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Comparative Studies on Grain Quality and Pesticide Residues in Maize Stored in Hermetic and Polypropylene Storage Bags

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Abstract: The conventional method of grain storage involving the use of polypropylene bags in conjunction with pesticides and hermetic bags are paramount in developing countries. However, there is limited information on grain quality and pesticide residue concentration of maize stored in such bags. This work determined grain quality and pesticide residue concentrations of maize stored in polypropylene and hermetic storage bags. Maize samples stored for a period of one year in polypropylene and hermetic bags were obtained from three major maize growing communities in the Ashanti region of Ghana and were analyzed for grain quality, aflatoxin content and pesticide residue concentration using standard methods. The amount of diseased, discolored, broken, insect-damaged, stained, germinated, shriveled, total defective, inorganic and organic matter of maize stored in hermetic bags was significantly lower than that of polypropylene. Levels of aflatoxin in maize stored in the polypropylene bags were significantly higher (13.9 ppb–20 ppb) than in maize stored in the hermetic bags (0.90 ppb–2.6 ppb). Out of 35 pesticides screened, only lambda-cyhalothrin was detected in polypropylene bags and deltamethrin in hermetic bags. The presence of these pesticide residues may be due to their long-lasting abilities. Levels of lambda-cyhalothrin residues were above the maximum residue limit (MRL) of 0.02 mg/kg, but have no significant effect on health. Deltamethrin residue concentrations in hermetically stored maize samples were below the MRL. In conclusion, maize grains stored in hermetic bags have higher grain quality and lower aflatoxin and pesticide residue concentrations than polypropylene bags. Education and promotion on the utilization of hermetic bags should be a priority in storing and supplying safe maize grains to consumers.

Keywords: maize grain storage; hermetic storage bags; polypropylene storage bags; quality attributes; pesticide residues

1. Introduction

Maize (*Zea mays* L.) is the most extensively produced and consumed cereal, accounting for over half of Ghana's entire grain harvest [1]. It is principally cultivated by small-scale farmers in most of the agro-ecological zones of Ghana, who depend predominantly on rainfall. Obaatanpa, Mamaba, Dadaba and Aburohoma are the common maize varieties grown by most farmers in Ghana [2]. Ghana's maize production capacity currently stands at 2.76 million MT with an annual growth rate of 8.06% [3]. Maize is used in many Ghanaian staples: poultry feed formulation, maize-grit production, alcohol brewing, baby food and breakfast cereal production [1,3]. There are basically two maize growing seasons (major and minor) along the transitional areas of Ghana, and usually one harvest season coincides with the rainy period, which threatens grain quality, particularly with respect to mold growth and insect pest infestation since most farmers rely on the sun for drying [4].

Maize storage is a major issue in maize production and a key contributing factor to post-harvest losses of maize across the globe. According to a report by FAOSTAT (Rome, Italy) [5], post-harvest losses of maize stand at 30%, with major causes being drying inefficiencies, poor post-harvest management, overdue harvesting and poor storage systems. Studies by Opit et al. [2] and Likhayo et al. [4] discovered that storage of maize in warehouses in Ghana is being affected by insects such as weevils (*Sitophilus zeamais* Motschulsky) and larger grain borer (*Prostephanus truncatus* Horn) owing to inappropriate moisture content, temperature and storage material and high gaseous exchange. Efforts by researchers in reducing post-harvest losses of maize have resulted in formulation of pesticides and invention of storage bags, silos, warehouses and others. However, studies have revealed that due to the high-cost nature and inefficiencies of some of these methods, farmers still use pesticides which are less expensive but have other deleterious effects on consumers' health. In late 2010, 15 farmers living in the Upper East region of Ghana died from consuming cereals suspected to have been treated with pesticides [6]. As a result, some of these pesticides have been banned in Ghana, yet some farmers use them secretly.

