Degradation of Lambda-Cyhalothrin in Spinach (*Spinacia Oleracea*) & Collard Green (*Brassica Oleracea*) Under Tropical Conditions

Leonia N. Henry[1], Jonas N. Ngowo[2]

Department of Science and Laboratory Technology, Dar es Salaam Institute of Technology (DIT), Dar es Salaam

Abstract: ***Degradation of Lambda-Cyhalothrin was studied in spinach (Spinacia oleracea) and collard green (Brassica oleracea) under tropical conditions. The two vegetables were grown at a selected area and known doses of Lambda Cyhalothrin were applied. Leaf samples were collected for fourteen days and the remaining concentration of the pesticide determined in the samples. Sample extraction followed standard procedures and analysis was done using Gas Chromatography tandem to Mass Spectroscopy (GC-MS). Faster degradation was noted in spinach with the mean degradation rate of 0.43mg/kg in 48hrs (two days) while in collard green the degradation rate of 0.38mg/kg in 48hrs (two days). The concentrations at 7th day, the day recommended by the manufacturer for observation before the consumption of vegetables, were found to be 0.1 and 0.5 mg/kg for spinach and collard green, respectively. Apparently, the concentration in collard green on the seventh day (0.5 mg/kg) was greater than the maximum residue limit (MRL) of lambda-Cyhalothrin in cabbage as set by WHO and FAO (0.3mg/kg). This concludes that degradation of pesticides can be influenced by the variation in environmental conditions. It is therefore recommended that degradation of pesticides should be studied in different environmental conditions to ascertain their valid observation time before consumption of the product.***

Keywords: Lambda-Cyhalothrin, Maximum Residue Limit (MRL), collard green, spinach, degradation, tropical conditions

1. Introduction

The prudent use of pesticides in agriculture is considered to be indispensable for the control of insect-borne diseases in order to enhance food supply for an increasing world population. Pesticide application in horticultural crops is found to be effective and reliable means for the protection of plants from pests, and has contributed significantly to enhance agricultural productivity and crop yield (Oerke & Dehne, 2004 & Ngowi, *et al* 2007). Much concern has been raised based on human exposure risk and environmental conditions due to the residues of pesticides that may persist many weeks or months after application (McConnell *et al*., 1998; Sparling *et al*., 2001).

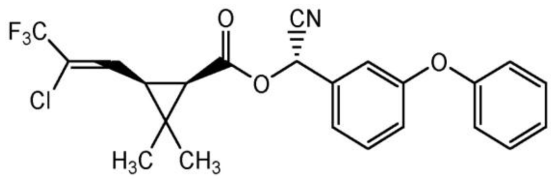

Figure 1: Lambda Cyhalothrin

Lambda-cyhalothrin is a synthetic pyrethroid insecticide containing a 1:1 mixture of two stereoisomers, (S)-α-cyano-3phenoxybenzyl-(Z)-(1R,3R)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2 dimethyl cyclopropane carboxylate and (R)-α-cyano-3-phenoxybenzyl-(Z) -(1S,3S)] (Fig.1). Lambda-cyhalothrin residues dissolved in water decrease rapidly if suspended solids and/or aquatic organisms are present because λ-cyhalothrin molecules are strongly adsorbed by particulates, thus posing a low risk to ground water contamination (Lu, 2010). Adsorbed λ-cyhalothrin molecules show decreased degradation rates because they are less accessible to breakdown than free molecules in the water column (He *et al*, 2008). On the other hand, λ-cyhalothrin adsorbed to suspended solids or bottom sediments may provide a mechanism to mitigate its acute toxicity to aquatic organisms by reducing their short-term bioavailability in the water column (He *et al*, 2008). Experience shows that, during the dry season there were higher levels of λ-cyhalothrin in vegetables than during the wet season that could be associated with wash off effect of the pesticides by rainwater immediately after application (Njagi, 2006). Lambda-cyhalothrin is highly stable to light and at temperature below 220°C (Hart, 1984). It is also stable in water at pH 7 and pH 9 and has a half-life of seven days; and there is racemization at the alpha-cyano carbon to yield a 1:1 mixture of enantiomer pairs (Hart, 1984). At pH 9, the ether bond is fairly readily hydrolysed (Collis and Leaheys, 1984). The field half-life of Lambda-cyhalothrin is close to 30 days in most soils (Wauchope, *et al*, 1992). In field studies of Karate, leaching of λ-cyhalothrin and its degradation in the soil was minimal (Royal Society of Chemistry, 1991& US EPA, 1988). Breakdown products formed in the soil environment were mainly via the hydrolysis of the central ester bond and oxidation (Royal Society of Chemistry, 1991). Cyclopropane acid is reported to be the major product of hydrolysis (2% at pH 7 and 73% at pH 9). Insecticidal products containing pyrethroids have been widely used to control insect pests in agriculture, public health, and homes and gardens (Amweg and Weston 2005; Oros and Werner 2005). A number of pyrethroids containing pesticides are commonly used in many parts of Tanzania (Ngowi, *et al* 2007). One of the commonly used pesticide in the northern Tanzania, is NINJA 5EC (5% λ-cyhalothrin) imported from China used in vegetables as an insecticide. According to the pesticides manufacturer's instructions the vegetables can be consumed seven days after application. However, with the number of variations in the environment that may affect the rate of degradation the observation time may vary from place to place owing to variation in environmental conditions. Apparently the degradation rate of the pesticide in spinach under tropical conditions is not well established. Therefore the study aimed to assess the degradation rate of λ-cyhalothrin in spinach and collard green under tropical conditions and hence advise on the observation time for consumption after application.

