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Residue analysis and associated risk assessment of hexythiazox and spinosad applied on strawberry plants

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Abstract

This work aimed to study the residue dynamics of two pesticides applied on strawberry plants and to assess their associated risks. Hexythiazox and spinosad were applied separately on mature-stage strawberry plants. Fruit and leaf samples were collected at different times from 2 h to 15 days after application and analyzed using HPLC. The results showed that strawberry leaves contained higher initial amounts of the tested pesticides than fruit. The rates of loss of the initial deposits were higher in strawberry fruit than in leaves. The half-life (t½) values of hexythiazox and spinosad were 2.23 and 3.24 days in strawberry fruit and 2.05 and 2.86 days in leaves, respectively. Regarding MRLs and risks, washed and unwashed fruits of strawberry could be consumed safely at 6 days of hexythiazox or spinosad application and after 2 h when harvested strawberry fruits were processed as jam.

Keywords: Strawberry, Hexythiazox, Spinosad, Residue, Risk assessment

1. Introduction

Strawberry fruits are well known for their human health benefits, as they are playing a valuable role in our diet. Strawberries contain few calories, as 100 grams of fresh strawberries contain only 32 calories. They enrich food with vitamins and minerals and strengthen the human immune system. In addition, strawberries are rich in antioxidants, soluble fiber, and contain a high amount of flavonoids, which are used as anti-inflammatory (McDougall and Stewart 2012; Kumar et al., 2020).

Pesticides are used in agricultural production to protect crops and control pests. Harvesting crops after pesticide application, especially fruit and vegetables, might lead to high levels of pesticide residues in food commodities, which might have chronic effects on human health upon consumption. Hexythiazox is an acaricide that is widely used to control eggs and larvae of many phytophagous mites on fruit, citrus, vegetables, vines, and cotton. Meanwhile, spinosad is used to control many pests such as Lepidoptera in row and vegetable crops. It is also used for pest control (e.g., Agrotis ipsilon and Spodoptera spp.), in turf and ornamentals (e.g., Lepidoptera, Liriomyza spp., thrips, sawflies, chrysomelid beetles), tree nurseries and plantations, for the structural control of drywood termites (e.g., Cryptotermes brevis, Incisitermes snyderi), and for fire ant (Solenopsis spp.) control, as well as effective bait for fruit flies (Ceratitis spp., Bactrocera spp., Rhagoletis spp., Dacus spp., etc.) (MacBean 2012).

Analysis of pesticide residues in food is a key tool for monitoring the levels of human exposure to pesticides (Tchounwou et al., 2002; Vasyliva et al., 2017; El-Sheikh and Ashour 2022). Maximum residue limits (MRLs) and acceptable daily intakes (ADIs) are the references used for monitoring residues of pesticides in food matrices and environmental samples. The MRL is an index that indicating the highest concentration (mg kg-1) of pesticide accepted in food, while the ADI represents the amount of a pesticide in food (mg kg-1) that can

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be ingested daily over a lifetime without cognizable health risk (FAO 2002).

The aim of this study was to investigate the dissipation rates of hexythiazox and spinosad in strawberry and the effects of washing and processing on residues. This would provide basic information for developing regulations regarding the safe use of hexythiazox and spinosad in pest management strategies and environmental protection. Health risk assessment of the two tested pesticides on strawberry fruit was also performed.

2. Materials and Methods

Pesticides

The pesticides used in this study were commercial formulations of the acaricide hexythiazox (Maccomite 10% WP; Nippon Soda Company, Tokyo, Japan) and the insecticide spinosad (Tracer 24% SC; Dow Agrosciences Company, Indianapolis, USA) at rates of 20 g/100 L and 20 ml/100 L, respectively.