Efforts to mitigate the use of pesticides in cereal or maize storage led to discovery of hermetic storage bags, which provide a pesticide-free and cost-effective storage system [7,8]. Hermetic storage technology operates on the principle of depleting O_2 and accumulating CO_2 concentrations in the interior of the bags by virtue of grain and pest metabolism [4]. Walker et al. [9] emphasized that the hermetic phenomenon thwarts evaporation and gaseous exchange, thereby adjusting the interior composition (O_2 and CO_2) of the container to eliminate insect pests. Nevertheless, the concept of hermetic storage has not been fully accepted by many stakeholders along the maize value chain because little information has been published on the relative advantages of hermetic bags over traditional (polypropylene) bags with respect to grain quality and pesticide residues.

A national approach in Ghana to attain food security via the introduction of the "Planting for Food and Jobs" initiative may increase maize production to meet domestic consumption as well as international market demands. Nonetheless, the full prospects of the initiative may be unattainable unless stakeholders along the maize supply chain are provided with the capacity to preserve maize and market excesses for profit [8]. The current overreliance of smallholder maize farmers on the storage of maize in polypropylene bags with pesticide application is overwhelming and has the tendency to increase the effect of pesticides on the health of the Ghanaian consumers and the international market. It is therefore vital to provide information on the concentrations of pesticide residues and the quality of maize stored in hermetic and traditional (polypropylene) storage bags in Ghana to offer farmers and other stakeholders the opportunity to make informed storage choices for maize and promulgate laws with respect to eliminating pesticide use for maize preservation, for the safety of consumers.

This research work seeks to determine and compare the quality characteristics and the pesticide residue concentrations of maize stored in hermetic and traditional (polypropylene) bags in the leading maize producing areas in the Ashanti region of Ghana.

2. Materials and Methods

2.1. Study Area

This research work was conducted in three leading localities (Ejura, Abofour and Asante-Akyem Agogo) in the Ashanti region of Ghana notable for their high volumes of maize production. The three municipalities were chosen as study areas because of their significant production, active trade and involvement in the maize supply chain.

2.2. Sampling

Maize samples stored for a period of one year were collected from traditional polypropylene bags and hermetic bags in two different warehouses in each locality. A random sampling was done by taking a minimum of the square root of the number of bags in the warehouse, to get a fair representative sample of the total consignment. Samples were collected from bags by inserting a sampler from the top to the bottom of the bag at multiple random points. They were then sealed separately in zip-lock bags and labelled.

2.3. Maize Grain Quality Determination

Moisture content, physical quality, pesticide residues and aflatoxin content of maize samples were determined in the Laboratory of the Pesticide Division of the Ghana Standards Authority, Accra, as follows:

2.3.1. Determination of Moisture Content

Sampled maize grains were combined and mixed thoroughly, and about 500 g was milled using a standard laboratory mill (SUS304, China) to obtain uniform particle sizes. About 50 g of the milled sample was analyzed for moisture content using a Dicky-John Instalab® 700 proximate analyzer (IL7101FG, USA). The procedure was triplicated and their mean values recorded for each sample.

2.3.2. Determination of Maize Grain Physical Quality

Cone and quartering method were used to sub-divide the mixed sample several times to get a representative amount of 100 g. Grains were sorted according to stated parameters or defects (diseased, discolored, broken/chipped, insect damaged, stained, germinated, shriveled, other grains, total defective, inorganic matter, organic matter). After thorough sorting, the percentage defects were then calculated using Equation (1):

$$\text{Percentage defective grains} = \frac{\text{Weight of defective grains (g)}}{\text{Weight of sample (g)}} \times 100 \tag{1}$$

The analysis was conducted in triplicate and the resulting average percentages for the various defects were then recorded and compared with the Ghana Standards Authority's grading specification.

