Endosulfan Pesticide Dissipation and Residue Levels in Khat and Onion in a Sub-humid Region of Ethiopia

Feleke K. Sishu[1(✉)], Elsabeth K. Thegaye[2], Petra Schmitter[3], Nigus G. Habtu[2], Seifu A. Tilahun[1], and Tammo S. Steenhuis[4]

[1] Faculty of Civil and Water Resources Engineering, Bahir Dar Institute of Technology, Bahir Dar University, Bahir Dar, Ethiopia
felek2004@gmail.com
[2] Faculty of Chemical and Food Engineering, Bahir Dar Institute of Technology, Bahir Dar University, Bahir Dar, Ethiopia
[3] International Water Management Institute, Yangon, Myanmar
[4] Departments of Biological and Environmental Engineering, Cornell University, 206 Riley Robb Hall, Ithaca, NY 14853, USA

Abstract. Endosulfan, a mixture of α- and β-isomers, is used by farmers in the wet and dry season for khat and onion production. Khat leaf samples were collected in farmer fields at intervals of 1 h; 1, 5, 9 and 14 d after application. The dissipation rate of α- and β-isomers and residue level in khat were compared with residue levels in onion. The extraction was done by using Quick Easy Cheap Effective Rugged and Safe (QuEChERS) method and analyzed by Gas Chromatography – Electron Capture Detector (GC-ECD). Greater residue α- and β-isomer endosulfan levels were found in khat compared to onion as khat leaves are sprayed repeatedly in two week. Residue levels of khat exceeded the tolerable EU limit of 0.05 $mg.kg^{-1}$ for leafy vegetables and herbs. For both raw and processed onion sample α- and β-endosulfan residues level were below the tolerable of limit EU regulation for bulb vegetables (i.e. 0. 1 $mg.kg^{-1}$). The mean half-life for the α-isomer of endosulfan was 3.4 d in the wet season and 3.6 d in the dry season whilst that for the β-isomer was 5.0 d and 5.4 d respectively. Both isomers dissipated fastest in the wet season under conditions of high humidity and precipitation. The β-isomer persisted longer and had a lower dissipation rate from plants surface compared to the α-isomer.

Keywords: Pesticide · Endosulfan · Dissipation · Residue · Khat · Onion · Ethiopia · East Africa · Sub-humid tropical

1 Introduction

Endosulfan α- and β is a widely used pesticide all over the world since 1960 [1]. It used to protect crops like cotton, soya bean, coffee tea and vegetables. But the residue in plant tissue and water causes both acute and chronic health risks for aquatic and terrestrials organisms including humans [2–4]. Hence, use of endosulfan in agriculture was banned

N. G. Habtu et al. (Eds.): ICAST 2019, LNICST 308, pp. 16–28, 2020.
https://doi.org/10.1007/978-3-030-43690-2_2

by the EU in 2007, UNEPA since 2012, and USEPA in 2016. Endosulfan is still used in countries like Ethiopia for irrigated vegetable production (i.e. onion, tomato, pepper) and khat [5, 6]. Khat (*Catha edulis Forsk, Celastraceae*) is a perennial cash crop where fresh leaves are harvested and consumed in the Horn of Africa and some Arabian countries as a mild narcotic stimulant [7–11].

The endosulfan belongs to the organochloride pesticide family and it is persistence in the environment. However, its persistence is influenced by environmental factors including temperature, humidity, precipitation and microbial activity [12–15]. Therefore, the half-life of residue levels in crops, soil and water vary with weather conditions. For instance, in cold sub-tropical and temperate regions, the half-life of endosulfan in soils was estimated between 39 and 42 d and took 238 d for 99% dissipation [16] and between 9.5 and 14 d in plant tissue [17]. However, half-life decreases in tropical hot humid climates to 3.3 to 21 d in soil [14, 18] and, between 3.3 and 3.6 d in plant tissue [18, 19]. Therefore, understanding the dissipation of pesticides under local weather conditions could help to determine appropriate consumption time after harvest to reduce potential human health risks associated with high dose intake.

Despite intensive applications of endosulfan on khat and vegetables in Ethiopia, data on dissipation and residue levels on plant surfaces under the sub-humid climatic condition are very limited. For that reason, we investigated the rate of dissipation for endosulfan pesticide used by farmers under repeated application on khat and compared residue levels in khat with onion. To address this we assessed: (1) the effect of seasonal variation on dissipation rate of pesticide (endosulfan α and β) from plant leaf; (2) the influence of repeated application of pesticide on residue levels, and (3) the residue level in khat compared to onion that only once treated by pesticide and consumed after processing such as peeling and cooking.

