Pesticide Residues and Their Degradation Products as Influenced by Acidity and Organic Matter in Kura Irrigation Farmland Soils

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Authors' contributions

The study was a collaborative research. Author COO managed sample collection, preparation and instrumental analyses. Author AAA designed the study, performed the statistical analyses and wrote the first draft of the manuscript. Author MW managed the literature searches, wrote the protocol and prepared the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

The aim of this research is to determine the insecticide and herbicide residues and their degradation products in Kura irrigation farmland soils. The analyses were carried out during the planting (before harvest) and after the harvesting periods. The insecticide residue analyses were undertaken using Gas chromatography-mass spectrometry (GC/MS) after extraction with a mixture of n-hexane and acetone (1:1) in a soxhlet extractor. The pH levels of the soil samples and the soil organic matter were also determined using standard analytical methods. The acidity and organic matter content of most of the soil samples increased slightly after harvest. The compounds detected as residues include 1-octadecene, 9-heptadecanone, (E)-3-eicosene, (Z)-5-nonadecene, heptadecane, 1-docosene, 1-nonadecene and 1-eicosene. Out of these residues, 1-octadecene and (E)-3-eicosene were detected during planting and after the harvesting periods, showing that they are the most persistent of the residues in the soil samples. The residues detected before harvest were totally different from the residues detected after harvest. This shows that the pesticides, after some time, degraded in the soil into completely different compounds and the total residues were detected in high percentages.
1. INTRODUCTION

Agriculture plays a significant role in the economic growth and development of nations as in the production of food, earning of valuable foreign exchange through the export of agricultural products and provision of employment [1]. One of the key sectors of the Nigerian economy that accounts for more than one-third of the total Gross Domestic Product (GDP) and labor force is agriculture and this sector has been recognized as a fundamental tool for spurring growth, overcoming poverty and enhancing food security [2,3]. The improved productivity is based on many important and often complementary determinants of agricultural productivity such as fertilizer, improved seeds and other inputs [4]. In agriculture, farmers’ efforts are often undermined by the activities of parasites, pathogens, fungi and weeds. They do not only compete with the farmers for space and food materials but are also agents of diseases to root crops, cereal crops, fibers, fruits, vegetables, stored grains and livestock. They reduce the farm yields to the level that make agricultural endeavors uneconomical to the farmers if not controlled [5]. They even sometimes inject toxic substances when they feed on the plants or create holes through which disease-causing bacteria or fungi may enter the plants which can be toxic to humans [6].

Farmers have therefore been compelled to explore ways of controlling these unwelcome fungi, insects, birds and weeds to curtail the losses. One of such is the application of pesticides to farmlands, crops and stored grains to protect and remedy the farm produce from the ravages of these organisms [5]. In agriculture, the use of insecticides such as dichlorodiphenyltrichloroethane (DDT) has been the dominant form of pest management since the 1950s to kill pests such as insects and nematodes [7]. The application of herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D) have also been on the increase throughout the globe [8].

The use of pesticides has multiplied over the past few decades and this has been estimated to about 5.2 billion pounds worldwide per annum not only in agriculture, but also employed in homes or buildings in form of sprays, poisons and powders for controlling cockroaches, mosquitoes, fleas, ticks and other harmful bugs [9]. Pesticides and their degradation products remain in or on crops after harvesting or during storage and can enter into the food chain [10]. These residues are found in the soil, air, surface and ground water; their degradation and transformation in the environment are dependent on their physicochemical properties, the environment in which they are found and their threshold levels [11,12].

Although, pesticides have substantially contributed to the control of pests and in increasing crop yields so as to meet the food demand of the increasing population and the control of vector-borne diseases, exposure to them is one of the problems farmers in developing countries are facing. In fact, the risks associated with their use have surpassed their beneficial effects [9,13,14]. Moreover, pesticides and their degradation products result in cancer, neurological defects, diabetes, respiratory diseases and genetic disorders depending on the degree and type of exposure [15]. Annually, there are millions of cases of pesticide poisonings worldwide [16]. Several families have been reported to have died or have been hospitalized as a result of contaminated foods in several parts of Nigeria due to improper handling and usage of insecticides [17,18,19].