2.3.3. Aflatoxin Analysis

- Source of Reagents
  ENVIROLOGIX QUIKSCAN® DB5 Buffer solution and Sodium Lauryl Sulphate were obtained from Portland-USA, and 50% *v/v* ethanol solution was prepared using absolute ethanol and distilled water.
- Cleaning of Glassware
  Preceding the analysis, glassware was cleaned using Ecolab® Food grade detergent and washed with deionized water. They were further cleaned with acetone, dehydrated and stored in dust free cabinets until required.
- Extraction and Purification
  The sample was mixed thoroughly to achieve a homogenous mixture. About 500 g of the sample was milled (SUS304, China) to attain a granulation of 841 microns. Then, 25 g of the milled sample was weighed into a beaker. One packet of extraction powder was added to the flour as well as 50 mL of 50% ethanol. It was then shaken vigorously for 2 min by hand and allowed to settle for 2 min for a clear separation into lipid and aqueous phases. Finally, 100 μL was pipetted from different portions of the lipid phase into a centrifuge tube and centrifuged for 1 min in a LabniqueTM centrifuge (Spinplus-6, China).
- Analysis
  First, 200 μL of buffer solution was pipetted into a reaction vial, and 100 μL of the clarified extract containing the analyte was pipetted, added and mixed thoroughly. A test strip was then added to the vial and allowed to run for 5 min. Test strips were immediately cut at the top of the arrow tape and inserted into a QuickScan® reader

with barcode facing down. A corn high sensitivity Matrix Group was selected and the result was read.

2.3.4. Pesticide Residue Analysis

Pesticide residue analysis was done using the QuCHERS method of analysis, which involved extraction, purification and quantification of the extract via the chromatographic method as described below.

1. Extraction
   Five grams of comminuted sample was weighed into a 50 mL centrifuge tube and 1 mL of deionized water was added, and then it was vortexed for 30 s. About 10 mL of acetonitrile was added, and it was vortexed again for 60 s. A mixture containing 4 g of 0.2 g magnesium sulphate anhydrous, 1 g of 0.05 g sodium chloride, 1 g of 0.05 g trisodium citrate dihydrate and 0.5 g of 0.03 g disodium hydrogen citrate sesquihydrate was added before being immediately vortexed for 1 min and centrifuged (Spinplus-6, China) for 5 min at 3000 U/min.
2. Dispersive Solid Phase Extraction
   A 6 mL aliquot of the extract was pipetted into a polypropylene centrifugation tube containing 150 mg primary and secondary amine and 900 mg magnesium sulphate. The tube was closed and shaken strongly for 30 s and centrifuged for 300 s at 3000 U/min. For matrixes containing low amounts of fat, freezing out and addition of 150 mg of carbon-18 was done.

About 4 mL of the cleaned extract was pipetted into a round bottom flask and the pH adjusted quickly to 5 by adding 40 µL of 5% formic acid solution in acetonitrile (*v/v*), and the filtrate concentrated below 40 °C on a rotary evaporator and 1 mL of ethyl acetate was added for re-dissolution. About 20 µL of 1% polyethylene glycol solution in ethyl acetate (*v/v*) was added and the extract transferred into a 2 mL standard opening vial for quantitation via GC-ECD and GC-PFPD. Qualitative confirmation for positive detection was done via GC/MS.

2.4. Data Analysis

Data from the study was analyzed for mean values, standard deviation and significant difference at 95% confidence level, using a one-way ANOVA from Statistical Package for Social Science (SPSS) software version 20.0.

3. Results

3.1. Grain Quality of Maize Samples

Grain quality traits employed in domestic transaction tend to imitate the grading categories stipulated by Ghana Standards Authority (GSA). Prominent quality parameters such as visual appearance, moisture content, grain color, dryness and cleanness are mostly paid attention to by stakeholders along the maize supply chain. The fraction of insect-damaged grains and organic and inorganic material are also considered by producers, aggregators, retailers and processors as the main maize grain quality parameters with reference to the Ghana Standards Authority criteria. Grain quality is also a function of the wholesomeness of grains as verified by several examinations from visual appearance to complex laboratory analysis. The quality standards for grain are country-specific, as different countries have different grades and standards to facilitate marketing and commercial values of produce [10].