2. Materials and Methods

2.1 Experimental Design and Sampling

A portion of land at Sanyajuu village was selected where seedlings (spinach and collard green) were grown. Known dose of λ-Cyhalothrin was applied after which the leaf samples of the vegetables were collected in an interval of two days for 14 days consecutively. Systematic sampling was employed to obtain duplicates representative samples, giving a total number of 16 samples.

2.2 Sample Preparation and Extraction:

The vegetable samples were stored at low temperature at -20^{o}C centigrade immediately after collection. Samples were extracted by QuEChER's technique as follows; 50gm of leaves sample (spinach) was blended to make homogenized sample. 15gm of sample was extracted by followed by 6gm of MgSO4 and 1.5gm of Sodium acetate, then 5 min centrifuge at 4000 rpm (Anastassiades, *et al*, 2003). This was followed by addition of 300mg of MgSO4 and 150mg PSA (primary second aryl amine), and finally graphitized carbon black (GCB) with 30sec hand shaking and 5min centrifuge at 4000rpm (Anastassiades, *et al*, 2003).

2.3 Sample Analysis

Analysis of lambda-Cyhalothrin in the sample was done by Gas Chromatography- Mass Spectrometry (GC-MS). The λ-Cyhalothrin peak at Retention time (RT) = 40.00 minutes in GC and fragments of m/z at 449 and 181 in MS representing the molecular ion peak and the base peak of λ-Cyhalothrin, respectively were the typical features used to confirm the presence of the pesticide in the samples. Quantitative analysis employed the values of the peak areas in the GC as compared to those of the standards. A Gas Chromatography-Mass Spectrometry, GC-MS-2010 Shimadzu operating in EI mode (MS) at 70ev, and FID detector for GC with a Restek-5MS column (30m x 0.25mm x 0.25µm) was used. The oven temperature program in GC was 40^{o}C, held for 2 minutes then raised at 6^{o}C per minute to 280^{o}C and held for 4 minutes. The injection temperature was 250^{o}C with split less injection mode. Helium was used as a carrier gas at a flow rate of 1.21ml min^{-1}. The ion source temperature and interface temperature in MS were 230^{o}C and 300^{o}C, respectively. Sample blanks and recoveries were done following the same procedures and all results were corrected to recoveries. Mean concentrations were determined graphically by excel graphs.

3. Results and Discussion

3.1 Determination of λ-Cyhalothrin in the samples

The peak at RT=40minutes in the GC compared well with that of λ-Cyhalothrin in the parallel standard. Furthermore, fragmentation of the same peak in the electron impact Mass Spectroscopy gave the m/z ratios of 449 and 181 as the molecular ion peak and base peak, respectively (Fig 2), the typical features for λ-Cyhalothrin mass fragmentation. The main reaction been hydrolysis of the esteric part of the molecule with the formation of the Cyclopropanoic acid (m/z = 209), subsequently followed by the loss of two methyl groups (m/z=30) resulting to the base peak (m/z=181). The percent recoveries of λ-Cyhalothrin in collard green and spinach were 84% and 85%, respectively. All the concentrations were corrected to the recoveries.

3.2 Lambda-Cyhalothrin residues in spinach

The initial mean concentration of λ-Cyhalothrin in spinach samples collected on the application day (0 hrs after application) was 5.2 mg/kg that decreased to 2.5891, 1.448, 0.536, 0.1004, 0.0728, 0.038 and 0.0242 mg/kg after 3, 5, 7, 9, 11, 13 and 15 days, respectively after application(Fig 4).

