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Determination of some herbicides in foreign and local rice brands obtained from Makurdi, Benue, Nigeria

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Abstract
Rice consumption has increased worldwide over recent decades, as it has become one of the most common foods. However, there is dearth of information regarding the analysis of pesticide residues in rice-grain. Thus, residues of some pesticides were determined in selected rice brands sold in three markets in Makurdi metropolis Benue State - Nigeria using gas chromatograpy mass spectrometry. Prior to the GC-MS technique analysis, Quick Easy Cheap Effective Rugged Safe (QuEChERS) method for extraction and clean-up was carried out. The results showed pesticides with most occurrences as; Dichloran, Heptachlor epoxide, Propyzamide, Chlorpyrifos, Diazinon, Endosulfan II, Methoxychlor and Mirex; followed by BHC, Aldrin, Trifluralin, Dieldrin, Endrin P, p – DDT, and Antrazine. Whereas, 2, 4 – D, Propanil, BHC and Trifluralin were not detected across all the samples. Occurrences of the residues in the rice samples were influenced more by pesticide type rather than rice brand. All cases of the detected pesticide residues were found to exceed the Maximum Residue Limits (MRLs) set by the European Union with Mirex having the highest concentration of 6.9255 mg/kg (which is 1385 times the MRLs) and heptachlor with the least concentration of 1.5831 mg/kg (which is like 158 times the MRLs).

Keywords: Pesticide Residues, Rice, EU, Maximum Residue Limits, *Oryza sativa*, Makurdi

1. Introduction

Rice (*Oryiza sativa*) is well-thought-out as the most frugally important food product in many developing countries and it's considered as a basic food source for about 2.4 billion people [1][2]. Thus is one of the most widely consumed foods in the world and its demand has increased in recent decades [3]. It is a crop that shows great adaptability to different soils and climate conditions. Rice plays a strategic role, both economically and socially; especially in populous nations such as Asia, Africa and Latin America [1][4]. Benue State known as the Food Basket of the Nigeria engages highly in agricultural activities including rice farming. Hence, many pesticides; herbicides, fungicides, insecticides, avicides [5][6][7]; are used in various combinations and at different stages of cultivation of rice to protect it against pests [8]. The use of pesticide chemicals has often increased the yield of rice production. However, due to bad agricultural practices while applying these chemicals, or different legislations between countries, residues of several pesticides can be found in rice. This can affect the quality of rice, hence a threat to human and the environment [5]. Therefore, contamination of the environment and food by pesticide residues has caught the attention of many globally [9-11]. According to Grewal *et al.* and Ouwa *et al.* [12, 13] the residues can affect non–target organisms along the food chain and pose a potential risk to human health due to their sub-acute and chronic toxicity. Zanella *et al.*[8] also observed that contamination of animal feed with pesticide residues can cause harmful health effects in the animals and may be harmful to human through secondary exposure. In fact, recently agricultural commodities from Nigeria were banned by the European Food Safety Authority because some of the food produce including beans, sesame seeds, melon seeds, dried fish and meat, peanut chips and palm oil were found to contain pesticide residues [8]. The prohibited beans were found to have concentration of dichlorvos ranging from 0.03 - 4.6 mg/kg, whereas the acceptable maximum residue limit is 0.01 mg/kg. Some of the commonly used pesticides include; cypermethrin (α-cyano-3phenoxybenzyl-2, 2-dimethyl-3-(2, 2dichlorovinyl) cyclopropanecarboylate), butachlor, aldrin, dieldrin, pendimethalin and propanil and alpa-HCH [8, 13]. In addition, physico-chemical properties can explain the occurrence of pesticides in rice commodities; lipophilic pesticides are frequently found in brown rice, whereas fungicides are mainly found in milled rice. Carbendazim, malathion, iprodione, tebuconazole, quinclorac and tricyclazole are the pesticides most frequently found in white rice, while buprofezin, hexaconazole, chlorpyrifos and edifenphos are most commonly found in paddy rice [5]. Pesticide-residue concentrations can be affected during rice processing-with concentrations generally lower in the final products [5]. By the way, due to the wide cry about health implication of the conventional pesticide residues, many have strongly advocated for greener alternative pesticides. The focus of the proposed greener pesticides is to reduce the usage of synthetic conventional pesticides, thereby preventing their adverse residual effects on human and the environment [14].