2 Materials and Methods

2.1 Description of Study Area

The study was conducted in Robit Bata watershed located in Northwest Ethiopian highlands, Lake Tana basin (3322523 N, 1291087 E) and an elevation of 1847 m (Fig. 1). Main rainfall season occurs from May to September. The average annual rainfall from 2014 to 2018 was 1420 mm a^{-1} at the Bahir Dar Zuriya weather station. According to [20], 82% of Robit Bata watershed is cultivated in the wet phase and 10% of the area is irrigated from wells in the dry season of which half is in khat (*Catha edulis Forsk, Celastraceae*), one fifth in hop and the remaining are vegetables.

The agricultural system is predominantly a mixed crop-livestock system with maize, millet and teff primarily cultivated during the rainy season [21]. Khat and vegetables, such as tomato, are irrigated through shallow groundwater pumping and surface water river diversion.

Pesticide Survey. Prior to field selection, a survey was conducted to determine the type of pesticides applied and their application rate. In total 5 farmers, 2 local pesticide sellers and 3 pesticides applicators were surveyed. Dimethoate, endosulfan with alpha and beta isomers, 2,4-D, chlorpyrifos and profenofos were used at different growth stages

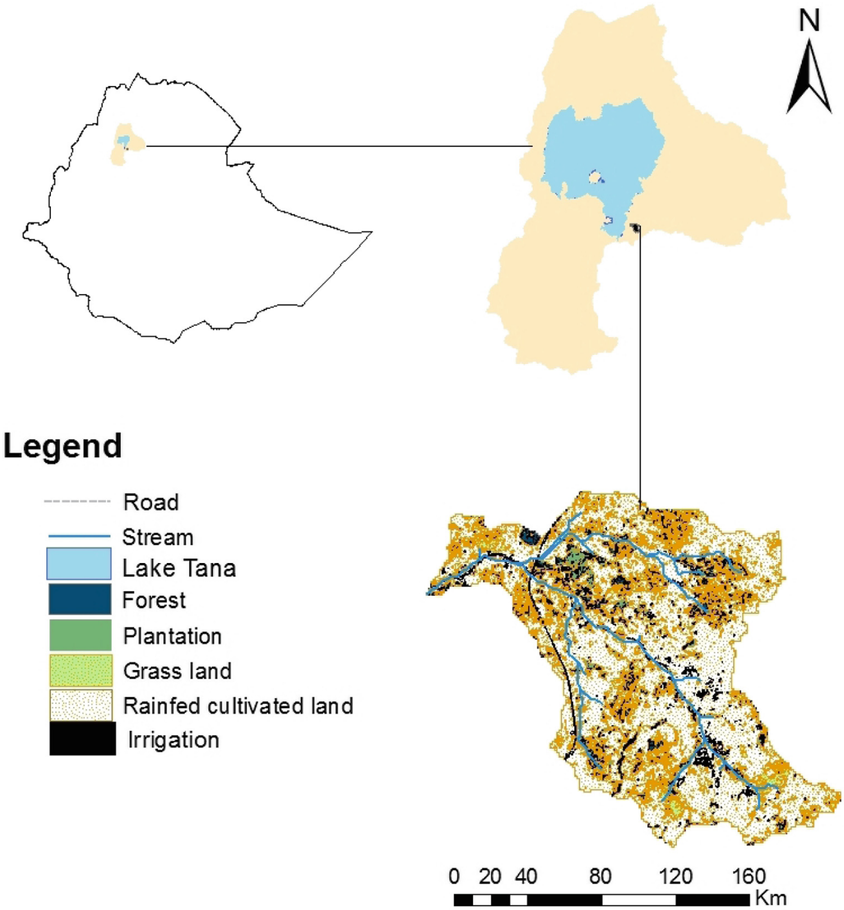

Fig. 1. Study area land use in Robit Bata watershed.

depending on the crop (Table 1). Due to its wide application in dry and wet seasons, endosulfan (containing a technical grade mixture of alpha 70% and 30% beta isomers) was selected for this study. Commercially, the formulation of endosulfan contains abundant the α-isomer and the less abundant but more volatile and less degradable metabolite than β [22, 23].