Field experiment and sampling

The research was conducted in the summer at a private strawberry field (Fragaria ananassa ver. festival) located at El-Slaheya Elgdeda, Sharkia Governorate, Egypt. The experiments were carried out in a randomized complete design. For each pesticide, three plots were established (50 m2 each) with a 2 m plot-to-plot distance. A motor sprayer (with a single-cylinder, 2-cycle engine, 2.6 KW/3.5 HP power, 108 dB pressure, and 20 L tank capacity) was used to apply the tested pesticides. Mature plants were sprayed with hexythiazox and spinosad once at the recommended rates of 20 ml/100 L for spinosad and 20 g/100 L for hexythiazox. The control plots were left unsprayed. Samples (fruit and leaves) were taken 2 h, 1, 3, 6, 9, 12, and 15 days later. In addition, fruit samples from the same periods were used to study the effect of washing with tap water (1 min washing) and air drying. Fruit samples were taken after 2 h for the jam preparation process. The reduction in pesticide residues or concentration during processing was evaluated by calculating the processing factor (PF) according to the equation PF = Cafter/Cbefore, where Cafter and Cbefore are the pesticide residue levels after and before processing, respectively (Chen et al. 2013). The PF values indicate a reduction when PF < 1, no change when PF = 1, or an increase when PF > 1 of the residues.

When residues were below the limit of quantification after processing, the PF value was set as zero (Aguilera et al. 2012). The jam was prepared by cooking a weighed amount of strawberry fruit with sugar (1:1 w/w), after which the jam was cooled to room temperature and acidulated with citric acid (3 g kg-1 sugar), filled into glass jars, and kept for residue analysis within 2 days (Kurz et al. 2008).

Residue determination

Extraction and clean-up of strawberry samples

In accordance with the method of Mollhof (1975), fruit samples of strawberries (50 g) and leaf samples (25 g) were extracted using methanol as a solvent for the extraction of hexythiazox and spinosad. Samples were cut into small pieces in a blender. A constant volume of distilled methanol (150 ml) was used for extraction. The sample was blended using a Hamilton Beach blender for 3 min with methanol at high speed, followed by filtering through a dry pad of cotton into a graduated cylinder. A known volume of the filtrate (100 ml) was taken and partitioned successively with 100, 50, and 50 ml of methylene chloride in a 500 ml separatory funnel after adding 40 ml of sodium chloride saturated solution. The combined methylene chloride phase was dried by filtration through a pad of cotton and anhydrous sodium sulfate, and then evaporated to dryness on a rotary evaporator at 40°C. The dry extract was then subjected to the clean-up procedure suggested by Mills et al. (1972) using a Florisil chromatograph column [40 cm × 18 mm (i.d.) glass column] filled with 10 g of activated Florisil (60-100 mesh) and topped with 2 g of anhydrous sodium sulfate and compacted thoroughly. The column was pre-washed using 50 ml of petroleum ether. The sample extract was dissolved in 10 ml of the same solvent and transferred into the column, followed by elution with 100 ml of the eluent (15% diethyl ether in petroleum ether). The eluent was evaporated to dryness by a rotary evaporator at 40°C and stored at −20 °C until residue determination.

HPLC conditions for quantitative analysis of hexythiazox and spinosad

Agilent 1100 HPLC with a UV photo diode array detector (DAD) has proven to be suitable for hexythiazox and spinosad determination.

Chromatographic separation was performed in the Kinetex system, with a 2.6 µ C18 100 A column (4.6 mm i.d. × 100 mm length). Detection at 245 ηm offers suitable chromatograms for the quantification of hexythiazox and spinosad. The mobile phase was acetonitrile:water (90:10 v/v) with a flow rate of 1 ml min . The column oven was kept at 25 °C. The volume of the injection loop was 10 µl. Under the previous conditions, hexythiazox and spinosad showed retention times of 3.93 and 4.75 min, respectively.

Recovery and statistical analysis

To estimate the recovery rates, known quantities of hexythiazox or spinosad were added to control samples of strawberry fruit and leaves at levels of 0.1 and 1 mg kg-1. The recovery rates in leaves and fruit for the two tested pesticides were 94.42% and 88.73% for hexythiazox and 91.68% and 86.39% for spinosad, respectively. The rates of degradation (K) of hexythiazox and spinosad and their half-lives (t½) (Gomaaa and Belal 1975) in fruit and leaves were calculated as follows: K = 2.303×slope, while t½ = 0.693/K.

