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CHEMICAL ANALYSIS OF SOME HERBICIDES CONTENTS OF MOST COMMON VEGETABLES AND AQUATIC ANIMALS IN MAKURDI METROPOLIS

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ABSTRACT

Vegetables, water snails and fish samples were collected from farmlands, river, streams, wetlands, and stagnant waters within Makurdi metropolis and analysed for two common herbicides (2,4-dichlorophenoxyacetic acid (2,4-D) and glyphosate) residues using GC-MS. This was to assess the impact of anthropogenic activities on the samples. The result of the analysis indicate only Tilapia fish (Oreochromis niloticus) to contain about 0.01mgL^{-1} of 2,4-D acid, while glyphosate was not detected in all the samples. The result of the study revealed that all the samples were free from the two herbicides except Oreochromis niloticus that was contaminated with 2,4-dichlorophenoxyacetic acid. This implies that these activities had not impacted sternly on the surrounding environment; however it is believed that long term exposure may result to some health threat.

Keywords: Herbicides, 2, 4-dichlorophenoxyacetic acid, Glyphosate, Farming, Analysis, Extraction

1. INTRODUCTION

The growing demand for food arising from the daily increase in population, has called for a more drastic means of combating the identified problems of agricultural productivity. In Nigeria, and elsewhere among developing countries, the problems of crop production among others include those of weeds and pests.

Over the years, various agrochemicals have been used to combat these problems with a view to improving overall yield in crops production per plot of land. Agricultural chemicals are chemical agents used in enhancing food production. Among such chemicals are herbicides, fungicides, insecticides, nematicides and fumigants. Broadly, they are referred to as pesticides [1]. Imoloame, et al. [2], reported that, chemicals used in controlling weeds had revolutionized farmers approach to weeds control in the world and it is one of the recent developments in crop production. The use of herbicides has been reported to be more profitable than hoe-weeding or hand weeding in the production of various crops in Nigeria. When herbicides are used judiciously, it reduces labour and increased crop yield. While the beneficial effects of herbicide applications are well known, the risks to man and the other living organisms that he considers beneficial to himself or his environment should not outweigh the benefits associated with the use of these chemicals. Therefore, distribution should be made between the consequences of an abuse and the benefits from a recommended use of chemical. Some of the risks posed by herbicides include, spray drift to sensitive crops, contamination of drinking water especially herbicides that are not biodegradable and easily leached from the surface of light soil, the reduction and killing of the population of soil inhabiting animals, the development of resistance in weeds due to repeated treatment on weeds with a particular class or family of herbicides, etc.

According to Asogwa and Dongo [3], the use of herbicides by farmers without scruple about the health implications may result to some aliments which may not be known immediately since herbicides are known to have widely variable toxicity. In addition to acute toxicity from high exposures, there is concern for possible carcinogenicity. Herbicides are known to cause a range of health effects ranging from skin rashes to death. They are also known to have negative impacts on bird's populations and order soil organism. For example, dioxin a herbicide used in defoliation by the American army was found to cause congenital deformation and mental effects to children born to the American soldiers and in the area over which it was applied. A minute amount of dioxin has the ability to cause cancer and chloracne.

The behaviour of herbicide in the soil is dependent on the soil properties and physico-chemical properties of chemical substances available. The interaction of the applied herbicides with the soil and the surrounding chemicals may result into a residual form of the herbicide which may be non-biogradable and most often toxic. As the residual herbicides remains in the soil, cultivated crops absorbed and accumulates them, as such people who depend on such crops may also absorb the residual form of the herbicides. Prolong exposure to herbicide residues through the consumption of contaminated crops could lead to disruption of numerous biochemical processes in the human body which will consequently lead to health threats to entire food chain.

The presence of herbicides in food and crops is fast growing especially in developing countries with serious repercussion on human health. According to Tahir, et al. [4], the irrational use of herbicides had led to the contamination of soil, water and air. Other effects include; destruction of non target organism especially soil microorganisms, destruction of wildlife and the ecosystem in general. Ahmad [5] reported that, human exposure to herbicides is usually estimated by measuring the levels in the environment (eg soil, water and food). According to Tariq, et al. [6], 60-70% of herbicides poisoning cases are due to occupational exposures.