Experimental Design and Sample Collection. Three experimental plots 8 m × 10 m were selected within a 25 m × 35 m farmer-cultivated khat plot. The plant spacing of khat was 50 cm by 50 cm. The farmer used an endosulfan mixture as described in Table 1 and applied the pesticide using a backpack sprayer on a biweekly basis.

Experimental investigation of the degradation rate was carried out during two consecutive application cycles in the dry period (May–June) and wet season (July–August). In each cycle, a plant sample was taken before application (background sample) followed by samples at 1 h and 1, 5, 9 and 14 d after application. From each experimental plot

Table 1. Trend in pesticide applications and formulation by local farmers in study area for maize, khat, and onion

Crop types	Dose (ha^{-1} in 40 L H_2O)	Frequency of pesticide application	Active ingredient formulation (mix)	Cropping season
Maize	256 ml	1 per cropping season	Profenofos	Wet season
Khat	1536 ml	2 to 3 times per month	Dimethoate (16 ml) + endosulfan(16 ml) + profenofos (16 ml)	Irrigated dry season
	1536 ml	2 to 3 times per month	Dimethoate (16 ml) + chlorpyrifos (32 ml) or endosulfan (32 ml)	Wet season
Onion	256 ml	1 per cropping season	Dimethoate (16 ml) + endosulfan (16 ml) + profenofos (16 ml)	Irrigated dry season

500 g of young leaves was collected at each sampling event. A total of 60 samples were taken to investigate the degradation rate.

During the dry season, six harvested onion samples were collected from two onion irrigated fields in the study area. The samples were put in polyethylene plastic bags, chilled and transported to the laboratory within 24 h for analysis. The endosulfan compound was analyzed in raw and boiled onion samples to evaluate the impact of processing such as cooking, peeling and washing before consumption in the reduction of pesticides.

The climate data, including daily temperature, rainfall amount between first day after application to up to date of sampling and humidity were collected (Table 2). A manual rainfall collector with a container of 2.5 L was installed to measure daily precipitation.

Sample Preparation and Pesticide Analysis. Pesticide (endosulfan) was extracted from khat leaves and onion peels using the AOAC Quick Easy Cheap Effective Rugged and Safe (QuEChERS) method [24]. The khat and onion samples were grounded to obtain homogenous mixture. Fifteen mL of acetonitrile containing 1% of acetic acid was added to 15 g of the homogenized sample and followed by shaking using vortex shaker for 30 s. After shaking, 1.5 g sodium acetate and 6 g of anhydride magnesium sulphate were added and centrifuged for 1 min at 4000 rpm for 5 min. Afterwards; 8 mL of the supernatant acetonitrile phase was transferred into 15 ml centrifuge tube. Given the high pigment concentration of khat, the sample was extracted using 125 mg mL^{-1} Primary and Secondary Amine (PSA) (Agilent Technologies group) and 125 mg mL^{-1} US

Table 2. Weather conditions during the field experimental period and pesticides application cycles in dry and wet seasons in 2018 in the Robit Bata watershed

Sampling season	Application cycles	Sampling date (2018)	Days after treatment	Weather conditions		
				Temp. (°C)	Humidity (%)	Cumulative rainfall (mm)
Dry	1	8 May	0	29	38	0
		8 May	1 h	32	30	0
		9 May	1 d	29	35	0
		12 May	5 d	26	54	0
		16 May	9 d	25	50	0
		21 May	14 d	29	47	0
	2	2 May	0	24	54	0
		22 May	1 h	31	39	0
		23 May	1 d	29	37	0
		26 May	5 d	21	49	0
		30 May	9 d	23	52	0
		4 Jun	14 d	23	66	0
Wet	1	25 Jul	0	22	85	0
		25 Jul	1 h	25	75	0
		26 Jul	1 d	18	74	31
		29 Jul	5 d	20	71	71
		2 Aug	9 d	16	92	84
		7 Aug	14 d	22	82	91
	2	10 Aug	0	18	74	0
		10 Aug	1 h	18	75	0
		11 Aug	1 d	24	72	3
		14 Aug	5 d	21	80	54
		18 Aug	9 d	23	76	112
		23 Aug	14 d	25	64	148

and Graphitized Carbon Black (GCB) (Waters, Ireland) and 150 mg $MgSO_4$. However, for raw and boiled onion samples, in the extraction and clean-up, the AOAC QuEChERS values described in [24] were taken.