Chromatographic methods are indispensable in the determination of pesticide residues [5]. A variety of selective detectors permit the analysis of compound mixtures or mixtures of parent compounds and degradation products. GC-NPD and -ECD are the dominant methods for routine control analyses [10]. These techniques have been largely replaced by GC and LC coupled to mass spectrometric techniques, especially by using tandem mass spectrometry [8]; and it has become a viable method of pesticides analyses [11][3]. A simple, easy, cheap and efficient analytical method for determination of multiple pesticide residues including organochlorine, organophosphorus, synthetic pyrethroids and herbicides in rice grain by capillary gas chromatography is reported. The quantification of residues was done by capillary gas chromatography with a µ-ECD detector and a HP-5MS capillary column [15]. Shah *et al.* [3] analyzed pesticides of interest using a simple QuEChERS sample preparation procedure and UPLC-MS/MS technique in rice samples. Again, for the first time pesticides were analyzed simultaneously in a single run using positive electrospray ionization with multiple reaction monitoring (MRM) after extraction with slightly modified QuEChERS method [16]. Furthermore, based on the European Union (EU) database, more than 3000 analyses of pesticide residues in rice have been performed by official EU laboratories over the past decade. Of these, 6% reported pesticide residues above the maximum residue limits (MRLs) [5]. A study was conducted to investigate the pesticide residues in unhusked and husked rice (*Oryza sativa* L.) on Basmati-385 and Irri-6 varieties in major rice growing areas of Punjab, Pakistan. The concentration of four pesticides was determined by gas chromatography with flame ionization detection (GC-FID). In all the 400 samples, four pesticides, *i.e.*, Karate, Malathion, Novacran and Padan were found in concentrations ranging from 19 to 148 ppm [17]. Furthermore, Onojoh *et al.* [11] observed no pesticide residues in most the samples of husked rice grain and rice plant leaves collected from Omala area, of Kogi State – Nigeria. Therefore, due to the high rate of rice consumption in Benue State - Nigeria, the Determination of some Herbicides in Foreign and Local Rice Brands obtained from Makurdi, Benue State-Nigeria is hereby reported.

2. Experimentals

2.1 Reagents/Apparatus

n–Hexane (JHL, 99.8%), acetone (Kermel, 99.5%), magnesium tetraoxosulphate (VI) ($MgSO_4$), sodium chloride (NaCl), distilled water, 2,4–dichlorophenoxyacetic acid solution (SELECT, 722 g/mL), mortar and pestle, Weighing balance (AE–ADAM), separatory funnel (Interflon, 250 mL), spatula, stop watch (Tecno N7 Digital Stopwatch), sieve, retort stand, measuring cylinder (Bomex 10 mL, 20 mL), glass sample bottles, refrigerator (Electrolux), crucible, volumetric flask (Bomex 10 mL).

2.2. Sample Collection

Six samples of rice i.e. four brands of foreign rice (RAS, MBG, CCR, MDR) and two brands of local rice Faro-61 and Faro-44 were purchased from each of the three major markets in Makurdi metropolis i.e. Wurukum, Wadata and Modern markets using composite sampling method. Samples of each brand were purchased randomly from the three markets. The samples were packaged in aluminum foil, labeled appropriately and taken to the laboratory at the Department of Chemistry, Benue State University Makurdi. The map of sampling area is given in Fig. 1