The most common used herbicides by farmers within the study area are dichlorophenoxyacetic acid (2,4-D) and glyphosate (roundup). The herbicide 2,4-D is 2,4-dichlorophenoxyamine salt, its molecular formula is $C_{10}H_{13}Cl_2NO_3$. When 2,4-dichlorophenoxyamine salt is applied, microbial degradation occur. This involves hydroxylation, cleavage of the acid side-chain, decarboxylation, and ring opening. The ethyl hexyl form of the compound is rapidly hydrolyzed in soil and water to form the residue 2,4-D acid. The acid is a chlorinated phenoxy compound, it function as a systemic herbicide and is used to control many types of broadleaf weeds. It is used in cultivated agriculture and in pasture and rangeland applications, forest management, home and garden situations and for the control of aquatic vegetation. A few commercial names for the products containing 2,4-D include Weedtrine-II, Aqua-Kleen, Barrage, Plantgard, Lawn-Keep, Planotox and Malerbane. 2,4-D. It is known to be in many forms or derivatives (esters, amines, salts) which vary in solubility and volatility. Studies have shown that the acceptable daily intake of 2,4-D for man is 0-0.3 mg/kg [7]. The herbicide can cause a range of aliment which may sometimes result to death [8].

The use of 2,4-D has had drastic affects for both agricultural and wildlife animals including, the deaths of cattle and horses grazing on treated plants, and the destruction of plant food sources for moose, gopher and voles [9].

Glyphosate (Roundup) is an aminophosphonic analogue of the natural amino acid glycine. It is the isopropylamine salt of N-(phophonomethly) glycine. It has a molecular formula $C_3H_8NO_5$. The molecule tends to exist as zwitterions where phosphonic hydrogen dissociates and joins the amine group. Glyphosate is soluble in water and hydrolysed to the residual form of the herbicide; aminomethylphosphonic acid (CH_4NO_3P).

Glyphosate or N-(phosphonomethyl) glycine is a widely used, non-selective herbicide. It is strictly used as a foliar spray and is systemic in nature. It is very effective for perennial weeds because of its translocation characteristics. It inhibits new plant growth by interfering with aromatic amino acid synthesis. Visible symptoms generally occur on annual plants in 2 to 4 days and on perennial plants in 7 to 10 days. Symptoms on the shoots include yellowing and wilting, progressing from the new to the older tissues. Human and animal exposure to glyphosate may result to a range of illness and sometimes death [10].

It is in the light of the above that this study consider it relevant to assess the levels of these herbicides; dichlorophenoxyacetic acid (2,4-D) and glyphosate (roundup) in some universal vegetables like *Telfairia occidentalis* (Fluted pumkin), *Amaranthus hybridus* (spinach), and *Abelmoschus esculentus* (okra) and also some aquatic animals like *Pilla ovate* (water snail), *Oreochromis niloticus* (Tilapia) and *Neochanna diversus* (Mudfish) in Makurdi metropolis hence the vegetables and the aquatic animals are staples food materials for majority of the residence of the town.

2. MATERIALS AND METHODS

2.1 Collection of Samples

Vegetables samples were collected from farmlands where the dry season farming is practiced (the river banks). Fresh samples of *Telfairia occidentalis* (Fluted pumkin), *Amaranthus hybridus* (spinach), and *Abelmoschus esculentus* (okra) were collected and analysed fresh. Fresh *Pilla ovate* (water snail) were collected from river, streams, wetland, and stagnant waters around farmlands, while Tilapia (*Oreochromis niloticus*) and Mudfish (*Neochanna diversus*) were bought from fishermen at the river. Sample were collected in clean polythene bags and taken to the laboratory immediately for analysis. Before the analysis, the samples were identified in the Department of Biological Sciences, Benue State University Makurdi. The analysis of vegetables was done for two dry seasons (January to February, 2010 and 2011) while the analysis of water snail and fish was done for two wet seasons (July to August 2010 and 2011).