The concentrations of hexythiazox and spinosad in strawberry samples were compared with the MRLs recommended by the European Union (FAO 2002). Estimated average daily intakes (EADIs) of pesticide residues and food consumption were used to determine long-term health risks to consumers. To calculate the risk of consuming strawberry fruit and processed products, a daily dose of 0.1 kg day-1 was used, based on the research conducted by Ashfield–Watt et al. (2003).

For each type of exposure, the EADI was obtained by multiplying the mean residual pesticide concentration (mg kg-1) in the food of interest by the food consumption rate (kg day-1) (Darko and Akoto 2008).

The health risk indices (HRIs) were obtained by dividing the EADI by the corresponding values of ADI (FAO/WHO 2010), assuming an average adult body weight of 80 kg (Ahmed et al. 2016; Taghizadeh et al. 2019).

The EADI and (risk quotient) RQ were calculated as follows:

EADI = CRL × FI × 100/bw RQ = EADI/ADI,

kg-1, respectively. Moderate degradation of the

Where CRL is the calculated residue level concentration of each pesticide in strawberry fruit (mg kg-1), FI is the daily intake of strawberries (0.1 kg), bw is the average body weight of 80 kg, and 100 is the safety coefficient (Malkate et al. 2014). When the health risk index is >1, the food involved is considered a risk to consumers, but when the index is <1, the food involved is considered acceptable (Hamilton and Crossley 2004; Darko and Akote 2008; Ahmed et al. 2016; Liu et al. 2019).

Results and Discussion

Residues of hexythiazox and spinosad in strawberry fruit and leaves

Residues of hexythiazox

Residues and loss rates of hexythiazox in and on strawberry fruit and leaves are illustrated in Table 1 and Figures 1 and 2. The initial deposits detected in strawberry fruit and leaves after 2 h of treatment were 2.321 and 4.621 mg kg-1, respectively. These amounts dropped to 1.248 and 4.079 mg kg-1 after 1 day of the application, indicating dissipation rates of 46.23% and 11.73%, respectively. Residues of hexythiazox in and on strawberry fruit and leaves gradually decreased to 0.626, 2.319; 0.214, 1.423; 0.112, 0.745; 0.041, 0.403; and 0.019, 0.169 mg kg-1, showing loss rates of 73.03, 49.82%; 90.78, 69.21%; 95.17, 83.88%; 98.23, 91.28%, and 99.18, 96.34%, respectively, after 3, 6, 9, 12, and 15 days of spraying. The t½ values were 2.23 and 3.24 days from the time of treatment with degradation rates of 0.319 and 0.214 for the strawberry fruit and leaves, respectively. Figures 1 and 2 indicate that hexythiazox was more highly degraded in fruit than in leaves. Data in the same table indicate that, despite the low t½ for hexythiazox in fruit (2.23 days), strawberry fruit could be consumed safely after 6 days of treatment. Concerning health aspects, the MRL of hexythiazox residues in and on strawberries according to the EU Pesticides Database (European Commission) was 0.5 mg kg-1.

Residues of spinosad

Residues of spinosad and their dissipation are shown in Table 2 and Figures 3 and 4. The results revealed that the initial deposits of spinosad on fruit and leaves of strawberry were 0.972 and 4.406 mg

tested insecticide residues in fruit and leaves was noted 1 day after application, with values of 28.29 and 33.00% dissipation, respectively. The initial deposits gradually decreased during the experimental period to reach 0.007 and 0.103 mg kg-1 at 15 days after spraying, reaching 99.28 and 97.66% reductions in fruit and leaves, respectively. According to the EU Pesticides Database (European Commission), the residue tolerance for spinosad in strawberry fruit is 0.3 mg kg-1. Comparing this level with the residue amounts detected in unwashed strawberry fruit at 6 days (0.141 mg kg-1) after spraying (Table 2), which showed that the amount of spinosad residue in unwashed strawberry fruit after 6 days of spraying was lower and thus could be used safely for human consumption after this period of time post-application.

