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TOXIC METALS LEVELS IN AGROCHEMICALS SOLD IN SABON GARI MARKET, KANO, NORTHWESTERN NIGERIA

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ABSTRACT

Heavy metals such as Cadmium (Cd), Nickel (Ni), lead (Pb), Zinc (Zn), and Copper (Cu) originate from various sources including agriculture. From agricultural sources, they comprise agrochemicals such as insecticides and pesticides. The study aimed at evaluating the levels of toxic metals in agrochemicals (pesticides) sold at Sabon Gari market, Kano. 42 brands of pesticides were obtained from the market. They were digested and then analyzed by Atomic Absorption Spectrophotometer for determination of Cd, Pb and Ni. Cd was found to be highest in LF (0.0833mg/l) and least in RCK (0.0015mg/l) while not detected in CBT, CPT, DDF, and PRF. Pb was found to be highest in FUP (2.995mg/l) and least in PRF (0.0434mg/l) while not detected in BF, CLV, CPF, CPT, DDF, GRF, LCH, LF, PK, and RV. Ni was only detected in DDF (0.305mg/l). Therefore, it is clear that the pesticides contain heavy metals slightly above the tolerable limits which could get into the soil subsequently accumulate overtime and pose serious threat to the plants and other living organisms.

Keywords: Agrochemicals, Heavy metals, Insecticides, Monitoring, Pesticides

INTRODUCTION

Heavy metals such as Cadmium (Cd), Nickel (Ni), lead (Pb), Zinc (Zn), and Copper (Cu) originate from various sources including agriculture. From agricultural sources, they comprise agrochemicals such as insecticides and pesticides (Masindi & Muedi, 2018).

Agrochemicals are major issue of current agricultural systems around the globe. Consequently, utilization of agrochemicals such as pesticides and fertilizers remained a major practice especially in most tropical countries. Major stakeholders have prevented the adoption of some pesticides in the environment in most developing nations as a result of their persistence but yet it is still in use in developing nations including Nigeria due to their low cost, ease of synthesis or obtained from developed nations. Several non-governmental organizations, consumer associations and international bodies opposed the existence of these pesticides in the environment which they perceive as destructive to water quality and human health (Jayaraj *et al*., 2016).

Agrochemicals are identified by their toxic nature, demur to degradation, accumulation and transfer capacity via water, air, and organisms, over the international boundaries and then reserved far the point of source. Some agrochemicals such as organophosphates, rodenticides, carbamates, and persistent organic pollutants compounds have caused critical concern for conservation species that are located on the top of the food webs (Ferreira *et al*., 2020; Miranda *et al*., 2022).

The most common types of agrochemicals used in Nigeria are imported mainly from Asian and European nations. Only a few industries formulate and package these chemicals such as Butachlor and Gammalin 20 (Lindane), and insecticides etc. During some formulations, there were performed mostly without regard for environment and human health during their handling, storage, use and disposal. Although there are nationally made legislative policies and instruments for managing the chemicals and their composition, however, enforcement and implementation remain inadequate as a result of limited national infrastructure (Oyekunle *et al*., 2017).

The World Health Organization (WHO) reported about three million cases of poisoning from agrochemicals in developing countries. The agrochemicals mostly negatively affect food safety, agricultural sustainability, soil biodiversity, functions and biochemical processes (Boedeker *et al*., 2020).

Accordingly, the use and fate of agrochemicals is of vital concern to the aquaculture sector as it could affect sustainable development of the agricultural industry (Yuen *et al*., 2021). Pham (2012) employed spatial and GIS models to evaluate the use, accumulation and distribution of agrochemicals in the lower Mekong Delta in Vietnam.

Therefore, it becomes imperative to produce metals-free and nutrition enriched agricultural products for the animal and human consumption without destroying natural resources (WHO, 1990).

The exposure of the public and environmental contamination by pesticides in food could result in great health risk. Insecticides cause the most damage to the soil and organisms among all categories of pesticides (Özkara et al., 2016). Outcomes of scientific research described that even in minute levels, the homogenized effect of synthetic persistent compounds such as pesticides diminish the hypersensitivity and immune response to chemical agents. In Nigeria, pesticides as components of agrochemicals employed in the farming industry traces back to the colonial times and have been an integral part of agricultural systems in the country. The aim of this work was to assess the heavy metals concentration in agrochemicals sold in Kano metropolis, Nigeria

METHODOLOGY

Study area

The study site is Sabon Gari Market, in Kano metropolis on latitude: 11° 06' 60.00" N and longitude 7° 43' 59.99" E.

