Assessment of Selected Pesticides Levels in Some Rivers in Benue State-Nigeria and the Cat Fishes Found in Them

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Abstract: *The levels of selected pesticides in some rivers in Benue State-Nigeria and the cat fishes in them, were assessed. QuEChERS method was used for sample clean-up and GC-MS was used for the actual quantitation of the analytes. Whereas in the water samples collected from the rivers, pesticides levels ranged between Not detected to 0.005 ppm, in the cat fish samples, pesticides residues ranged between Not detected to 0.024 ppm. The results obtained show that, where pesticides were present, they were present only in trace amounts, that were below their respective guideline values in drinking water or their maximum pesticide residue limit in food. Hence, there are no immediate risks of the toxicities associated with these pesticides if water or cat fish from rivers in the study area were consumed. However, fishes from River Otobi are more likely to be associated with a wider spectrum of pesticides toxicity following a prolonged bioaccumulation than fishes from River Royongo, seeing as the former contains the highest number of pesticides residue types (7) while the latter have the least (4).*

Keywords: pesticides, water, pesticide residues, cat-fishes, rivers

INTRODUCTION

Pesticides are chemicals used in agriculture to protect crops against insects, fungi, weeds and other pests (Picó, 2006; Giliomee, 2009; Akashe, 2018; Anjum, 2017; Salem *et al*., 1988; Bordin et al., 2016). The term ‘’pesticides residue’’ applies to substances or mixtures of substances in food which result from the use of pesticide(s) and includes any derivatives, such as degradation and conversion products, that are considered to be of toxicological significance. Pesticides and their residues are potentially toxic to humans [Ccanccapa et al., 2016; Darko & Akoto, 2008; Guo et al., 2008; Vega et al., 2005). They may induce adverse health effects such as cancer and other harmful effects on the reproductive, immune or nervous systems (Akoto et al., 2016; Khan et al., 2008; Asgha et al., 2016; Hayden et al., 2010; Thany, Reynier, & Lenaers, 2013; Sabrina et al., 2012; Claudine, 2008; Rojas, Ojeda, Barraza, 2000; Koutros et al. 2009) From farmlands, pesticides may leach into soils and thereafter, find their way via rain and surface runoffs and other anthropogenic activities into streams, rivers and lakes. As such, the main environmental concerns associated with pesticides use are water, soil and air pollutions which causes harm to non-target organisms including plants, birds, wildlife, fish and crops (BCMA, 2017). Also, inappropriate application of pesticides as well as improper disposal of pesticide containers can cause pesticides-related pollution (Katagi et al., 2010). Processes such as adsorption, transfer, breakdown and degradation determine the fate of pesticides in the environment. Transfer refers to processes that move the pesticide away from the target site. Bioconcentration occurs when pesticides enter aquatic organisms directly from water, through the gills or epithelial tissues (BCMA, 2017) but bioaccumulation occurs via an uptake through food consumption or intake of bottom sediments (Katagi, 2010). Both bioconcentration and bioaccumulation are important factors in the overall process leading to the toxicity of pesticides as the rate at which they occur, affects how soon toxicity appears (Akoto et al., 2016).

Although several studies (Vega et al., 2005; Zabik et al., 1995; Racke et al., 1997; Kent & Johnson, 1979; Kafilzadeh et al., 2012; Fisk et al., 1998), have been carried out on pesticides and their residue levels in the environment and foods, yet, there continues to be a dearth of literature regarding different aspects of the subject matter. This is because, the degree of pesticide usage in different farming communities differ (Rahman & Chima, 2018) and the levels of environmental contamination from pesticides and their residues also differ, and so do their toxicities. This means that each community would need to from time to time, perform its own assessment of the levels of pesticides occurring in environmental components of interest, such as, water, soil, air and foods. Such would provide the empirical basis for reviewing the guidelines on pesticides uses and related safety measures. This work is one such study.

MATERIALS AND METHODS

Fifteen catfish samples weighing 8.43 kg were randomly collected from five rivers in the study area, between August and October 2019. Six litres each, of 3 composite water samples, were also collected from each river from where the fishes were caught. Each sample was processed and analysed for BHC, Aldrin, Trifluralin, Dichloran, Heptachlor Epoxide, Dieldrin, Endrin, Mirex, P,P- DDT, Endosulfan II and Methoxychlorusing QuEChERS method withGC-MS.