This research is a novel one carried out in Kura, in Kano State Nigeria. Kura is one of the locations of major irrigation schemes in Nigeria. This irrigation scheme runs throughout the dry season to increase food production and has been in existence for about five decades [20,21]. Most farmers in Kura are not literate and do not follow the instructions of extension workers as per the manufacturers’ specifications on pesticide application hence the need to assess the insecticide and herbicide residues, the degradation products as well as correlate the levels of pH and organic matter to the pesticide adsorption and degradation in some of the farmland soils.

2. MATERIALS AND METHODS

2.1 Study Area and Sample Collection

2.1.1 Study area

Kura Local Government Area of Kano State has the coordinates latitude 11°46'20.35"N longitude 046°20.35"E.
8°25'32.72"E. Kura is one of the major locations known for rice cultivation in Kano State. The study sites chosen were the ones consisting farmlands that were already being prepared for rice cultivation as at the time of this research. The study area was divided into 8 farmlands which were marked F1 – F8. Farms F1 – F6 were mostly waterlogged throughout the planting season which made sample collection difficult.

In Farms F1 and F6, grazing commenced just immediately after harvest prior to sample collection while only the farmer in Farm F3 applied animal dung on his farm before planting.

The pesticide solutions were applied to the farmlands both during the land preparation and during planting using the spraying method.

2.1.2 Sample collection

The soil samples were collected using a soil auger at a depth of 0-15 cm during the planting season of rice and after harvest between August and December. A grid was established by dividing each farmland into 5 rows, 10 paces apart with 4 core samples taken per row for a total of 20 cores [22]. The cores were mixed thoroughly for each farmland and a subsample was collected from the cores. A total of these samples were obtained for each rice farmland which were 8 during the planting season and 8 after the harvest. Coning and quartering method was used to obtain a representative analytical sample [23].

Samples of the insecticides and herbicides used in the area and in all the rice farmlands during the planting season were purchased and used as standards. These were compared with those found in the soil extracts. The most common insecticides and herbicides used in Kura farmlands which were used in this study with their active ingredients include: Best Up (glyphosate), Buta Force (Butachlor), Orizo Plus (propanil, 2,4-dichlorophenoxyacetic acid) and Sharp Shooter (profenofos, cypermethrin).

![Map of Kura and Azore showing the sampling sites](image-url)

Fig. 1. Map of Kura and Azore showing the sampling sites
2.2 Sample Treatment and Analyses

The soil samples (75 g for each sample) were air-dried at about 22°C in a drying room of the laboratory and subsequently placed in an oven at about 30°C for 24 hrs. Using wooden mortar and pestle, the sample was ground and divided into two parts; one part was sieved using 2 mm sieve and the other part, using 0.5 mm sieve. Twenty grams of the 2 mm sieved soil was used to determine the pH using the Jenway 3501 Digital pH Meter using water [24]. The pH meter was standardized with standard solutions of pH 4.0 and 9.0. These pH values were chosen because most nutrients are available to plants at pH 5.5 – 6.5 in soils [25]. Two grams of the 0.5 mm sieved soil was used to determine the organic matter content by titration method [24].

Twenty-five grams of the sample was extracted with acetone and n-hexane mixture (1:1 v/v 250 cm 3) using soxhlet extractor for 6 hrs. The eluent collected was passed through a column containing 50 g of granular sodium sulphate to absorb any residual moisture from the soil. This was then concentrated to about 60 cm 3 using a rotatory evaporator prior to GC/MS analysis [24, 26].

The soil extracts as well as the purchased insecticides and herbicides samples were analysed using Agilent Gas Chromatograph/Mass Spectrophotometer 5975C equipped with a triple axis detector and an auto injector (10 μl syringe). Pre-purified hydrogen was used as the combustion gas with the pre-purified air as the supporting gas. Helium gas was used as the carrier gas and all chromatographic separations were performed on capillary column having the specifications: length; 30 m, internal diameter 0.2 μm, thickness; 250 μm. The chromatogram was run on a programmed mode with column temperature starting at 35°C for 5 min and increased to 250°C at the rate of 20°C/min and then held for 5 min. MS Solution software provided by the supplier was used to control the system and to acquire the data; identification of the compounds was carried out by comparing the mass spectra obtained with those of the standard mass spectra from NIST library.

Samples of an insecticide (Sharp Shooter with specified actives as cypermethrin and profenofos) and herbicide (Best Up with specified active as glyphosate) were chromatographed as above.

3. RESULTS AND DISCUSSION

3.1 Soil pH and Organic Matter

The soil pH values were between 6.3 – 9.5 before harvest while after harvest, the soil pH values were between 5.0 – 8.2 as seen in Fig. 2.