Table 1. Residues of hexythiazox detected in strawberry fruit, leaves, and processed products.

Days after treatment	Unwashed fruit		Washed fruit			Processing as jam			Leaves	
	Residues (mg/kg)	% loss	Residues (mg/kg)	Loss by washing	PF	Residues (mg/kg)	% reduction	PF	Residues (mg/kg)	% loss
2 h	2.321	-	1.285	44.64	0.554	0.190	91.81	0.082	4.621	-
1	1.248	46.23	0.742	40.54	0.595				4.079	11.73
3	0.626	73.03	0.407	34.98	0.650				2.319	49.82
6	0.214	90.78	0.098	12.5	0.458				1.423	69.21
9	0.112	95.17	0.043	12.24	0.384				0.745	83.88
12	0.041	98.23	UND	-	-				0.403	91.28
15	0.019	99.18	UND	-	-				0.169	96.34
K	0.310905								0.214179	
t½	2.23								3.24	

PF = Processing Factors; UND = undetectable amounts

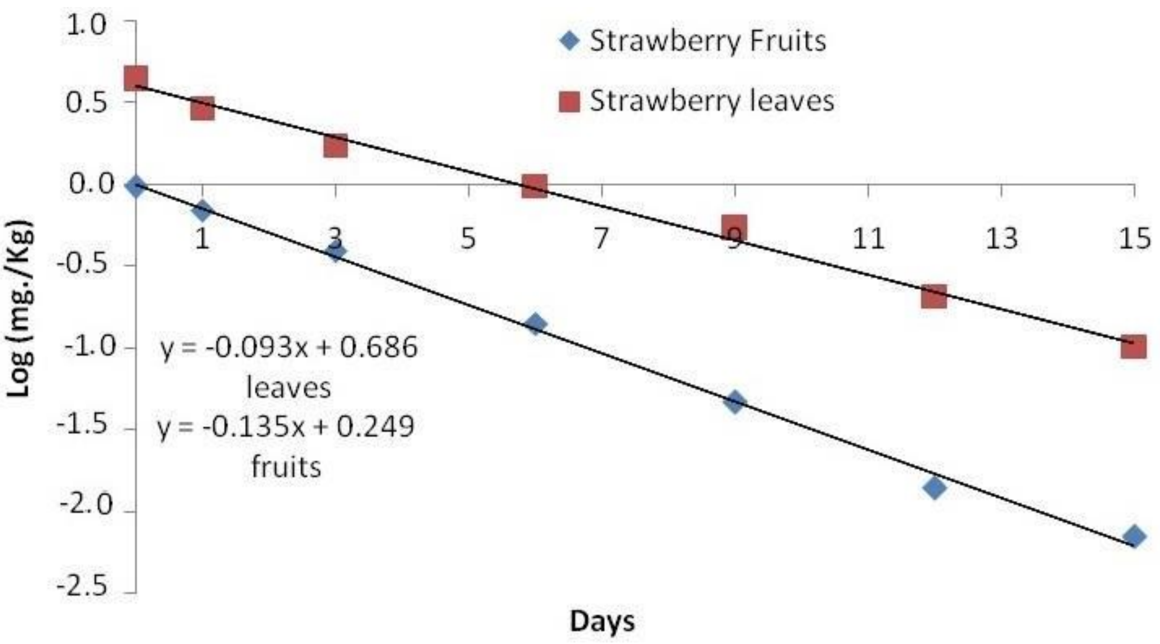

Fig. 1 Log residue-day regression line of hexythiazox in strawberry fruit and leaves