Each fish sample was separately homogenized in distilled water using a food blender before oven drying to a constant weight and ground into powder form using a feed mill. Thereafter, 10g of each oven dried fish sample was separately weighed into an extraction bottle and 10mL Methylene Chloride/Hexane/Acetone (2:2:1) v/v was added to each sample tube followed by 5g of anhydrous Sodium Sulphate. The mixtures were sonicated for 1 hour on a sonicator at 40^0C. Each resulting extract was decanted and concentrate d using a rotary evaporator to 2 mL. Extract clean-up was done separately by passing 1mL of extract through a column preconditioned with n-hexane. The extract was eluted 5 times and pesticides residue eluent was collected and concentrated into 1mL. The selected pesticide residues in each sample eluent, were then determined separately, by injecting 1µL portions into a GC-MS (HP 6890 -MS model) right after the instrument had been calibrated with standards in the linear range of the Pesticides concentrations. Accustandards (USA) was used for the calibration of the pesticide's residue defining window.

For the determination of pesticides in water sample, 100mL of the sample was measured into a separating funnel and 10mL of methylene chloride in hexane (1:1 vol/vol) was added. The mixture was then shaken vigorously for 2mins and allowed to stand for 10 mins for phase separation to occur. The organic phase was transferred into a 2 cm outer diameter (OD) column containing 8cm of anhydrous sodium sulphate eluting into a 10mL concentrator tube. The sample was concentrated to 2mL in a hot water bath at 90^0C. The extract was then collected into a vial. 1µL of the sample extract was then injected into a GC-MS (HP 6890 -MS) for analyte determination. Standards in the linear range of the Pesticides concentrations were injected for calibration and this was used to calculate the concentration of pesticides in the water samples. Accustandards (USA) was used for the calibration of the pesticides defining window.

RESULTS AND DISCUSSIONS

Table 1 shows the levels of some pesticides in water from selected rivers in Benue State Nigeria and Table 2 shows the pesticides residue levels of cat fishes in selected rivers in Benue State.

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Table 1: Pesticides residue levels in water from selected Rivers in Benue State

S/N	Pesticide	Residue Levels in water (ppm)					
		River Benue	River Royongo	River Ochobo	River Otobi	River K-Ala	Guideline Value in water (ppm) Hamilton et al., 2006; CODEX, 2021)
1.	BHC	ND	ND	ND	ND	ND	1.00
2.	Aldrin	ND	ND	ND	ND	ND	0.03*
3.	Trifluralin	0.005 ± 0.001	0.003 ± 0.001	ND	ND	ND	20.00
4.	Dichloran	ND	ND	ND	ND	ND	-
5.	Heptachlor Epoxide	0.003 ± 0.001	0.003 ± 0.001	ND	ND	ND	0.04
6.	Dieldrin	ND	0.002 ± 0.001	ND	ND	ND	0.5*
7.	Endrin	ND	0.002 ± 0.001	0.002 ± 0.001	0.003 ± 0.001	0.005 ± 0.001	2.0
8.	Mirex	ND	0.003 ± 0.000	ND	ND	ND	-
9.	P,P- DDT	ND	ND	ND	ND	ND	0.06
10.	Endosulfan II	ND	ND	0.001 ± 0.001	ND	ND	0.05
11.	Methoxychlor	ND	ND	ND	ND	ND	0.20

Key:

Results are mean± standard deviations of duplicate determinations
ND – Not detected as concentration was < 0.001 ppm
* Health Advisory limit per day

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Table 2: Pesticides residue Levels of cat fishes in selected Rivers in Benue state

S/N	Pesticides	Residue Levels in Fishes (ppm)					
		River Benue	River Royongo	River Ochobo	River Otobi	River K-Ala	Maximum Residue limit in food (ppm)(CODEX, 2006;CODEX, 2021)
1.	BHC	0.015 ± 0.001	ND	ND	ND	ND	-
2.	Aldrin	ND	ND	0.023 ± 0.001	0.014± 0.001	0.005± 0.000	0.02- 0.20
3.	Trifluralin	0.009 ± 0.001	0.024 ± 0.001	0.012 ± 0.001	0.014 ± 0.001	0.004± 0.001	0.05-3.00
4.	Dichloran	ND	ND	0.023± 0.001	0.008 ± 0.001	ND	0.20-7.00
5.	Heptachlor Epoxide	ND	ND	ND	ND	ND	0.01 - 0.2
6.	Dieldrin	0.007 ± 0.001	0.014 ± 0.001	0.016 ± 0.000	0.015 ± 0.001	0.005 ± 0.001	0.02 - 0.2
7.	Endrin	0.017 ± 0.001	0.015 ± 0.000	0.012 ± 0.001	0.015 ± 0.001	0.005 ± 0.001	0.05- 0.1
8.	Mirex	ND	0.012 ± 0.001	ND	0.013 ± 0.001	0.003 ± 0.001	-
9.	P,P- DDT	ND	ND	0.013 ± 0.001	0.003 ± 0.001	0.003 ± 0.001	0.02- 0.3
10.	Endosulfan II	ND	ND	ND	0.011 ± 0.001	0.002 ± 0.001	0.004 - 0.50
11.	Methoxychlor	0.003 ± 0.001	ND	ND	ND	ND	

Key

Results are mean± standard deviations of duplicate determinations

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ND – Not detected as concentration was < 0.001 ppm

Table 1 shows that, BHC, Aldrin, Dichloran, P,P- DDT and Methoxychlor were not detected in all the Rivers assayed. This seems to suggests that, the pesticides in question are not among the pesticides commonly used by farmers in the study area. Hence it is somewhat plausible to posit that dwellers in these localities are not at risk of the toxicities associated with these pesticides.