The solution was centrifuged 5 min at 4000 rpm and 2 mL of the final extract containing the solvent and pesticide compound was taken and transferred to a GC vial. The 2 mL solution was evaporated to dryness under a stream of gentle flow of nitrogen in water bathe at 40 °C to make more concentrated and ready for GC injection. The dried extract was reconstituted in 200 μL of acetonitrile and the vials were kept at −18 °C until analysis.

GC-ECD GC-ECD Operating Conditions. A 2 μL sample was injected into the gas chromatograph-electron capture detector GC-μECD and analyzed according the stated GC parameters. The capillary column HP-5 length 30 m, 0.25 mm i.d., and 0.25 μm film was used. Detector temperature was 300 °C. The temperature program was: initial temperature 70 °C hold for 1 min, 10 min to bring the temperature to 160 °C then hold for 5 min, finally, by 24 °C min^{-1} to 280 °C hold for 9.5 min. The total analysis time was 30 min and the equilibration time 0.5 min. Nitrogen was used as a makeup and carrier gas at a constant flow of 50 ml min^{-1}.

Method of Validation and Quality Control. The linearity of the methods for targeted pesticides was evaluated by analyzing a reference standard and spiked samples. Endosulfan-α and-β, standards (Sigma Aldrich) were prepared in series 30, 60, 90, 120 and 150 μg L^{-1} and analyzed for six-points of calibration. The recovery and precision (repeatability) of the method was evaluated before the samples were analyzed. Five replication of blank samples for method blanks and (MB) and five spiked samples were analyzed for laboratory control sample (LCS). Control samples were prepared spiking 15 g of khat with a known amount of a standard mixture of 1 ml target pesticides at concentration of 90 μg L^{-1}. The GC with ECD chromatograms of standard sample peaks for α- and β- isomers are shown in (Fig. 2). The mean percent recovery for endosulfan-α was 84–88% and for endosulfan-β was 81–85%. The relative standard deviation for repeatability (RSD) endosulfan-α was 7 μg kg^{-1} Endosulfan-β was with 11 μg kg^{-1} which is less than 20% according to USEPA method 508 [25]. The limit of detection (LOD), a signal-to-noise of 3 [26] for endosulfan-α and β were 0.22 and 0.8 μg g^{-1}, respectively.

Determination of the Pesticide Half-Life in Plant Samples. Pesticides dissipation rate from plant surface, soil and sediment undergoes first order kinetics [5, 12, 17, 22, 27]. The dynamic was calculated using first order kinetics for both endosulfan α and β for each of cycles and seasons.

$$C(t) = C_o e^{-kt} \tag{1}$$

Where $C(t)$ is the concentration of pesticides on the khat leaf at time t, C_o is the concentration of pesticides at time $t = 0$, and k is the dissipation rate constant. Using natural log fit of concentration ratio versus t of Eq. 1, the k values were calculated from the slope of linear graph for each cycle. Finally, solving Eq. 1 for the field half-life ($t_{1/2}$) yields.

$$t_{1/2} = \frac{0.69}{k} \tag{2}$$

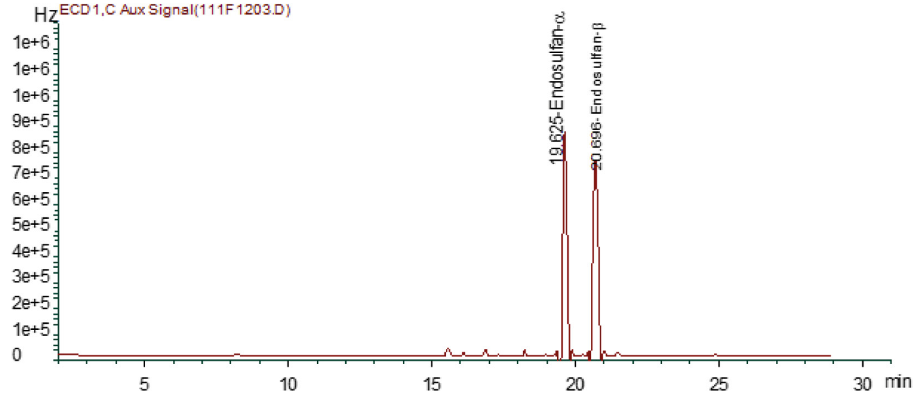

Fig. 2. GC-ECD chromatogram of pure reference sample.