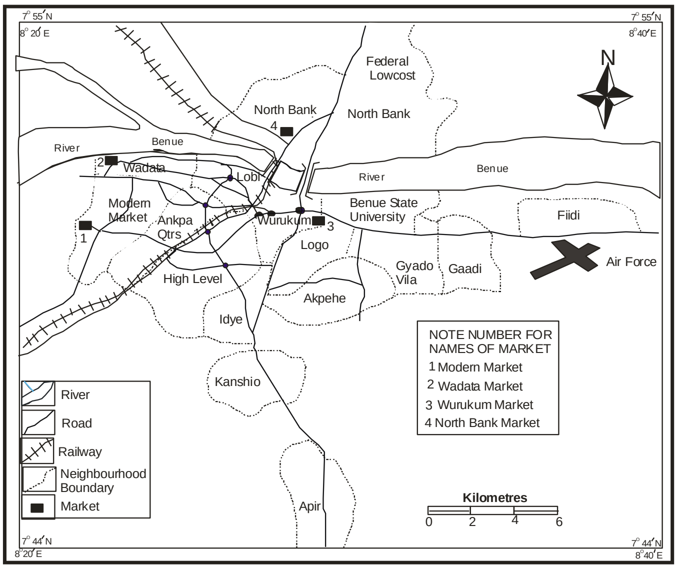

Figure 1: Map of Makurdi Metropolis showing the location of sampling areas

2.3. Sample Preparation

Each of the rice samples were pulverized using mortar and pestle, sieved and packaged in aluminum foil, labeled accordingly and stored in plastic containers.

2.3.1. Sample Extraction

About 5 g of rice sample was measured into a crucible using a weighing balance and transferred into a separatory funnel. 10 mL of distilled water was added, 10 mL of n-hexane was added using a measuring cylinder. Also, 1 g of sodium chloride (NaCl) was weighed and added. 6 g of magnesium tetraoxosulphate (VI) $MgSO_4$ was added to the solution and 20 mL of acetone was added using a measuring cylinder. The solution was then shaken vigorously for 20 minutes and allowed to settle down for 10 minutes. The tap was opened carefully to collect the extract into the labeled glass sample bottle. The bottle was immediately kept under a cold condition in a refrigerator; this process was repeated for all the samples [18].

2.4. Cleanup Process

Clean up process was carried out in order to remove any interfering substances that were co-extracted with the herbicide residues in the rice sample. A column of about 15 cm (length) × 1 cm (internal diameter) was packed first with glass wool and then with about 7.5 g activated silica gel prepared in a slurry form in acetonitrile. About 5 g of anhydrous sodium sulphate was placed at the top of the column to absorb any water in the sample or the solvent. Pre-elution was done with 15 mL of acetonitrile, without exposing the sodium sulfate layer to air, so as to prevent the drying up of the silica gel adsorbent. The reduced extract was run through the column and allowed to sink below the sodium sulfate layer. Elution was done with 3 × 10 mL portions of the acetonitrile. The eluate was collected, dried with anhydrous sodium sulfate and evaporated to dryness under a stream of analytical grade nitrogen (99.99%) for GC-ECD analysis [18].

2.6. Preparation of Pesticide Standards

Stock solution of 2, 4-D herbicide was prepared in 10mL volumetric flask by accurately weighing 1mL of the herbicide solution into the volumetric flask, 9mL of n-hexane was then added up to the mark and thoroughly shaken [18].

2.7. Column Type and Conditions

The dried eluate was reconstituted with 1 mL 2, 2,4-trimethylpentane (isooctane). With the aid of a micro syringe, 1 µL of the 1.0 mL purified extract was injected into the injection port of a gas chromatograph coupled with a ^{63}Ni electron capture detector (GC-ECD, Hewlett Packard 7890A series II). The column consisted of a DB-17 fused silica capillary column (30 m×0.32 mm i.d.× 0.25 m (film thickness). The temperatures of the injector and detector were 250 ℃ and 300 ℃ (held for 5 min), respectively. Oven temperature programme started from 60 ℃ (1 min) and continued at 20 ℃/min to 150 ℃ and at 5 ℃/minute to 280 ℃ held for 4 min injected sample volume was 1µL. The injection was carried out on a split less injector at 200 ℃ and the purge activation time was 30 s. The carrier gas was N_2 at 30 mL /min; and the split less flow rate was 19.6 mL /min. The run time was 23 min. The individual organochlorine pesticides were identified by comparing the elution time of standard organochlorine pesticides with those in the samples, while each organochlorine pesticide was quantified by comparing the peak areas of the organochlorine pesticides in samples with those in standard [19].

