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Assessment of deposition and residues of unstabilized pyrethrins in maize grains

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Abstract
Chemical insecticides are mixed with maize grains to offer protection against insect pest infestation during storage period. The insecticides are deposited onto the surface of the maize grains preventing possible insect pests from crawling and burrowing the maize grains and therefore causing damage. Chemical insecticide residues have raised environmental and food safety concerns on the possible adverse effects they may induce. Research studies have been done on alternative insect control methods including ethnobotanicals. Pyrethrum plant powder containing *pyrethrins* used since antiquity for formulation of household insecticides was assessed. *Pyrethrins* are unstable on light exposure and increased temperatures and suitable mostly for indoor applications. In the current study, *pyrethrins* in incremental ratios were assessed for initial deposition onto maize grains and residue levels over a six-month period at 28 ± 2 ºC and 65 ± 5% RH storage conditions. The *pyrethrins* in the powder were standardized at 1%$^{w}/_{w}$. Monitoring of residue levels provided an indication of unstabilized *pyrethrins'* ability to protect maize grains against insect pest infestation. Initial deposition was determined on treatment day (24hrs). Residue levels were determined at 90th and 180th day after application. Initial *pyrethrins* deposition onto maize grains was quantified using HPLC and compared with *pyrethrins* quantity before application using chi square (χ^2). Results showed that initial deposited *pyrethrins* onto the maize grains showed no significant difference with the quantity of *pyrethrins* before application. Residue levels at three and six month showed that *pyrethrins* degraded in large proportion over this period. Milled grains still showed residue levels although at lower quantities indicating further degradation on milling process. Based on this study it is recommended that unstabilized *pyrethrins* be utilized as grain storage protectant.

Keywords: *Pyrethrins,* Initial deposition, Degradation, Residues, Maximum Residue Levels

1. Introduction
The use of chemical insecticides in grain protection spans over many years. Chemical insecticides are mixed with maize grains to offer protection against insect pest infestation during storage period. The insecticides are deposited onto the surface of the maize grains preventing possible insect pests from crawling and burrowing the maize grains and therefore causing damage. Most pesticide residues detected in food grains arise from contact chemical insecticides or fumigants, deliberately applied to protect the grain from postharvest insect attack. Residual chemical grain protectants, chiefly organophosphate, pyrethroid and Carbamates insecticides have been used on a world-wide scale in management programs of insect pests in stored raw agricultural commodities (Arthur, 1996) [1].

These chemical insecticides may persist in the form of toxic residues in the treated maize grains and their consumption by man and animals, even in small quantities, presents a potential risk to consumer health (Halliday, 1989; Sgarbiero *et al.* 2003) [8, 12]. Concerns have also been raised over the use of chemicals and their effects on environmental balance since over-use and abuse of insecticides impose serious costs on a nation's economy while eroding the ecological foundations and thriving agro-ecosystems (Gadzirayi *et al*. 2006) [5]. Guidelines on control of pesticides in foods are generally based on the maximum residue levels (MRL) or tolerance and safety intervals established on case by case. Studies on the effects of storage and some commercial processing techniques regarding residues in foods are part of the requirements for pesticide registration in many countries.

The effects of chemical insecticides poisoning in animals can result in both systemic and topical symptoms which may include constriction of the eye pupils, blurry vision, headache and severe irritation and reddening of the eyes (Lorenz, 2009) [10]. Alternative grain insect control methods including ethnobotanicals have previously been investigated. Research on use of extracted *pyrethrins* formulated and stabilized with antioxidant chemicals as stored grain protectants have been found to offer sufficient protection against stored grain insect pests (Greening 1983; Warui *et al.* 1985; Kimani and Sum 1999; Mulungu *et al.* 2010) [6, 14, 9, 11].

Exposure of *pyrethrins* to light and high temperatures accelerate their degradation (Todd *et al.* 2003; Gunasekara 2004; Atkinson *et al.* 2004) [13, 7, 2]. This is desirable property of *pyrethrins* from human health risk and environmental effects stand point as it reduces possible dietary intake in foodstuffs and minimal environmental pollution. Chesang *et al*. (2015) [4], previously, investigated unstabilized *pyrethrins* formulation on maize grain protection against maize weevil and found to offer appreciable protection.

The aim of the current study was to assess the initial *pyrethrins* deposition and residue levels of unstabilized *pyrethrins* in pyrethrum powder in maize grains over a six month period as an alternative to the longer persisting insecticides used in grain protection.

2. Materials And Methods

2.1 Maize Grains

Clean and dry maize grains were obtained from a farmer in Njoro, Nakuru County, Kenya.

2.2 Pyrethrum Powder

Finely ground pyrethrum powder with 1%$^{w}/_{w}$ *pyrethrins* was obtained from Pyrethrum Board of Kenya (PBK) in Nakuru, Kenya and sieved using 106µm sieve.