3 Results and Discussion

3.1 Temporal Variability of Residue Level of Endosulfan α and β Isomers

The results of residue levels in khat, conducted for two spraying cycles in the dry and wet seasons are shown in (Table 3). One hour after spraying, the α-endosulfan was more abundant than β isomer endosulfan in all cycles of the experiment. In every cycle the residues of α-endosulfan were greater than 50 μg.kg^{-1} during one hour interval sampling whilst maximum levels for β-endosulfan were recorded at 41.8 μg kg^{-1}.

Slight differences in residues levels were observed in the dry and rain monsoon seasons for samples collected at the same sampling time after application between the two cycles. For instance, residue concentrations found in the dry season one hour after spraying in cycle one for β-isomer was 38.8 μg.kg^{-1} and increased to 41.8 μg.kg^{-1} in cycle two. Similar trend was observed for α-endosulfan dry period cycle one spray residue was 63.8 μg.kg^{-1} but in cycle two it increased to 65.1 μg.kg^{-1}. This was probably due to the residue left in first cycle on the biomass increase residue level in samples of the second cycle. A previous study found that photolysis did not significantly affect endosulfan degradation in duplicate experiments in the dark and direct sun light [28]. Temperature, which increases degradation rate, was slightly greater in the dry than in rain season (Table 2). Despite this endosulfan concentration was less in the wet season indicating that the greater humidity that increase moisture in the wet season had the greatest effect on increasing the degradation rate and precipitation wash off the pesticides from plant surface reduce the residues level.

Based on results in Table 3, the amount dissipated from plant surface was smaller in the dry season than in the wet season and faster for the α-isomer than the β-isomer (Fig. 2). For example in the first 24 h after spraying during a 80% of the sprayed α isomer dissipated from plant surface in the wet season while only 50% was degraded in the same time span during the dry season (see Fig. 3). Similarly, for the β-isomer 68% degraded within one day after spaying in the wet season whilst only 35% degraded within the first 24 h in the dry season. Pesticide dissipation was favored by an increase in humidity (wet season range 71–92%; dry season range: 30–54%) and the occurrence of

Table 3. Residue levels of α- and β-endosulfan isomers (μg.kg^{-1}) in khat leaf samples collected at 1 h to 14 d after spraying for two spraying cycles in wet and dry season.

Sampling season	Application cycle	Sampling date (2018)	Days after treatment	α-isomer	β-isomer	α + β-isomers
				Mean ± SD	Mean ± SD	
Dry	1	8 May	1 h	63.8 ± 1.5	38.8 ± 1.02	102.6
		9 May	1 d	32.4 ± 0.96	25.2 ± 0.71	57.7
		12 May	5 d	20.8 ± 0.56	11.2 ± 0.70	32.1
		16 May	9 d	9.3 ± 0.15	9.4 ± 0.42	18.7
		21 May	14 d	3.5 ± 0.53	5.4 ± 0.49	8.8
	2	22 May	1 h	65.1 ± 0.63	41.8 ± 0.84	106.9
		23 May	1 d	36.8 ± 0.60	28.5 ± 1.52	65.3
		26 May	5 d	24.5 ± 0.70	14.9 ± 0.97	39.5
		30 May	9 d	12.3 ± 0.80	10.4 ± 1.58	22.7
		4 Jun	14 d	3.6 ± 0.43	6.4 ± 0.74	10.0
Wet	1	25 Jul	1 h	50.3 ± 0.73	34.0 ± 1.30	84.3
		26 Jul	1 d	22.7 ± 0.52	14.1 ± 2.12	36.8
		29 Jul	5 d	12.6 ± 0.45	9.82 ± 0.72	22.5
		2 Aug	9 d	5.7 ± 0.45	5.26 ± 0.81	11.0
		7 Aug	14 d	2.5 ± 0.24	3.2 ± 1.36	5.7
	2	10 Aug	1 h	50.8 ± 0.40	34.1 ± 1.29	84.9
		11 Aug	1 d	14.3 ± 0.74	15.9 ± 1.72	30.2
		14 Aug	5 d	9.9 ± 0.56	7.7 ± 1.74	17.6
		18 Aug	9 d	5.2 ± 1.02	5.7 ± 0.75	10.96
		23 Aug	14 d	1.7 ± 0.79	4.5 ± 0.67	6.1

rainfall. Microbial degradation of pesticides could increase with an increasing humidity and temperature. The moisture creates a conducive environment for microbial activities [29, 30]. Studies have found that endosulfan degraded to its major metabolite due to microbial degradation of the two isomers [31, 32]. Furthermore, precipitation washes the pesticide from plant surface more easily as their affinity to the plant surface is lower compared to the soil [19, 33].