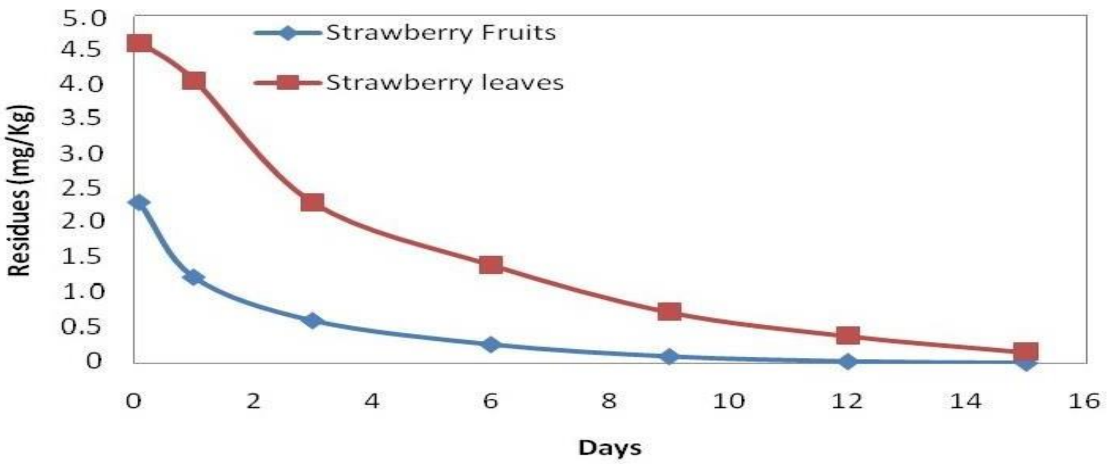

Fig. 2 Dissipation pattern of hexythiazox in strawberry fruit and leaves

The previous results indicated that the amount of residue of hexythiazox was greater than that of spinosad. Similar results were obtained by Abd– Alrahman (2012), who reported an initial deposit of 0.76 mg kg^{-1} following the application of hexythiazox at the recommended dosage in bean pods. Guo et al. (2012) mentioned that the t½ of hexythiazox was 6.8 days in peach. In addition, Abd El-Hamid et al. (2015) studied the dissipation rate of hexythiazox on strawberry under Egyptian climatic conditions. Their results showed that the initial deposit was 3.64 mg kg^{-1} and the calculated t½ was 2 days. However, the pre-harvest interval (PHI) of strawberry was 4 days for hexythiazox. Huan et al. (2015) studied the dissipation and residues of an eco-friendly bio- pesticide, spinosad, in cowpea under field conditions. The dissipation of spinosad (sum of spinosyn A and spinosyn D) fitted well to first-order kinetics with t½ of 0.9-1.5 days. The highest residue (HR) at PHI of 12 h was 0.321 mg kg^{-1}. Compared with the MRL set by Codex, a PHI of at least 24 h was recommended. Majumder et al. (2015) found that the t½ values of hexythiazox in brinjal were in the range of 1.42 to2.32 mg kg^{-1} and pre-harvest periods were found to be in the range of 3-5 days, irrespective of dose and location. Ramadan et al. (2016) investigated the residual level and dissipation behavior of spinosad in tomato. The spinosad residue was determined after application three times at the recommended rates. The value of t½ of spinosad was 1.7 days. The results indicated that tomato fruit could be safely consumed the two targets were similar. Figures 1 to 4 of the degradation rates of the two tested pesticides as well as the t½ support this, showing that the degradation after < 1 day of the application of spinosad at recommended rates according to the recommended EU MRLs. Saber et al. (2016) evaluated the use of hexythiazox on strawberry fruit under field conditions, and their results suggested that hexythiazox's t½ ranged from 3.43 to 3.81 days. They stated that final residues on strawberry were below the Codex MRL (6 mg kg^{-1}) when analyzed after 3 days of application. Also, these researchers found that storage and processing play a vital role in influencing the level of hexythiazox residues in the strawberry matrix and thus in reducing exposure risk. The effect of thiophanate-methyl on strawberry fruit was studied by El-Hefny et al. (2017) who reported that the residue in strawberry was below the Codex MRL (0.1 mg kg^{-1}) after 4 days of application, with a t½ value of 1.26 days.