Moisture content of maize is normally beyond 18% at harvest, and further reduction to 13% (ideal for storage) is achieved through drying [11]. Maize samples stored in hermetic and polypropylene bags for a period of one year from the three study locations recorded moisture content in the range of 10.9–12.1% and 13.8–14.9%, respectively. The moisture contents of maize stored in polypropylene bags were above the GSA specification (≤13%), whereas those of hermetic storage were within the acceptable range.

All the maize grains sampled from the polypropylene and hermetic bags recorded low concentrations of organic and inorganic matter, stained, germinated and other grains (Figure 1). Maize grains sampled from the hermetic bags had lower defects in the grain quality attributes. The presence of other grains and organic and inorganic matter in a bag of maize informs the quality (purity) and level of adulteration. For this study both polypropylene and hermetic bags recorded low amounts of other grains (0.78 and 0.75%), inorganic matter (2.17 and 1.31%), organic matter (5.27 and 3.19%) and shriveled grains (3.52% and 1.45%), respectively. The differences were not significantly different ($p < 0.05$), implying equivalent levels of defects. However, the percentages of diseased grains in the polypropylene bags (1.54%) were significantly ($p < 0.05$) higher than those in the hermetic bags (0.04%). Similar observations of significant difference ($p < 0.05$) were recorded for polypropylene and hermetic bags for discolored maize grains (3.70% and 0.79%), broken/chipped maize (7.85% and 6.04%), insect-damaged grains (9.75% and 1.96%) and total defective grains (30.49% and 9.58%), respectively.

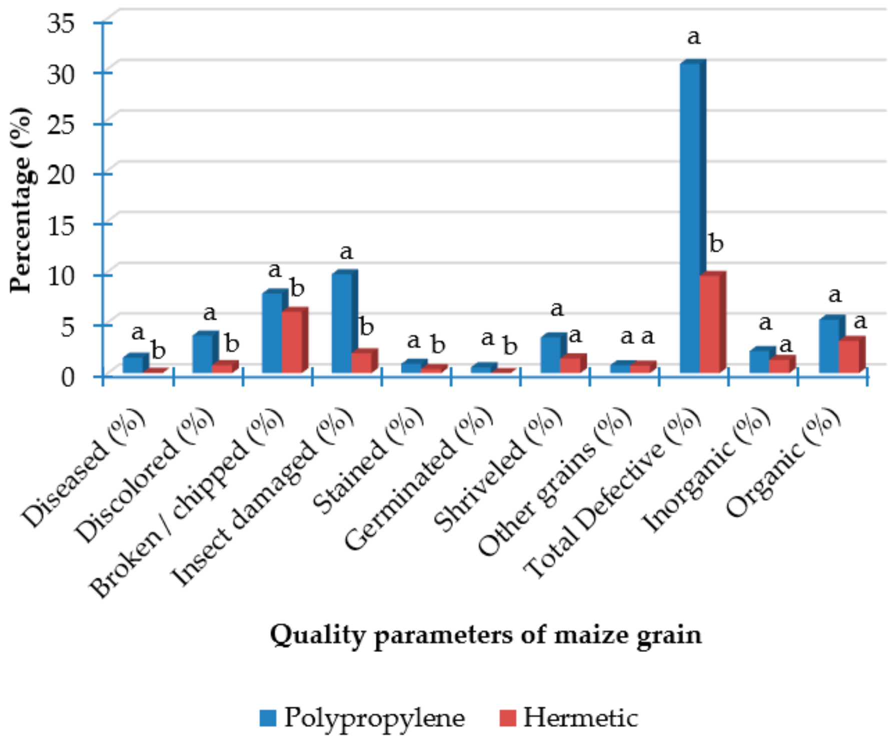

Figure 1. Percentage defects in grains stored in hermetic and PP bags. Means within the graph followed by the same letter are not significantly different at $p < 0.05$ (ANOVA: *t*-test).