Total residue (α + β) after one day of application in the wet period was below the tolerable limit (50 μg.kg^{-1} or 0.05 mg.kg^{-1}) of the EU commission regulation for leaf vegetables and herbs [27]. However, in the dry period a longer timespan was needed for the residue levels to fall below the threshold.

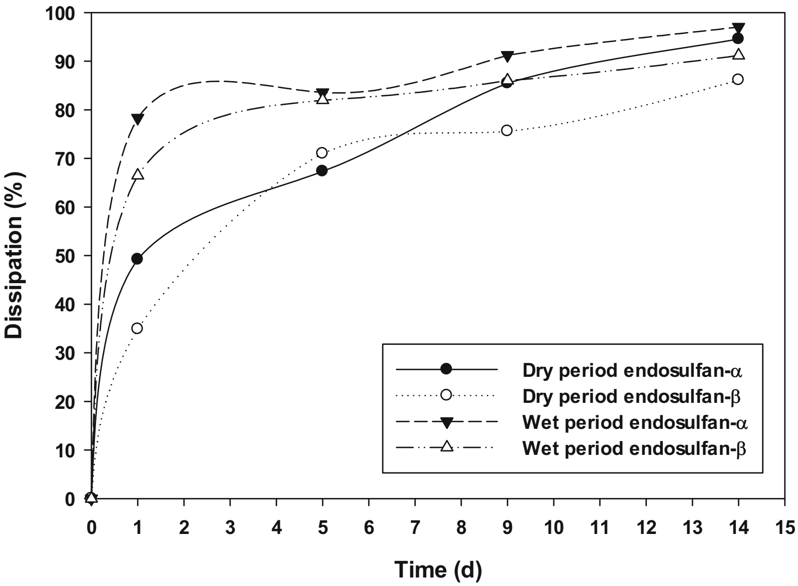

Fig. 3. α- and β-endosulfan isomer degradation during dry and wet seasons.

3.2 Kinetics and Half-Life of α- and β-Isomers

The dissipation rate and half-life of pesticide were related to season of application and the isomer type (see Table 4). For α isomer, the half-lives were shorter during the wet season with an average of 3.4 d compared to 3.6 in the dry period whilst for β- isomer the average value in the wet season was 5.0 compared to the 5.4 d in the dry season. This suggests that α-isomer is dissipated faster compared to the β- isomer in both the dry and wet season. These results correspond with others findings [16, 34]. The estimated half-life for α-isomer in Ethiopian sub-humid tropic in both the dry and wet season was similar to the 3.6 d half-life observed in Benin, West Africa tropical climate [19].

3.3 Comparison of Dry Period Residue Levels in Onion and Khat

The residue levels were higher in khat than raw and boiled onion (Fig. 4). This difference can be explained by the fact that for onion the pesticide is mixed with irrigation water and only applied once, hence dependent on pesticide uptake from the roots and the allocation within the onion bulb. For khat, on the other hand, pesticides are repeated applied in 14 d cycles directly on the leaf tissue. Farmers sprayed pesticides on khat at levels six times more than commercial recommendations for maize (Table 1). Pesticides are repeatedly applied on khat, a cash crop which is harvested frequently. To retain the shine on chewable fresh leaves, the farmers harvest khat within 3 d of the last spraying application. However, according to the findings in the study at least 3.3 d are required for the α-isomer to reach its half-life. But, a pre-harvest interval at least 2 week are suggested for persistence pesticides given a commercial dose of application [35]. On the other hand, onion was below the EU pesticide regulation for α- and β- endosulfan

Table 4. α- and β-endosulfan isomers dissipation kinetics on khat leaf surfaces and the half-life during different application cycles in dry and wet seasons