The initial amounts of each pesticide in leaves were much higher than those in fruit. These variations may be attributable to the differences in plant area, morphology, and chemistry of the recipient leaf surfaces. Ali et al. (2016) and Ramadan et al. (2016) recorded that lower content of insecticide residues was detected in fruit than in leaves in vegetable and field crops. It was also found that the rates of loss of residues were higher in strawberry fruit than in leaves. This loss may be due to the increase in the growth rate of fruit, which dilutes the residue uptake in fruit, and differences in metabolism, since the roles of natural degradation in rates of fruit were higher than those of leaves and the opposite was observed for t½ (Romeh and Hendawi 2014; Sleem 2015; Ali et al. 2016).

Table 2. Residues of spinosad detected in strawberry fruit, leaves, and processed products.

Days after treatment	Unwashed fruit Residues (mg/kg)	Unwashed fruit % loss	Washed fruit Residues (mg/kg)	Washed fruit Loss by washing	Washed fruit PF	Processing as jam Residues (mg/kg)	Processing as jam % reduction	Processing as jam PF	Leaves Residues (mg/kg)	Leaves % loss
2 h	0.972	-	0.436	55.14	0.449	UND	-	-	4.406	-
1	0.697	28.29	0.455	34.72	0.653				2.952	33.00
3	0.394	59.47	0.311	21.07	0.789				1.746	60.37
6	0.141	85.49	0.116	17.73	0.823				0.984	77.67
9	0.047	95.16	0.039	17.02	0.830				0.541	87.72
12	0.014	98.56	0.012	14.29	0.857				0.208	95.28
15	0.007	99.28	UND	-	-				0.103	97.66
K	0.338541								0.241815	
t½	2.05								2.86	

PF = Processing Factors, UND = undetectable amounts

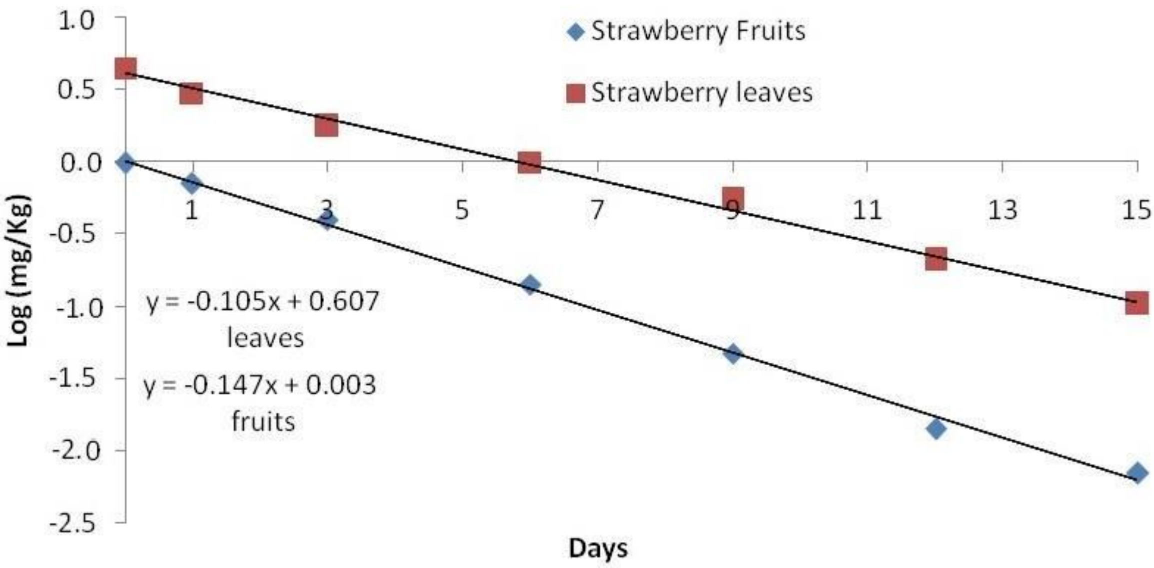

Fig. 3. Log residue-day regression line of spinosad in strawberry fruit and leaves