Collection of Pesticides

A total number of 42 pesticides comprising 3 from 14 different kinds. The pesticides were bought from Sabon Gari Market in their complete packs.

Preparation of Samples

For powdered pesticides, 1 g of sample was weighed using an electronic weighing scale and transferred to a conical flask. Wet digestion was performed by adding a mixture of 12 cm^3 HNO_3 and 4 cm^3 HCl to dryness at 105 ° for 2hrs on a hot

plate (Singh *et al*., 2010; Turek *et al*., 2019). The subsequent solution was then filtered through a medium filter paper into a 100 cm^3 volumetric flasks and filled to the mark with deionized water.

For liquid samples, 2 ml of the sample was added into a conical flask followed by addition of aa combination of 12 cm^3 HNO_3 and 4 cm^3 HCl and digested under same conditions as above (Turek *et al*., 2019; Sani *et al*., 2020). All chemicals used were of analytical grade.

Metal Analysis

The heavy metals levels including Cd, Pb, and Ni were determined by Atomic Absorption Spectrophotometry (Agilent 240FS AA model, Australia).

Data Analysis

The data generated were analyzed statistically by t test using the Sigma Stat v.3.5. Statistical significance was taken at $p < 0.05$.

RESULTS

Among the pesticides sampled, 28.6% (4 out of 14) were herbicides which include acetanilide, organophosphate, viologen and benzoic acids. Meanwhile, 71.2% (10 out of 14) were insecticides belonging to pyrethroid, organophosphate and neo-nicotinoid (Table 1). Chlorpyripos has the highest number (4 out of 14), followed by lambda-cyhalothrin (2 out of 14), cypermethrin (1 out of 14), Nicosul/furo (1 out of 14), imidacloprid (1 out of 14), and dichlovos (1 out of 14). Cd was found to be highest in LF (0.0833mg/l) and least in RCK (0.0015mg/l) while not detected in CBT, CPT, DDF, and PRF. The Cd levels in LCH and LF were greater than the FAO/WHO permissible limit (Table 2). Pb was found to be highest in FUP (2.995mg/l) and least in PRF (0.0434mg/l) while not detected in BF, CLV, CPF, CPT, DDF, GRF, LCH, LF, PK, and RV. The Pb levels in CBT, FUP, PRF and RCK were higher than the FAO/WHO permissible limit (Table 2). Ni was only detected in DDF (0.305mg/l) and was found to be above the tolerable limit of WHO (0.003 mg/L) (IARC, 2012) (Table 2).

Table 1: Nature and brands information of pesticides sold at Sabon Gari market, Kano

S/N	Brand name	Acronym	Active ingredients	Nature	Country	Category	Class
1	Buta force	BF	Buta chlor 30% wp	Powder	Lebanon	Herbicide	Acetanelide
2	Captor	CPT	Chlorpyrifos 20% EC	Liquid	China	Insecticide	Organophosphate
3	Chlorview	CLV	Chlorpyrifos 40% ES	Liquid	China	Insecticide	Organophosphate
4	Combitex	CBT	2% imidacloprid	Liquid	China	Insecticide	Neo-nicoticonoid
5	Cyper force	CPF	Cypermethrin 10% EC	Liquid	China	Insecticide	Pyrethroid
6	DD force	DDF	Dichlovos (RDVP 1009/LEC)	Liquid	China	Insecticide	Organophosphate
7	Force up	FUP	Glyphosate Ammonium	Liquid	China	Herbicide	Organophosphate
8	Guard force	GRF	Nicosul/furo 75% WDG	Liquid	China	Insecticide	Organophosphate
9	Lambda-Cyhalothrin	LCH	Lambda–cyhalothrin	Liquid	China	Insecticide	Pyrethroid
10	Lara force	LF	Lambda–cyhalothrin	Liquid	Indonesia	Insecticide	Pyrethroid
11	Parac Force	PK	Paraquet di chloride	Liquid	China	Herbicide	Viologen
12	Perfect killer	PRF	Chlorpyrifos 2% EC	Liquid	China	Insecticide	Organophosphate
13	Rice view	RCK	Bispyribac sodium 100g	Liquid	China	Herbicide	Benzoic acids
14	Rocket	RV	Chlorpyrifos 30%EC	Liquid	China	Insecticide	Organophosphate

The table below described the presence of Heavy metals in some selected agrochemicals sold at Sabon Gari Market, Kano.