Sampling seasons	Cycles in season	α-isomer			β-isomer		
		Kinetics	Half-life (d)	R^2	Kinetics	Half-life (d)	R^2
Dry	1	$C(t) = 64e^{-0.193t}$	3.6	0.98	$C(t) = 39e^{-0.131t}$	5.2	0.93
	2	$C(t) = 65e^{-0.189t}$	3.7	0.97	$C(t) = 42e^{-0.128t}$	5.4	0.96
	Mean	$C(t) = 64e^{-0.190t}$	3.6	0.98	$C(t) = 40e^{-0.129t}$	5.4	0.95
Wet	1	$C(t) = 50e^{-0.214t}$	3.5	0.96	$C(t) = 34e^{-0.13t}$	4.6	0.91
	2	$C(t) = 51e^{-0.182t}$	3.3	0.91	$C(t) = 34e^{-0.127t}$	5.3	0.83
	Mean	$C(t) = 51e^{-0.202t}$	3.4	0.94	$C(t) = 34e^{-0.139t}$	5.0	0.87

residue in bulbs and vegetables at the time of harvest. The EU pesticides regulation for α- and β-endosulfan residue in bulbs and vegetables recommended a tolerance level of 100 $\mu g.kg^{-1}$ [27].

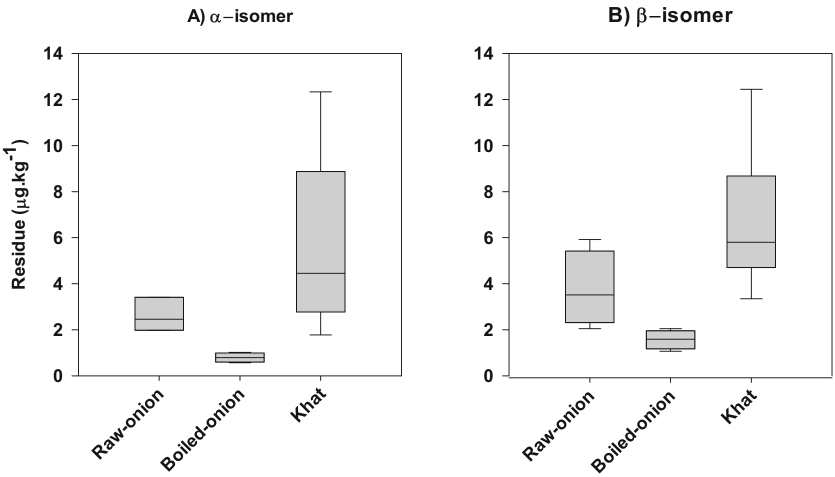

Fig. 4. Comparison of endosulfan α- and β-isomer residue in khat 14 d after application for raw and processed onion

The raw onion contained higher residue levels than boiled onion. Fruit and vegetable processing, such as peeling, boiling, and washing before consumption significantly reduces pesticides residue levels [36, 37]. Both raw and processed onion sample α- and β- endosulfan residues levels were below tolerable limit of EU guidelines for α- and β- endosulfan of bulbs and vegetables.

4 Conclusion

The dissipation rate of endosulfan isomer applied by farmers under sub-humid tropical conditions was investigated during dry and wet season. A shorter half-life was noted in the wet season compared to the dry because of increased humidity and precipitation, which likely increased hydrolysis, microbial degradation and pesticide loss during precipitation from plant surfaces. The α-isomer was less persistent compared to the β-isomer. Fourteen day after application, residue levels of β-isomer on khat were higher compared to the α-isomer in the wet and dry seasons. The residue level in khat 14 day after spraying was compared with onion grown locally under endosulfan application. We observed that the residue levels of the two isomers on khat were higher than the residue on onion. Whereas, the residue for onion was lower than EU endosulfan MRL in bulb fruits at harvest those of khat were well above. Therefore, with the current farmers' pesticide formulation and repetition of spraying, the residue levels in khat are a risk to the consumer. The risk for onion consumption both in raw and boiled form is less but not insignificant.

Acknowledgement. The study was made possible through the support of the Feed the Future Evaluation of the Relationship between Sustainably Intensified Production Systems and Farm Family Nutrition (SIPS-IN) project (AID-OAA-L-14-00006), a cooperative research project implemented through the United States Agency for International Development (USAID) in support of the Feed the Future (FtF) program. The study did not apply pesticides, but monitored the fate of pesticides from farmer application. The research was implemented under a collaborative partnership between the International Water Management Institute and Bahir Dar University. The contents of the paper are the responsibility of the authors and do not necessarily reflect the views of USAID or the United States government.

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