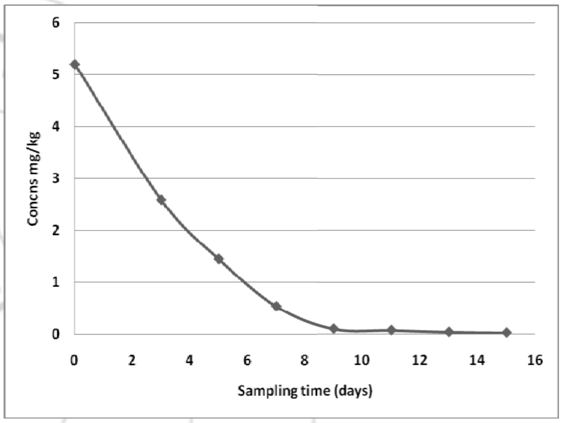

Figure 2: Variation of mean concentrations of λ-Cyhalothrin in Spinach for 15 days

Degradation of λ-Cyhalothrin in spinach was approximated from the figure 3 above from which the $t_{1/2}$ (2.6mg/kg) was observed after 72hrs (3 days after application). At the 7th day that was set by manufacturer as the observation time before the treated vegetables can be consumed, the concentration was about 0.5mg/kg (Fig. 2). Apparently, this is beyond the MRL set by WHO/FAO for λ-Cyhalothrin residues in vegetables (0.3mg/kg).

3.3 Lambda cyhalothrin Residues in the Collard Green:

The initial mean concentration of λ-Cyhalothrin in collard green samples on the application day (0 hrs after application) was 5.0 mg/kg that decreased to 2.33, 1.53, 0.727, 0.495, 0.299, 0.124 and 0.072 mg/kg after 4, 6, 8, 10, 12, 14 and 16 days, respectively (Fig 3).

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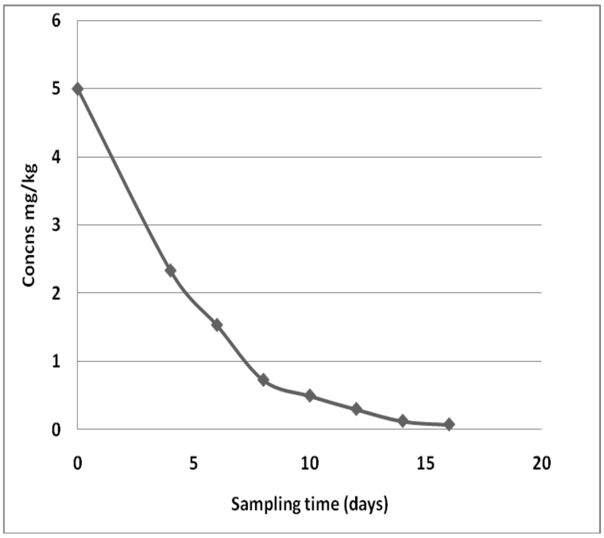

Figure 3: Variation of mean concentrations of λ-Cyhalothrin in collard green for 15 days.

Estimation of the degradation rate of λ-Cyhalothrin in collard green gave a half life of the pesticide of four days (96hrs) that is $t_{1/2}$ (2.5 mg/kg)=96hrs. The mean residual level after the seven days in edible portion of collard green was 1.2 mg/kg that is far beyond the MRL set by WHO/FAO (0.3mg/kg) of cyhalothrin residues in vegetables. The WHO and FAO indicate the maximum residue limits for cabbage and collard green species not to exceed 0.3mg/kg. Results obtained in this study showed different degradation rates of λ-Cyhalothrin between spinach and collard green both under the same climatic conditions. This concludes that different vegetables may have different characteristics that alter the rates of degradation of different pesticides.

4. Conclusion and Recommendations

4.1 Conclusion

Under the same tropical conditions λ-Cyhalothrin demonstrated faster initial degradation rates in spinach ($t_{1/2}$=72 hrs) compared to collard green ($t_{1/2}$=96hrs). The formulated pesticide NINJA 5% EC is recommended for vegetables with the observation time of seven (7) days after application and MRL of 0.3mg/kg in cabbage. The seven days were found unrealistic for this study where the residues on spinach and collard green were 1.2 and 0.5 mg/kg, respectively. Both were above the recommended maximum residue limit (MRL) for that pesticide. This suggests further that the geographical location, seasons, type of vegetable and specific pesticide has a significant influence in the degradation behavior of the pesticide in a plant.

4.2 Recommendations

Based on the findings of this study it is recommended that the observation days proposed by manufacturers for users to be taken as just a base line. However, more studies should be done to ascertain the valid observation time in specific edible products and specific climatic conditions. Further studies should focus on individual pesticides commonly used for edible products. Manufacturers should indicate the observation time and areas where it was tested to be valid. Apparently, the application dose may also differ in wet season compared to dry season where in the former more pesticide is expected to be lost into the soil by rain water (Njagi, 2006).

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