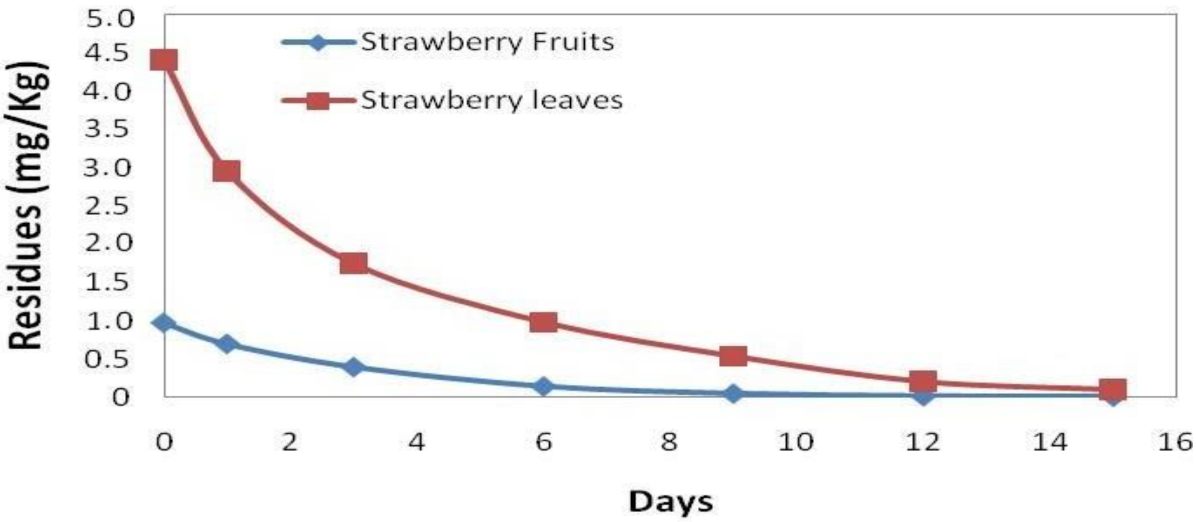

Fig. 4 Dissipation pattern of spinosad in strawberry fruit and leaves

3. Effect of washing and processing as jam on hexythiazox and spinosad residues

Data presented in Table 3 clearly show the effect of home processing (washing and converting to jam) on the reduction of hexythiazox residues in strawberry indicated that the residue of hexythiazox in unwashed strawberry fruits at 2 h after application was 2.321 mg kg-1. Washing reduced the amount of hexythiazox to 1.285 mg kg-1 (44.64% removal). This amount decreased gradually to 0.742, 0.407, 0.098, 0.043, undetected (UND), and UND mg kg-1 at 1, 3, 6, 9, 12, and 15 days after spraying, respectively, corresponding to losses of 40.54, 34.98, 12.50, 12.24, 0.00, and 0.00%. The detected hexythiazox residue was 0.190 mg kg-1 in the jam indicating a 91.81% reduction in residues due to processing. The safe consumption time was found to be 6 days after application, which could be shortened by converting fruit into jam.

Data in Tables 2 and 3 indicate that the residues of the two tested pesticides in strawberry fruit were affected by washing. Recorded PF ranged from 0.384 to 0.650 for hexythiazox and from 0.449 to 0.857 for spinosad. In the case of preparing strawberry fruit as jam, the residues were 0.082 and 0.000 for hexythiazox and spinosad, respectively. These PFs for the pesticide residues depend on the water partition coefficient (Kow) for the pesticides. In this regard, the pesticide with low octanol (Kow) was more easily removed by washing or processing (Guardia et al. 2007; Zhao et al. 2014).