The pH values of the soil samples before harvest ranged between 6.33 – 9.50 while after harvest, the values ranged between 5.03 – 8.17. The minimum value of pH before harvest was still within the FAO standard (5.5 – 6.5) which supports good cultivation while the minimum pH value after harvest was below the FAO standard. After harvest, farms F7 and F8 had pH values 5.03 and 5.17 respectively which were below the FAO standard. Before harvest, farms F7 and F8 had the pH values 6.43 and 6.33 respectively indicating that plant nutrients were all available during planting activities since these values were within the FAO standards.

It was observed that waterlogging slightly affected the pH range of farms F1 – F6 as the pH before harvest ranged between 7.47 – 9.50 while after harvest, the pH values ranged between 5.60 – 8.10. A significant decrease was observed in the pH of farm F3. Before harvest, it was 9.50 and it was 5.60 after harvest. This decrease can be attributed to the nature of microbial activities on the farm as it was the only farm where organic manure was applied [27, 28].

Results from ANOVA statistical test shows that there are no significant differences between the pH values of the studied farms i.e. F (5.47, 1.41) = 3.88, p = 0.05.

Before harvest, the soil organic matter ranged between 0.46% - 1.28% while after harvest, it ranged between 0.79% - 2.4% as shown in Fig. 3. The organic matter levels increased in most of the farms after harvest except for Farm F1 where the value stood at 0.94% before and after harvest. This increase can be attributed to the plant debris addition after harvest [29]. The increase in soil organic matter helps in the further adsorption of pesticides in the soil [30].

After harvest, the organic matter content in Farm F2 was observed to be the highest in relation to the other farms. This observation can be attributed to the long periods of water saturation on the farm plot as the soil was paddy throughout
the year [31]. Also, the crop yield from the farm was very high hence there was very high plant debris [32].

In Farm F1, there was no significant change in the organic matter content deposited in the soil and it was observed that the crop yield was low hence, the plant debris deposited was not much. There was immediate grazing of cattle on the farm after harvest which could explain the insignificant change in the organic matter content determined [32].

**Fig. 2.** The levels of soil pH from the farm plots before and after harvesting of rice as against the FAO pH standard

**Fig. 3.** Distribution of organic matter content within the farm plots before and after harvest
Farm F3 had the least content of organic matter before harvest. This can be attributed to the active microbial degradation taking place in the soil due to the application of animal dung.

In Farm F6, there was a reduction in the organic matter content which was not so in other farms. It was observed that the crop yield was low; hence the plant debris deposited was not much. There was also immediate grazing of cattle on the farm after harvest which could explain the insignificant change in the organic matter content determined [32].

Results from ANOVA statistical test shows that there are no significant differences between the organic matter contents of the studied farms i.e. $F(0.32, 0.16) = 2.00, p = 0.05$.

Noting the similarities in the results of some pairs of farms in relation to their organic matter contents, the n-hexane/acetone extracts of farms F1 and F4; farms F5 and F6 and farms F7 and F8 were combined and chromatographed as individual samples. As a result, the total sample extracts chromatographed were now 5 before harvest and 5 after harvest. Farms F2 and F3 were left as obtained because of their unique organic matter content before and after harvest.

The chromatograms of the soil extracts gave twenty-two (22) different prominent peaks. These include compounds in the soils before harvest as shown in Fig. 4(a) and after harvest Fig. 4(b). Out of these compounds, eight (8) were detected before harvest (1-octadecene; 9-heptadecanone; (E)-3-eicosene; Phthalic acid, di (2-propylpentyl) ester; bis (2-ethylhexyl) phthalate; octadecanoic acid ethyl ester; diisooctyl phthalate and cyclooctane as shown in Fig. 5 while fourteen (14) other compounds were detected in the farms after harvest (1-octadecene; di-sec-butyl phthalate; (E)-3-eicosene; phthalic acid isobutynonyl ester; (Z)-5-nonadecene; hexadecanoic acid methyl ester; 1-eicosene; cyclotetracosane; heptadecane; 1-docosene; heptadecyl trifluoroacetate; phthalic acid-2-ethylhexylphenyl ester; 1-nonadecene and phthalic acid-2,4-dimethylpent-3-yl isobutyl ester) as shown in Fig. 6.