Table 1 also shows that, trifluralin was not detected in Rivers Ochobo, Otobi and K-Ala, thus implying there may be no risk of trifluralin toxicity in both these locations. Nonetheless, trifluralin was found to be 0.005 and 0.003 ppm in Rivers Benue and Royongo respectively. But these levels are far below the guideline value of 20.00 ppm for Trifluralin in drinking water (Bardash, 1994) hence, there is no immediate risk of trifluralin toxicity arising from drinking water from the aforementioned rivers. Also, Table 1 shows that, heptachlor epoxide was not detected in Rivers Ochobo, Otobi, and K-Ala, but was 0.003 ppm in both Rivers Benue and Royongo. Since this amount is less than the guideline value of 0.04 ppm for Heptachlor epoxide in drinking water (Bardash, 1994), it is plausible to assume that, these Rivers pose no risk of Heptachlor-epoxide toxicity. From Table 1, it can also be seen that, dieldrin was only detected in R. Royongo but, at a concentration (0.002 ppm) that is significantly less than the Health Advisory limit per day (0.5 ppm) (Bardash, 1994) for dieldrin in drinking water and hence, pose no toxicity to locals in the study area. Endrin seemed to be the most common pesticide residue in the study locations as it is present in all the Rivers assayed except River Benue. However, the endrin concentrations found were all significantly below the guideline value for Endrin in drinking water (2.0 ppm) (Bardash, 1994) and hence may pose no risk of toxicity as well. Mirex and endosulfan II where only detected in Rivers Royongo (0.003 ppm) and Ochobo (0.001 ppm) in trace amounts that are much less than any of the quoted guideline values in Table 1.

Table 2 shows that, only heptachlor epoxide was not detected in fish samples from all the Rivers assayed. However, because Table 1 shows that heptachlor epoxide is present in Rivers Benue and Royongo, it is suggestive that this pesticide residue has the highest xeno-metabolic clearance rate in cat fishes or it has the lowest rate of bioaccumulation compared with the other pesticide residues.

Whereas, BHC, Aldrin, Dichloran, P,P-DDT and Methoxychlor are among the pesticide residues which were not detected in water samples from all of the rivers assayed, Table 2 shows that these pesticide residues are present in fish samples obtained from these rivers. This observation appears to negate the possibility that these pesticides are not used in the study location, but in the event that they are, then it may be that, they are nonpersistent in the environment. It is also plausible that these pesticides residues are found in the fishes only because they have migrated from other water bodies where these pesticides residues are present and have bioaccumulated prior to transmigration.

Trifluralin, Endrin and Dieldrin are present in fishes from all the rivers assayed but their levels are all below their respective recommended maximum residue limits in foods (CODEX, 2006; CODEX, 2021) as is with the other pesticide residues which are only present in fishes from some of the rivers. This implies that there is no immediate risk of the toxicity of these residues in populations consuming fishes from these rivers. Whereas, fishes from Rivers Otobi have the highest number of pesticides residues types present in them (7), fishes from River Royongo have the least (4), implying that the former is more likely to be associated with a wider spectrum of toxicity than the later as bioaccumulation progresses.

CONCLUSION

The pesticides assessed were either not detected in all the Rivers or cat fishes assayed or they were present only in trace amounts, far below the guideline values for each pesticide in drinking water or pesticide residue in food. Hence there are no immediate risks of the toxicities associated with these pesticides if water or cat fishes from the rivers in the study area is consumed. Heptachlor epoxide likely have the highest xeno-metabolic clearance rate in cat fishes or bioaccumulates the least. BHC, Aldrin, Dichloran, P,P-DDT and Methoxychlor are likely pesticides not used in the study area but may have been present in some of the cat fishes only because they had migrated from other water bodies where these pesticide are present and have bioaccumulated in them prior to transmigration. Whereas fishes from Rivers Otobi have the highest number of pesticides residues types present in them (7), fishes from River Royongo have the least, hence, the former is more likely to be associated with a wider spectrum of toxicity than the later following a prolonged bioaccumulation.

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