It was mentioned the importance of washing as one of the most studied treatment methods. Washing has an critical role in removing a large amount of pesticides that are loosely attached to the surface (Abou-Arab 1999). In addition, the amounts of pesticide removed from vegetables and fruit by washing were affected by the washing time, the temperature of washing water, and the initial concentration of pesticide (Youssef et al. 1995). The differences between the tested insecticides by washing with tap water on the removal of residues from treated strawberry fruit may be depend on the physicochemical properties of hexythiazox and spinosad, such as their solubility levels in water, which equal 0.5 mg L-1 and 235 mg L-1 at 20°C (MacBean 2012). Saber et al. (2016) studied the effect of PFs (washing, juicing, and cooking) on hexythiazox residues in strawberry fruit. They found that the entire processing could reduce the residues of hexythiazox in strawberry. Shalaby (2016) found that washing with tap water reduced the residues of abamectin and cyflufenamid in squash fruit, with removal rates ranging from 5.13% to 14.74% and 0.00% to 9.17%, respectively. Lozowicka et al. (2016) investigated the effects of washing with tap water and boiling on residue levels of 16 pesticides (10 fungicides and 6 insecticides) in raw strawberries at different processing times (1, 2, and 5 min). Their results showed that washing with tap water reduced pesticide residues from 19.8 to 68.1%, while boiling decreased the residues of most compounds from 42.8 to 92.9%.

Table 3. Health risk assessment of hexythiazox and spinosad on treated strawberry fruit.

Days after treatment	Hexythiazox				Spinosad			
	Residues	EADI	HRI	Health risk	Residues	EADI	HRI	Health risk
2 h	2.321	0.209	9.671	Yes	0.972	0.122	5.063	Yes
1	1.248	0.156	5.20	Yes	0.697	0.087	3.630	Yes
3	0.626	0.078	2.608	Yes	0.394	0.049	2.052	Yes
6	0.214	0.027	0.892	No	0.141	0.018	0.734	No
9	0.112	0.014	0.467	No	0.047	0.006	0.245	No
12	0.041	0.005	0.171	No	0.014	0.002	0.073	No
15	0.019	0.002	0.079	No	0.007	0.0008	0.036	No

EADI = estimated average daily intakesHRI = health risk indices
Acceptable daily intake for hexythiazox was 0.03 and 0.024 for spinosa

Data from the current study show that washing of strawberry fruit resulted in the removal of reasonable amounts of residues. This could be elucidated based on the increased rate of permeability with the passing of time. Several studies showed that the washing process resulted in the removal of certain amounts of different pesticides present on the surface of many vegetables, fruit, and field crops (Radwan et al. 2005; Shiboob et al. 2014; Shalaby 2017).

4. Dietary intake risk assessment of strawberry

Estimated average daily intakes (EADIs), hazard risk indices, and health risk assessment for hexythiazox and spinosad in the treated strawberry fruit are summarized in Table 3. The hazard index values showed that the two tested pesticides during the first three dates of sampling after spraying were >1 and after that during the four later dates were <1; therefore, the treated strawberry fruit from the 6th day after spraying to the end of the experiment are considered acceptable for human consumption. These results are in agreement with the data presented in Tables 1 and 2 when comparing the residue amounts with the MRL for the two tested pesticides. In other words, the contaminated strawberry fruit could be fit for human consumption at 6 days after pesticide application and at 2 h after application if the contaminated fruit are prepared as jam. These results are in agreement with those obtained in previous studies (Sójka et al. 2015; Song et al. 2020; Wang et al. 2015; Saber et al. 2020).

Conclusions

The residual of hexythiazox and spinosad is demonstrated in this study after field application and fruit processing. Results of this study showed that halflife of pesticides removal was rapid with hexythiazox compared with spinosad either in fruits or leaves of strawberry. The risk of pesticides was very low after 6 days of application, which can be shorten with the processing procedures. It was clearly noticed that the safety period of 6 days after treatment could be shortened to only 2 h after spraying when the harvested contaminated strawberry fruits were prepared as jam. These results are clearly indicating the importance of processing practices in pesticides removal from strawberry fruits and subsequently reducing the health risks.

Authors' contributions

Aly Shalaby, El-Sayed El-Sheikh, and Didair Ragheb designed the experiments; Ahmed Refaat, Aly Shalaby, and El-Sayed El-Sheikh carried out the experiments; Aly Shalaby, El-Sayed El-Sheikh and Didair Ragheb analyzed the experimental data and wrote the manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

Availability of data and materials Not applicable

Ethical approval Not applicable

Consent to participate Not applicable

Consent to publish Not applicable

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