repetitive nerve impulses. It also inhibits a variety of nervous system enzymes in it ATPase, inhibition results in increased release of the neurotransmitter, acetylcholine [11]. Permethrin inhibits respiration (the process by which cells use sugars as an energy source) in a manner similar to other neurotoxic drugs. It is therefore not surprising that permethrin causes a wide variety of neurotoxic symptoms. At relatively high doses, these neurotoxic symptoms of permethrin include tremors, incoordination, hyperactivity, paralysis and an increase in body temperature. Permethrin affects both male and female systems. It binds to receptors for androgen, a male sex hormone, in skin cells from human males [11]. The concentrations of permethrin in the different parts of watermelon from the three agricultural locations were higher than the Codex 2009 EU set maximum residue limit (MRLs) of 0.02 µg/g [3].

When deltamethrin gets on the skin, it causes skin sensations like tingling, itching, burning or numbness at that spot. These sensations usually go away within 48 hours. Deltamethrin can be mildly irritating if it gets in the eye. If enough deltamethrin is inhaled, it causes headaches and dizziness. Although not common, individuals who have ingested large amounts of deltamethrin have experienced nausea, vomiting, abdominal pain and muscle twitches. The concentrations of deltamethrin in the different parts of watermelon samples were higher than the Codex 2009 EU set maximum residue limits (MRLs) of 0.03 µg/g [3].

5. Conclusion

The presence of the tested pesticides was detected in all the watermelon and soil samples from the three agricultural locations. The concentrations were observed to be higher in the peel of the watermelon samples, while the root had the lowest concentrations from the three agricultural locations. The concentrations of all the pesticides in the soil samples were observed to be higher at the depth of 21-30 cm, while the lowest concentrations were detected at the depth of 0-10 cm. The concentrations of dichlorvos, diazinon, chlorpyrifos, fenthion, malathion, fenitrothion, bifenthrin, permethrin and deltamethrin in the watermelon and soil samples from the three agricultural locations were observed to be at alarming levels, much higher than the European Union (EU) set maximum residue limits (MRLs) and acceptable daily intake values (ADIs) set for vegetables and soil by the European Union (EU).

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