3.2. *Aflatoxin Content of Maize Samples*

Levels of aflatoxin in maize samples stored in polypropylene and hermetic bags ranged between 0.9 and 20 ppb, as shown in Figure 2. Results from the aflatoxin analysis revealed that maize sampled from polypropylene bags had relatively higher aflatoxin levels (13.9–20 ppb) than those from hermetic bags (0.90–2.60 ppb). These values were significantly different ($p < 0.05$). Similar observations were made for aflatoxin levels in grains sampled at Ejura, PP bag (18 ppb), hermetic bag (2.6 ppb), and Asante Akyem Agogo, PP bag (13.9 ppb), hermetic bag (1.6 ppb), respectively.

All maize samples stored in the traditional (polypropylene) bags had aflatoxin concentrations above the recommended limit (15 ppb) for human consumption as reported by Omari et al. [12] whereas those of hermetic storage bags were below the limit.

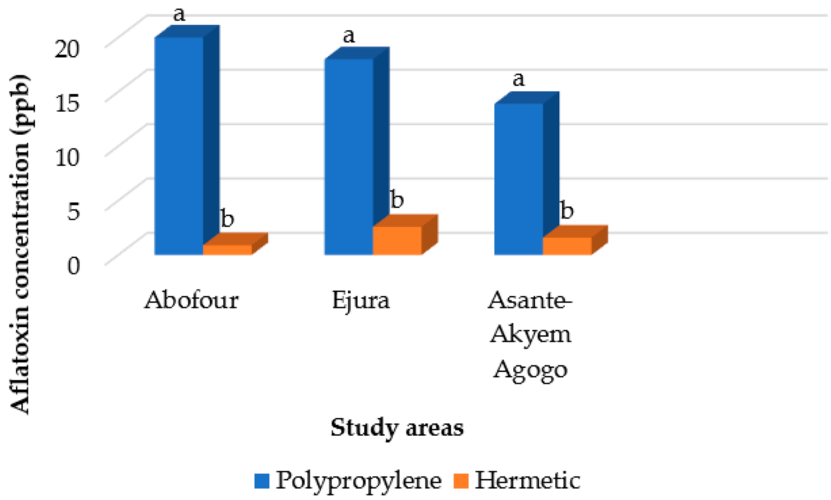

Figure 2. Aflatoxin concentration of maize stored in hermetic and polypropylene storage bags. Means within the graph followed by a different letter are significantly different at $p < 0.05$ (ANOVA: *t*-test).

3.3. Pesticide Residue Concentration in Maize Samples

Detected concentrations of the various pesticide residues in each maize sample from the three research areas (Abofour, Ejura and Asante-Akyem Agogo) are presented in Figures 3 and 4. Thirty-five pesticide residues were analyzed for two storage bags from each of the study areas. A total of 33 residues representing about 94.29% of the residues that were screened were found absent. These included bifenthrin, chlorpyrifos, dimethoate, permethrin, fenvalerate, profenofos, delta-HCH, fenpropathrin, p,p′-DDT, cyfluthrin, fonofos, ethoprophos, malathion, methoxychlor, chlorfenvinphos, heptachlor, lindane, p,p′-DDD, fenitrothion, dieldrin, endosulfan sulfate, alpha-endosulfan, p,p′-DDE, endrin, aldrin, beta-endosulfan, beta-HCH, diazinon, methamidophos, pirimiphos-methyl, gamma chlordane and parathion. The absence of organochlorine pesticide residues in the maize samples could be attributed to farmers' adherence to the ban on the application of organochlorine pesticides [13].

Lambda-cyhalothrin was detected in all maize samples stored in polypropylene and all were above the EU maximum residue limit of 0.02 mg/kg. Deltamethrin residues were detected in hermetic bags and were below the EU maximum residue limit of 2.0 mg/kg as reported by Milne [14].