2.3 Experimental Set up

The experiment was carried out at the Entomology Laboratory of Pyrethrum Board of Kenya in Nakuru, Kenya. Five different weights of pyrethrum powder (50mg; 100mg; 150mg; 200mg and 250mg weights of 1%$^{w}/_{w}$ *pyrethrins*) were weighed. Maize grains were weighed in portions of 100g and placed into clean glass jars. The weighed pyrethrum powder were poured into each glass jar and mixed thoroughly by shaking. There were 4 replicates in each of the 5 treatments denoted as T_1, T_2, T_3, T_4 and T_5. Experimental design was set in a completely randomized design. The laboratory temperature and RH were maintained at 28±2 ºC and 65±5% throughout the storage period.

Immediately after mixing and setting the experiment, 25g of treated maize grains in the glass jars was drawn from each replicate of a treatment level (25g x 4 replicates) and combined to obtain 100g. This was homogenized before a sample of 25g was drawn and extracted for initial *pyrethrins* deposition analysis. This procedure was repeated at 90th and 180th day for analysis of *pyrethrins* residues. The quantity of *pyrethrins* residues were analyzed using HPLC (Varian 5000) instrument. The quantified residues of initial pyrethrins deposited were compared with the *pyrethrins* before application onto the maize grains using chi square (χ^2).

3. Results

In all the treatment levels, it was observed that the initial *pyrethrins* deposition were lower than the levels of *pyrethrins* before application with percentage deposition levels of 84.8; 86.1; 85.27; 88.9 and 87.84% for T_1; T_2; T_3; T_4 and T_5 respectively as indicated on table 1 below.

Table 1: Initial deposition levels of *pyrethrins*

Treatment Level	*Pyrethrins* before application (mg/kg)	Initial *Pyrethrins* Deposited in Grain (mg/kg)	% Deposition
T_1	5.00	4.24	84.80
T_2	10.00	8.61	86.10
T_3	15.00	12.79	85.27
T_4	20.00	17.78	88.90
T_5	25.00	21.96	87.84

The initial deposition of *pyrethrins* data was subjected to Chi-Square (χ^2) analysis to establish if there was any significant difference between the *pyrethrins* before application and the initial deposited *pyrethrins* onto the maize grains as quantified.

The results indicated that the Chi-Square calculated from the initial pyrethrins deposition data ($\chi^2 = 1.251$) was less than the Chi-square table value ($\chi^2 = 9.488$) (df = 4; $\alpha = 0.05$) implying that the *pyrethrins* content initially deposited onto the maize grains was not significantly different from the *pyrethrins* content before the application. Over the 90-day and 180-day storage period, the proportion of degradation of *pyrethrins* from the initial deposition in the maize grains revealed that *pyrethrins* degrade in varying proportions (Table 2)

Table 2: Residue of *pyrethrins* in maize grains during storage period

Treatments	Time after Treatment (Days)				
	(24hrs) Grain (mg/kg)	90 Grain (mg/kg)		180 Grain (mg/kg)	
T_1	4.24*	3.07	(27.59)	0.82	(80.66)
T_2	8.61*	5.88	(31.71)	0.96	(88.85)
T_3	12.79*	6.83	(46.60)	1.20	(90.62)
T_4	17.78*	7.98	(55.12)	2.41	(86.45)
T_5	21.96*	9.08	(58.65)	3.97	(81.92)

*Initial deposition; Figures in parentheses indicate % reduction based on initial deposition

4. Discussion

The results from the study demonstrated that in all the admixture treatments, the initial *pyrethrins* deposited and determined within one day after application was lower than *pyrethrins* content values before application. Subjecting the initial *pyrethrins* deposition data to chi-square analysis indicated that this drop in *pyrethrins* content was not significantly different from the *pyrethrins* before application. This corroborates Caboni *et al*. (2007) [3] findings when they studied the degradation of *pyrethrins* residues on stored durum wheat after post-harvest treatment and found that in all trials, the initial deposition of *pyrethrins* levels, were below the maximum residue level of 3mg/kg. This reduced quantity of *pyrethrins* could be attributed to possibility of uneven distribution of the *pyrethrins* on the maize grains. Other contributory factors leading to lower deposition is the possible translocation of the powder during the storage period to the bottom of the test jars and incomplete extraction of the insecticide.

There was further reduction in *pyrethrins* residues in all the treatment levels in maize grain with increase in storage

period. This supports a study by Atkinson *et al*. (2004) [2] who found out that *pyrethrins* degraded during storage period by identifying the possible causes as generation of heat, presence of moisture, oxygen and microbial activity. The study also showed that treatment levels with more pyrethrum powder, showed larger degradation of *pyrethrins* within the first 90 day period.

5. Conclusion

The study also showed that actual initial deposition of *pyrethrins* was lower than the *pyrethrins* content before the application but not significantly different. Increased storage period leads to further degradation of unstabilized *pyrethrins* as evident from the data of residue levels at 90th day and 180th day. Detection of unstabilized *pyrethrins* residues at 180th day indicated that maize grain protection would be possible using unstabilized pyrethrins even within a six month period.

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