2.2 Extraction of Samples

a) Vegetable Samples [11, 12]

The fresh vegetables were chopped using a blender. 10g of the finely chopped sample was weighed into a 250cm^3 conical flask, 50cm^3 and 100cm^3 of acetone and hexane respectively were added to give a ratio of 1:2 acetone: hexane mixture. The mixture was mounted on a rotary shaker for 1hour. The extract was obtained after centrifuging for 10 minutes at 5000 RPh. The residue was washed with 20cm^3 solvent mixture and combined with first extract, 2g of anhydrous sodium sulphate was added to remove water and the extract kept in plastic containers for cleanup process.

b) Animal Samples

The viscera of *Pilla ovate* (water snail) and the gills, intestines and livers of *Oreochromis niloticus* (Tilapia fish) and Mudfish (*Neochanna diversus*) were chopped using a blender to obtained smooth samples. 10g of the sample was weighed into a 250cm^3 conical flask and 5g of anhydrous sodium sulphate and sand were added and the mixture ground using a mortar and pestle until a granular, friable mixture was obtained. 50cm^3 of hexane was added and the mixture warmed on a steam bath and stirred for 30minutes. The extract was obtained after centrifuging for 10 minutes at 5000 RPh.

2.3 Cleanup of Samples [13] (Method 3500C 2000)

To remove interference substances from the extracts, each of the samples were partitioned three times with 20cm^3 of acetonitrile. The acetonitrile extracts were combined and concentrated, after which 10cm^3 iso-octane was added the mixture evaporated to 2-3cm^3 for GC-MS analysis [14, 15]. GCMS-QP2010PLUS SHIMADZU JAPAN was used for the study.

3. RESULTS AND DISCUSSIONS

The result of herbicides analysis (Table 1.0) indicate that in all the sample analysed, it was only Tilapia fish (*Oreochromis niloticus*) that 0.01mgL^{-1} of 2,4-D acid was detected during the first year of analysis, while glyphosate was not detected. During the second year of the study, neither 2,4-D acid nor glyphosate was detected in any of the samples. The absence of the herbicides in the samples could not necessarily be that these samples cannot or did not absorbed the herbicides, but the levels of the herbicides in the samples could be in minute quantities (below the detection limits).

Studies have shown that 2,4-D acid may further decomposed in the soil resulting to other compound expected to be of low occurrence in the environment and of low toxicity. These compounds include; 1,2,4-benzenetriol, 2,4-dichlorophenol (2,4-DCP), 2,4-dichloroanisole (2,4-DCA), 4-chlorphenol, chlorohydroquinone (CHQ), volatile organics, bound residues, and carbon dioxide. The result of the study did not indicate the presence of any of the above compound in the samples. Also there was no traces of aminomethylphosphonic acid (CH_4NO_3P) which is the residual and toxic form of glyphosate in all the samples analysed.

4. CONCLUSION

The study revealed that the samples had not been harshly contaminated, since in most of the samples, the residues were not detected. The implication is that, farming activities at the river bank and elsewhere within wetlands in the metropolis has not impacted sternly on the surrounding environment; however long term exposure of this crops and animals to these faming activities could lead to some health threat.

5. RECOMMENDATION

It is therefore recommended that awareness should be created to farmers on the need to stick to the prescribe dosage in the applications of agricultural chemicals. Since most of them believed that the greater the quantity and concentration of the farming chemical apply, the more effective it will be, as such, the doses that are often use are not the doses recommended by the manufacturer thereby exposing the whole population to some health risks that are not amply perceived by health authorities.

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Table-1. Herbicides content of vegetables and aquatic animals

Samples	**2, 4-D (mgL^{-1})**		**Glyphosate (mgL^{-1})**	
	2010	**2011**	**2010**	**2011**
Tilapia fish (*Oreochromis niloticus*)	0.010	ND	ND	ND
Mudfish (*Neochanna diversus*)	ND	ND	ND	ND
Water snail (*Pilla ovate*)	ND	ND	ND	ND
Fluted Pumpkin(*Talfairia occidentalis*)	ND	ND	ND	ND
Spinach (*Amaranthus hybridus*)	ND	ND	ND	ND
Okra (*Abelmoschus esculentus*)	ND	ND	ND	ND

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