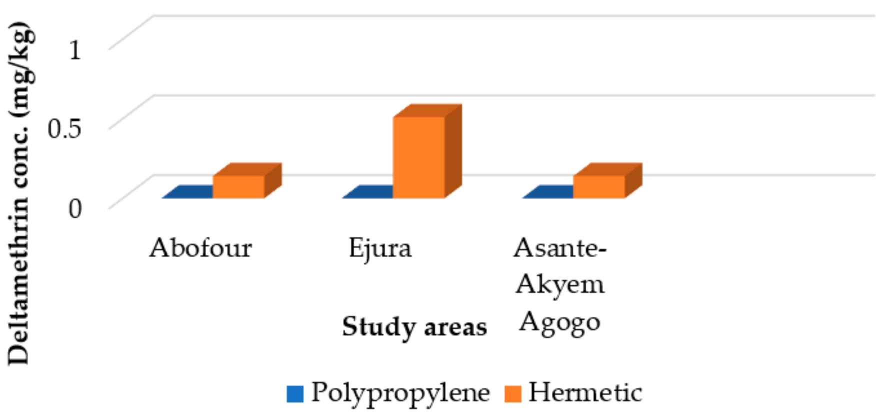

Figure 3. Deltamethrin residue in hermetic and polypropylene bags among study locations.

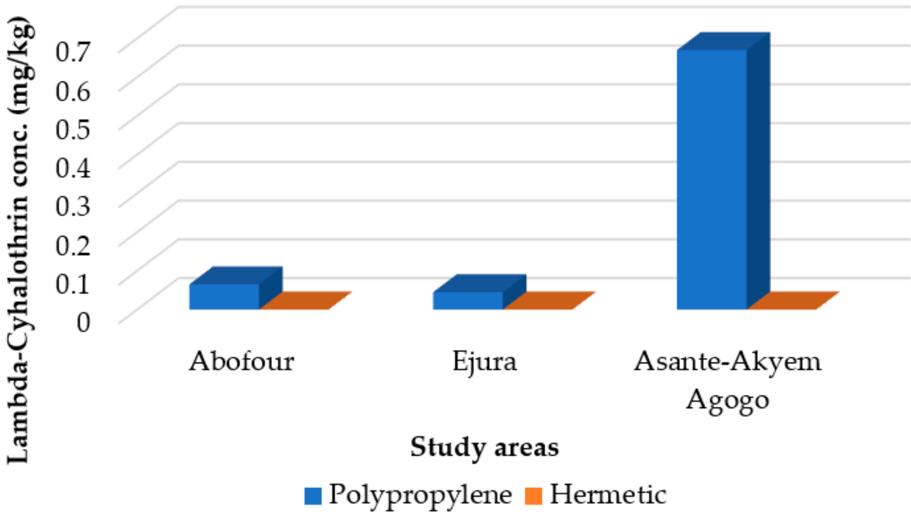

Figure 4. Lambda-cyhalothrin residue in hermetic and polypropylene bags among study locations.

4. Discussion

4.1. Grain Quality of Maize Samples

Generally, the recorded moisture content of the samples suggests adequate drying of the grains before storage by the warehouse operators; however, the relatively higher moisture content of maize samples stored in the polypropylene bags could be due to the gaseous exchange between the maize samples and the immediate environment in the storage area. Polypropylene bags have been reported to be porous in nature and therefore allows for moisture absorption or loss unlike hermetic bags that have a restrictive gaseous interchange barrier [9]. Moisture content beyond 13% encourages microbial growth and favors mycotoxin development, implying that maize grains stored in polypropylene bags will be susceptible to microbial and aflatoxin contamination compared to those stored in hermetic bags [8]. Gasparin et al. [10] and Bewley et al. [11] reported that control of maize grain moisture is the surest way of sustaining its viability, quality and safety throughout storage.