3. Results and Discussion

The results of the pesticide residues from the Wurukum, Modern and Wadata markets in Makurdi of Benue State-Nigeria are as represented in Figures 2 – 4, respectively.

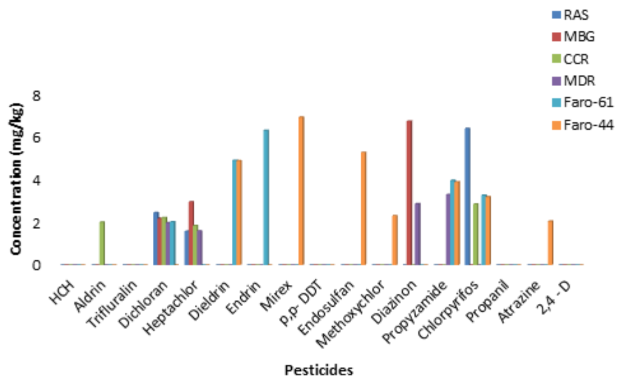

Figure 2: Pesticide concentration in rice samples from Wurukum Market

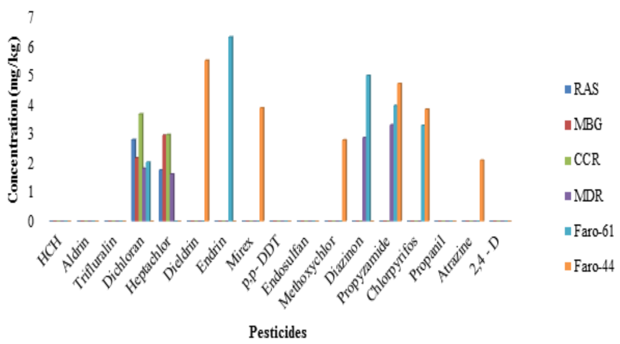

Figure 3: Pesticide concentration in samples from Modern Market

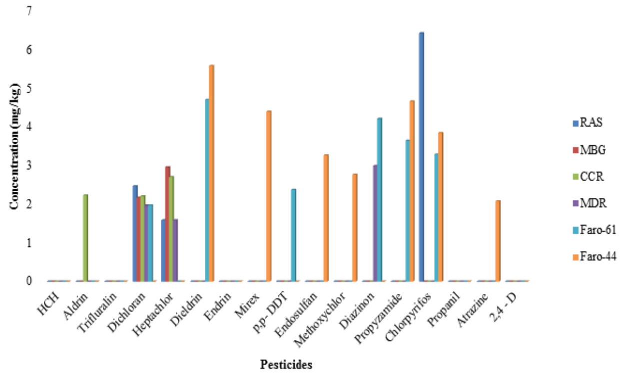

Figure 4: Pesticide concentration in samples from Wadata Market

Results from the Figures 2-4 above indicate that hexachlorohexane (HCH), trifluralin, propanil and 2, 4–D were absent in all the samples obtained from the three (3) markets. Aldrin was detected in CCR from Wurukum market with concentration of 2.003 mg/kg, while Faro-44 from Wadata market contained aldrin at 2.2181 mg/kg, aldrin was absent in Faro-44 from Modern market. The values determined were however higher than EU Maximum Residues Limit (MRLs) for aldrin which is 0.1 mg/kg. Ize–Iyamu and coworkers [20] also quantified the level of organochlorine pesticide residues in fish from Ovia river in Edo state and found aldrin to be present with a concentration of 0.027 mg/kg which was however below the EU–MRLs. p,p–DDT was absent in all rice samples from Wurukum and Modern markets, but present in Faro-61 from Wadata Market at concentration of 2.3661 mg/kg which exceeds the EU Maximum Residues Limit for p,p-DDT which is 0.01mg/kg. Tibor and Szogyi [21] determined pesticides in foods and food products in Hungary and found the level of p,p–DDT to be 0.1035 mg/kg, which was still higher than the MRLs approved by EU. In the case of endrin pesticide, its concentrations in Faro-61 were; 6.3004 mg/kg (Wurukum Market), 6.3004 mg/kg (Modern Market) and not detected (Wadata market).The results were far above the EU MRLs for endrin (0.01mg/kg). Bosnir *et al.*, [22] quantified the level of organochlorine pesticide residues in kaymak and butter marketed in Turkey. Endrin was found with a concentration of 7.31 ng/g which was however lower than the Turkish National residues limit. Chlorpyrifos was found in rice samples from Wurukum Market as follows: RAS (6.3960 mg/kg), CCR (2.8537 mg/kg), Faro-61 (3.2745 mg/kg) and Faro-44 (3.1884 mg/kg). The rice samples from Wadata Market showed varying concentrations of chlorpyrifos as follows: RAS (6.3960 mg/kg), Faro-61 (3.2475 mg/kg) and Faro-44 (3.8280 mg/kg) while Faro-61 and Faro-44 samples from Modern Market contained chlorpyrifos at 3.2744 mg/kg and 3.8280 mg/kg respectively. All the concentrations determined were above the EU approved MRLs for chlorpyrifos in foodstuffs which is 0.05mg/kg. Rohan and coworkers [23] determined pesticide residues in fruits and vegetables in India. From their analysis, chlorpyrifos was found to have a concentration of 0.5 mg/kg which was higher than the MRLs adopted by EU. The concentration of dieldrin in Faro-61 and Faro-44 from Wurukum Market were (4.9053 mg/kg and 4.8900 mg/kg, respectively). Dieldrin concentration in Fro-61 from Wadata Market was 4.6840 mg/kg while for Faro-44, the concentration was 5.5560 mg/kg. For the rice samples from Modern Market, dieldrin concentration in Faro–44 was 5.5015 mg/kg. The results were above the EU approved Maximum Residues Limit for dieldrin in foodstuffs which is set at 0.05 mg/kg, indicating that the samples were highly contaminated with pesticides. Bosnir and coworkers [22] quantified the level of organochlorine pesticide residues in kaymak and butter marketed in Turkey. Dieldrin was found with a concentration of 12.69 ng/kg which was lower than the EU MRLs. Heptachlor epoxide was found in rice samples from Wurukum Market as follows; RAS (1.5831 