Fig. 4(a). Chromatograms showing the peaks of detected compounds before harvest in farm F1
Fig. 4(b). Chromatograms showing peaks of detected compounds after harvest in farm F1

Fig. 5. Percentage levels of compounds detected before harvest
Six (6) of the compounds detected before harvest (9-heptadecanone; phthalic acid di (2-propylpentyl) ester; bis (2-ethylhexyl) phthalate; octadecanoic acid ethyl ester; diisooctyl phthalate and cycloeicosane) were found to have been completely degraded as they were not detected after harvest as seen in Fig. 6. 1-octadecene and (E)-3-eicosene were found to be in the soils before and after harvest though 1-octadecene formed about 90% of the common residues detected in all the farmlands.

Metabolites with cultures of Aspergillus niger yielded 1-octadecene and (E)-3-eicosene, amongst numerous others. (E)-3-eicosene has also been detected in soils with cultures containing Streptomyces sp. SCA 7 [33].

The residues detected before harvest were totally different from the residues detected after harvest. This shows that the pesticides, after some time, degraded in the soil into completely different compounds and the total residues were detected at high percentages (from 54 – 100%). Comparing the chromatograms of some raw insecticide and herbicide samples (chromatograms in Fig. 7(a) and 7(b)) and that of the soil extracts (Fig. 4(a) and 4(b)), the compounds detected were completely different from those detected in the soil extracts. This could be attributed to the transformation of the active components into other compounds even before their application in the farmlands due to the improper storage.

1-octadecene and (E)-3-eicosene which had been detected in the farmlands throughout the planting season would be said to be as a result of the action of Aspergillus niger as well as Streptomyces sp. SCA 7 on organic content of the soils [33,34]. This means that 1-octadecene and (E)-3-eicosene are not degradation products of the insecticides and herbicides but rather plant debris. More so, these long-chain hydrocarbons are known to have low solubility and mobility in the environment which explains their persistence in the farmland soils throughout the year [35].

Among the compounds detected before and after harvest, some are common to some farms while some are not. For instance, before harvest as shown in Fig. 5, 1-octadecene was found in all the farms; 9-heptadecanone and cycloeicosane were found in four of the farms; (E)-3-eicosene, octadecanoic acid ethyl ester; bis (2-ethylhexyl) phthalate and diisooctyl phthalate were each found only in one of the farms.

Similarly after harvest, 1-octadecene was found in four of the farms; 1-docosene, di-sec-butyl phthalate and phthalic acid, isobutyl nonyl ester were found in two of the farms while heptadecane, phthalic acid, 2,4-dimethylpent-3-yl isobutyl ester, 1-nonadecene, phthalic acid, 2-
ethylhexylphenyl ester, (E)-3-eicosene, cyclotetrasane, (Z)-5-nonadecene, 1-eicosene, hexadecanoic acid methyl ester and heptadecyl trifluoroacetate were each found in just one farm.

From Fig. 5, four compounds were detected with prominent peaks in farms F1, F2 and F4 before harvest showing that the levels of pesticide residues have direct relationship with the organic

Fig. 7(a). Chromatogram showing the peaks of compounds in the herbicide (best Up)

Fig. 7(b). Chromatogram showing the peaks of compounds in the insecticide (sharp shooter)
matter content in the soil. Although, more compounds were detected after harvest, averagely, the concentrations were lower than those that were detected before harvest. This can be attributed to degradation.

4. CONCLUSION

Farms F1 – F6 were waterlogged throughout the planting season, hence the reason why the pH values did not drop below the FAO standard for agricultural soils after harvest. This is in contrast to Farms F7 and F8 whose values dropped below the FAO standard after harvest as the farms were not waterlogged throughout the planting season.

The organic matter content of most of the farms increased after harvest except for farms F1 and F6. The increased organic matter content helps in the adsorption of pesticides in the soil. After harvest, the organic matter content of Farm F1 remained unchanged and that of F6 reduced due to the low crop yield in both farms and the immediate grazing of cattle on the plant debris.

The residues from the soil extracts were completely different from those of the insecticide and herbicide samples showing that the residues of the soil extracts had completely degraded into different compounds in the soil. The two compounds that were detected before and after harvest from the farms 1-octadecene and (E)-3-eicosene were not degradation products but rather plant debris resulting from some microbial activities on the farms. These compounds are long-chain hydrocarbons with low solubility and mobility in the environment; hence their persistence in the farmland soils throughout the year.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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