The variability in the organic and inorganic matter and stained and other grain qualities assessed could be attributed to decreased metabolic respiration/activity of mold in the hermetic bags compared to the polypropylene bags. Inorganic matter constitutes the presence of inanimate objects like stones, metals, plastics, cloth, etc. whereas organic matter takes into account wood, cobs, leaves, sticks, etc. in maize grains [15]. Both organic and inorganic matter are given keen attention by stakeholders in the maize value chain as they pose food safety threats to humans and animals aside from increasing the cleaning costs of processing industries. The decomposition of organic matter in maize adds to filth, stain and discolor of maize grains. The presence of diseased grains was significantly higher in the polypropylene bags than the hermetic bags. According to [16] this could be attributed to bacterial or fungal infections due to the presence of insect activities in the bag.

Discolored maize is grain that has an alteration in its regular (white or yellow) coloration to red, brown or a dark smear, which is usually influenced by excessive heat and/or excessive respiration [17]. The percentage of discolored grains in the polypropylene bags (3.70%) was significantly ($p < 0.05$) higher than that of the hermetic bags (0.79%). The observed discoloration could be attributed to respiration from insect and fungi activity within polypropylene bags and is an indication of a higher population of insects and fungi present in maize stored in the polypropylene bags compared to the grains in the hermetic bags. Fungi that occur in maize storage include members of the genera Aspergillus and Penicillium; their adaptation leads to the colonization of the embryo, which causes discoloration and rotting due to increased fatty acid content, oil rancidity and heating of the seed mass [18]. The grain quality analysis conducted on the stored maize samples revealed a significant ($p < 0.05$) concentration of broken/chipped maize in polypropylene bags (7.85%)

as compared to grains in hermetic bags (6.04%) in all the three study communities. The difference could be ascribed to the high moisture content of grains and poor post-harvest handling practices such as shelling, cleaning and winnowing. High moisture content has been found to significantly contribute to breakage of grains during shelling [19]. A similar study by Adu et al. [3] established that traditional shelling where maize cobs are packed in sacks and beaten with sticks usually results in an uncontrolled breakage of maize grains.

Mutungi et al. [7] reported that hefty sums of broken grain facilitate insects and microbial development and hence are undesirable in grain lots projected for longstanding storage. Maize grain processors lay emphasis on the amount of broken/chipped maize in their decision to accept or reject raw materials (maize) since it has the tendency to increase percentage grain losses in cleaning processes.

Maize samples stored in polypropylene bags recorded a higher amount of insect damaged grains (9.75%) in comparison to 1.96% recorded of sampled grains from the hermetic bags. Invasion of insects such as the maize weevil and the larger grain borer is responsible for such observation and was very profound in polypropylene bags due to its porous nature, permitting influx of oxygen for insect activity. These insects feed on maize endosperm leading to reduction in grain weight and end-product yield [8]. The lower insect damaged grains recorded in hermetic bags shows that it is better to store maize grains in hermetic bags than in polypropylene bags. The results further inform stakeholders along the maize value chain of the benefits of hermetic storage in the quest to reduce post-harvest losses in maize due to insect activity, which contributes to about 90% of post-harvest losses of maize globally according to [19].

Shriveled maize grains are underdeveloped, thin and papery in appearance, potentially resulting from a couple of factors such as soil and nutrient condition, moisture deficiency, drought and incidence of diseases [20,21]. Limiting growth factors that affect biomass and photosynthetic potential hinder the development of the reproductive organs of maize and consequently affect grain sizes. Results from the comparative analysis revealed that the percentages of shriveled grains in the polypropylene bags (3.52%) were not significantly different ($p > 0.05$) from those of the hermetic bags (1.45%), informing that the parameter is independent of the method of storage.

Maize grain quality assessment between the two methods of storage revealed a significant difference between the overall or total defective grains found in the polypropylene (30.49%) and hermetic bags (9.58%). The lower percentage of total defective grains in hermetic bags makes it a better option over polypropylene bags for maize storage.