mg/kg), MBG (2.9583 mg/kg), CCR (1.8481 mg/kg) and MDR (1.5925 mg/kg). Meanwhile, heptachlor epoxide quantified in rice samples of the Wadata Market showed; RAS (1.5831 mg/kg), MBG (2.9442 mg/kg), CCR (2.6936 mg/kg) and MDR (1.5925 mg/kg). The rice samples from Modern Market had varying concentrations of heptachlor epoxide as follows; RAS (1.7554 mg/kg), MBG (2.9442 mg/kg), CCR (2.9598 mg/kg) and MDR (1.6082 mg/kg). The concentration of heptachlor epoxide in all the rice samples was above the EU approved MRLs for heptachlor in foodstuffs which is 0.01 mg/kg. Akan and coworkers [24] also determined organochlorine pesticide residues in *Ethmalosa fimbriata* from Lagos lagoon. From their analysis, the concentration of heptachlor epoxide detected was 0.63 ng/kg which was at safe limit for consumers. Endosulfan concentrations found in Faro-44 from Wurukum Market was 5.2755 mg/kg and 3.2553 mg/kg in Faro-44 from Wadata Market. It was not detected in samples from Modern Market. The concentration was much higher than the EU approved Maximum Residues Limit for endosulfan which is set at 0.01 mg/kg. Methoxychlor concentration detected in Faro-44 from Wurukum Market was 2.3038 mg/kg. For the samples from Wadata Market, methoxychlor concentration in Faro-44 was 2.7511 mg/kg. Rice samples from Modern Market, methoxychlor concentration in Faro-44 was 2.7735 mg/kg. The concentration of methoxychlor was low when compared to other pesticides but was still above the EU MRLs for methoxychlor in foodstuffs which is 0.01 mg/kg. Dichloran concentration found in Wurukum Market were; Faro-61 (2.0203 mg/kg), MDR (1.9810 mg/kg), RAS (2.4564 mg/kg), CCR (2.2233 mg/kg) and MBG (2.1831 mg/kg). Dichloran was detected in rice samples from Wadata Market at varying concentrations as; Faro-61 (1.9632 mg/kg), MDR (1.9612 mg/kg), RAS (2.4564 mg/kg), CCR (2.1967 mg/kg) and MBG (2.1634 mg/kg). Rice samples from Modern Market showed varying concentration of dichloran as follows; Faro-61 (2.0202 mg/kg), MDR (1.8106 mg/kg), RAS (2.7900 mg/kg), CCR (3.6675 mg/kg) and MBG (2.1634 mg/kg). The concentration of Dichloran in rice samples from the various markets exceeded the EU approved MRLs for dichloran which is 0.01 mg/kg. Anzene and coworkers [25] quantified the level of organochlorine pesticide residues in post-harvest grains. Result of their analysis indicated dichloran was present at 0.01mg/kg in maize, guinea corn and millet samples. Mirex occurred only in Faro-44 from Wurukum, Wadata and Modern markets at concentration of 6.9255 mg/kg, 4.3762 mg/kg and 3.8798 mg/kg, respectively. The concentrations were above the EU approved MRLs for mirex which is 0.005 mg/kg. It is worthy to note that most of the pesticides that were detected in the rice samples from the different markets were among the list of banned pesticides by the National Agency for Food Drug Administration and Control (NAFDAC). Such pesticides include Endosulfan, Endrin, Mirex, Heptachlor, Benzene hexachloride, Aldrin and Dieldrin [26]. The pesticides determined and found present in the foodstuffs may be due to their illegal application by farmers during cropping seasons. Most of the pesticides have long half-life which makes them persist in foodstuffs after a long period of application. Aldrin has a half-life of 369 days, trifluralin has 60 days, and heptachlor epoxide has half-life of 3.5 years. Other pesticides such as dieldrin have half-life of 5 years, while endrin has a half-life of 4 years, mirex has a half-life of 12 years, p,p-DDT has a half-life of 2 years. Also, 2,4-D has half-life of 10 days, atrazine has half-life of 60 days, chlorpyrifos has 30 days, methoxychlor has 37 days and endosulfan have a half-life of 50 days [27].