Table 2: Heavy Metals Concentration (mg/l) in pesticides sold at Sabon Gari Market, Kano

S/N	Sample ID	Cd (mg/l)	Pb (mg/l)	Ni(mg/l)	Category	P value
1	PK	0.0102	ND	ND	Herbicides	
2	RCK	0.0015	0.0594	ND		
3	BF	0.0066	ND	ND		
4	FUP	0.0056	2.995	ND		
5	CBT	ND	2.058	ND	Insecticides	
6	CLV	0.0018	ND	ND		>0.05
7	CPT	ND	ND	ND		
8	GRF	0.0029	ND	ND		
9	LCH	0.065	ND	ND		

10	LF	0.0833	ND	ND
11	PRF	ND	0.0434	ND
12	RV	0.0073	ND	ND
13	CPF	0.014	ND	ND
14	DDF	ND	ND	0.305
	Tolerable limit (FAO/WHO)	0.03	0.02	0.01

Key: ND = Not Detected

DISCUSSION

From results, 28.6% were herbicides, meanwhile, 71.2% (10 out of 14) were insecticides as seen in Table 1. Abdel Khalek *et al*. (2018) revealed herbicides, and insecticides were among the major pesticides used in agricultural lands.

The pesticides sampled were in the following pattern in terms of their respective numbers Chlorpyripos > Lambda-cyhalothrin > Cypermethrin, Nicosul/furo, Imidacloprid, and Dichlovos. Also, in another study by Norina Farms, they reported that the most common pesticides used included paraquat dichloride, glyphosate, chlorpyrifos, and cypermethrin (Udoh & Gibbs, 2022). Moreover, chlorpyrifos were also reported in crops like maize, cassava, and millet (Raimi, 2021).

The levels of Cd in LCH and LF were greater than the FAO/WHO permissible limit (Table 2). Similarly, Gimeno-García *et al*. (1996) found Cd in most of the pesticides analyzed. Consequently, accumulation of Cd in the soil is a problem that came from general sources due to improved and revolutionized agricultural technology such as the development of pesticides (Alengebawy *et al*., 2021).

The levels of Pb in CBT, FUP, PRF and RCK were higher than the FAO/WHO permissible limit in Table 2 to which contrarily, Gimeno-García *et al*. (1996) reported highest levels of Pb in the herbicides and suggested that significant contributions of heavy metals the soil receives come from agricultural sources of which the pesticides form a grand carved niche. BF been an herbicide, was revealed to have undetectable levels of Pb. Pb is known to be among the major toxic metals that has been classified due to its toxicity profile (Uzu *et al*., 2009; Chauhan *et al*., 2020). Even at low concentration, it could result in devastating effects to plant growth, crop yield, and general productivity (Ashraf *et al*., 2017; Abdullahi *et al*., 2021). These is due to the fact that Pb reduce nutrient uptake, induce DNA damage, destroys shoot and root, deactivate the membrane permeability and degenerate the activities of enzymes (Reddy *et al*., 2005; Gichner *et al*., 2008; Ashraf *et al*., 2015).

Ni was only detected in DDF and was found to be above the tolerable limit of WHO (IARC, 2012). Although, Ni is extensively distributed in nature, its sources include anthropogenic and agricultural systems which agrochemicals belong to. Better yet, it is categorized as Group 1 human carcinogen which causes lung cancer, nasal and paranasal sinuses (ATSDR 2011). There was no significant difference between the pesticides classified as herbicides and insecticides ($p>0.05$). Although several of these heavy metals are found naturally in nature, humans may increase heavy metal-associated pollution via activities from industries as well as using metal containing pesticides and fertilizers in agricultural systems (Mitra *et al*., 2022). Such activities discharge metals into the environment through their products' application, run-off, and disposal, which could then get into the terrestrial system via surface water, aerial deposition, or soil (Ishaq *et al*., 2013). Pesticides is among the major agricultural sources of heavy metals (Alloway, 2013). These heavy metals generally result in greater harm to human health via food chain transfer (Cho-Ruk *et al*., 2006; Tangahu *et al*., 2011).

CONCLUSION

Cd and Pb were relatively detected in most pesticides although Pb concentration was much higher and calls for concern. Ni was found only detected in one insecticide. Therefore, it is clear that the pesticides contain heavy metals slightly above the tolerable limits which could get into the soil subsequently accumulate overtime and pose serious threat to the plants and other living organisms. Lastly, regulations on the formulations and extent of usage of these pesticides should be reinforced.

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