4.2. Aflatoxin Content of Maize Samples

Aflatoxin contamination in maize usually occurs in two different phases: pre-harvest and post-harvest contamination. High humidity, insufficient grain drying, high temperatures and poor storage surroundings are typical causes of aflatoxin development [9]. Efficient post-harvest management of maize is an important factor in mitigating post-harvest storage-related losses. Aflatoxin in maize significantly affects the market value of maize and threatens consumer health and food security. A study by Bakoye et al. [22] revealed that aflatoxin contamination is not directly correlated to moisture content but emphasized moldy grains, foreign materials, and the prevalence of insects as a function of aflatoxin contamination in grains.

Mutambuki et al. [23] explained that hermetically sealed containers operate on a phenomenon of restricting O_2 availability to microbes and insects already in cereal grains upon storage. The elimination of oxygen is primarily achieved through the exchange of gases between cereals, insects and microbes inside airtight containers; respiration within the airtight container leads to a reduction in oxygen volumes with an increase in carbon dioxide volumes, causing suffocation and subsequent death of insects and microbes. Gaseous exchange within polypropylene sacks is unrestricted, as the porosity of the bags allows free movement of oxygen and carbon dioxide in and out of the bag, ensuring balance in respiration among maize grains, insects and microbes [24]. The accessibility of oxygen by microbes (fungi) supports their growth and consequently increases aflatoxin levels in the maize samples stored in the polypropylene sacks. The results obtained from the present study show that hermetic storage bags have competitive advantages over polypropylene bags in terms of aflatoxin prevention.

4.3. Pesticide Residue Concentration in Maize Samples

The detection of lambda-cyhalothrin and deltamethrin, all belonging to the synthetic pyrethroid class of pesticides, in sampled maize grains could be as a result of the substitution of organochlorines with a more biodegradable option of synthetic pyrethroids. Results from this study corroborate a study by Bempah et al. [25] that detected pyrethroid residues in fruits and vegetables, which emphasizes a signal of a paradigm shift in the usage of pesticides in Ghana from organochlorine to less toxic, biodegradable pyrethroid pesticides. Dziembowska et al. [26] reported that pyrethroids have a high efficacy of about 2250 counts and are particularly lethal to insects compared to advanced animals. The detection of lambda-cyhalothrin above its stipulated maximum residue limit of 0.02 mg/kg suggests the possibility of misapplication and abuse of the insecticide. The detection could also originate from environmental contamination as a result of previous agricultural activities (such as chemical spraying against weeds and insects) in the growing communities. Pyrethroids usually exhibit low toxicity with respect to humans, characterized by a speedy breakdown in adults, as they do not bio-accumulate in adult tissues and are expelled out of the body through urine [26]. Since pyrethroid insecticide residues have shown some form of toxicity to humans, bioaccumulation along the food chain may subject an exposed population to harmful long-term health hazards.

5. Conclusions

The study discovered that maize grains stored in hermetic bags recorded lower aflatoxin and pesticide residue concentrations and higher grain quality than those stored in polypropylene bags with respect to diseased, discolored, broken/chipped, insect-damaged, stained, germinated, shriveled, other grains, total defective, inorganic and organic matter. Only lambda-cyhalothrin and deltamethrin were detected in maize stored in polypropylene and hermetic bags, respectively. Lambda-cyhalothrin showed residue levels higher than its maximum residue limit (MRL) of 0.02 mg/kg and this poses safety issues for consumers, whilst maize samples stored in hermetic bags had deltamethrin residues below the MRL of 2.00 mg/kg. The findings point to the many benefits of the use of hermetic bags over polypropylene bags in maize grain storage and the urgent need to establish reliable monitoring programs for pesticides so that any exceedance in concentration over quality standards can be detected with appropriate actions taken.

Further research could focus on evaluating pesticide residue concentrations of maize from production through to the point of entry into the market to establish at what point(s) along the maize supply chain pesticides are being introduced.

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