4. Conclusion

Pesticides are used globally in farming sector to control weed and other crop diseases, it is no doubt that pesticides are of great significance to modern agriculture since they help to boost food production. However, their use or misuse leads to serious contamination of the environment. Worthy of note, is the fact that the concentration of pesticide residues found in these rice brands were high and pose a heavy threat to man or animals that eat them as their concentrations were above the European Union (EU) approved Maximum Residue Limits (MRLs) for cereals as adopted by NAFDAC. The pesticide residues continuously accumulate in the body system of man and animals that consume them which can lead to serious health problems. Routine supervision of these pollutants in rice and other food stuff is required for the prevention, control and reduction of pollution to minimize health risks.

5. Recommendations

Environmental regulatory agencies should brace up in monitoring against the indiscriminate use of pesticides in agricultural production. In order to ensure this, only licensed dealers should be allowed to sell pesticides. Also banned pesticides should not be allowed to be sold out to farmers. A comprehensive data bank for symptoms of pesticide infections should be made available by NAFDAC so as to educate the public on the possible ways to quickly detect and avert them. Good Agricultural Practices (GAP) should be adopted by farmers; such practices include: using only recommended pesticides at the specified doses and at the right time. The Nigerian Pesticide Action Network (NiPAN) should be established with the aim of educating the public on the side effects of pesticides and strictly monitor the excess applications.

6. Acknowledgements

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7. Conflict of interest

The authors have no conflict of interest about this work.

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