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Persistence of imidacloprid, acetamiprid and methomyl in qat leaves

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Summary Qat leaves are chewed on a daily basis by approximately 10 million inhabitants of different countries. This study investigated the persistence of three insecticides most used in qat production, imidacloprid, acetamiprid and methomyl. These chemicals were applied separately on plots of ten qat trees each at the recommended application rates. Samples of qat leaves were collected separately at time 0 (1 h post-treatment) and 1, 3, 7, 12, 19, 26 and 37 days after application. The residues of the investigated pesticides were extracted and then quantified by liquid chromatography (LC-MS/MS). The half-lives of imidacloprid, acetamiprid and methomyl were 12.2, 11.7, and 5.1 days, respectively. Overall, our findings showed that imidacloprid and acetamiprid were more persistent than methomyl in qat leaves. Taking into account the maximum residue limits (MRL) in lettuce, due to lack of MRL in qat leaves, the residue concentrations were below MRL for imidacloprid 7 days after application, and 1 day after application for acetamiprid and methomyl.

*Additional keywords***:** chat, degradation, half-life, insecticide, khat, qat

Introduction

Qat (*Catha edulis*, Forsk) is a perennial shrub, also known by the common names khat or chat, cultivated only in specific regions of a few countries encompassing the Red Sea: Yemen, southwestern Saudi Arabia, Ethiopia, Eritrea, Djibouti, Kenya, and Somalia (Alvi *et al*., 2014; Gebissa, 2010). The fresh qat leaves are chewed for 3–6 hours on a daily basis (usually in the afternoon) by around 10 million inhabitants of these regions; this habit is referred to locally as "takhzeen al-qat" (Hassan *et al*., 2013; Al-Motarreb *et al*., 2010). Moreover, the habit of qat chewing has recently been introduced to other African countries, such as Uganda, Burundi, and Rwanda (Numan, 2012), as well as to the United States, Great Britain, and Western Europe by the Eastern African and Yemeni communities of these countries (Bongard *et al.,* 2015; Al-Motarreb *et al.,* 2010).

The principal active component in qat leaves is cathinone (*(S)*-2-Amino-1-phenyl-1-propanone, $C_9H_{13}NO$), which is known for its mild stimulatory effects; recently, synthetic cathinones have been sold worldwide under the name "bath salts" (Katz *et al.,* 2014; Daba *et al.,* 2011). Qat is moderately used as a traditional medicine by indigenous people of East Africa, but neither the plant itself nor its isolated active ingredients have been widely recognised for their therapeutic use (EMCDDA, 2016). According to the literature, qat-chewing is linked to adverse health effects, such as liver toxicity, an increased risk of cardiovascular events, reproductive problems, psychosis, and periodontal problems (Date *et al.,* 2004; Al-Hebshi and Skaug, 2005).

Qat has been reviewed by the WHO Expert Committee on Drug Dependence (ECDD) on a number of occasions. *Catha edulis* remains outside international control, although cathinone and cathine, which arises from the metabolism of cathinone in the mature plant, have been listed in the 1971 UN Convention under Schedules I and III, respectively, since the early 1980s. Qat is controlled in a number of European countries including Belgium, Denmark, Germany, Greece, France, Ireland, Italy, Latvia, Lithuania, Poland, Slo-

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venia, Finland, Sweden, Norway, Switzerland and recently in U.K. (The Misuse of Drugs Order, 2014; EMCDDA, 2016).

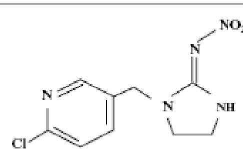
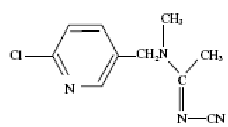
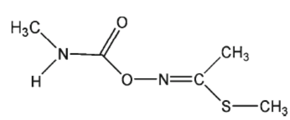
The high demand for qat, combined with the limited amount of cultivated lands, has raised its value in recent years. Its price has increased dramatically to approximately \$150–\$200/kg, depending on its variety and origin. An individual chews about 100–300 g of fresh leaves daily (Nakajima *et al.,* 2014; Date *et al.,* 2004).

The use of pesticides in qat production is indispensable in protecting the plants from different insects and fungi. Consequently, qat production consumes about 70% of the pesticides used in Yemen; some of these pesticides are banned (e.g. DDT) but continue to be used illegally in the production of qat and other crops (Date *et al*., 2004). Imidacloprid, acetamiprid and methomyl are the most commonly used insecticides in the production of qat; some of their key properties are presented in Table 1. Imidacloprid (*N*-{1-[(6-Chloro-3-pyridyl)methyl]-4,5-dihydroimidazol-2-yl}nitramide; $C_9H_{10}ClN_5O_2$), the most-used insecticide worldwide, and acetamiprid (*N*-[(6-chloro-3-pyridyl)methyl]-*N′*-cyano-*N*-methyl-acetamidine; $C_{10}H_{11}ClN_4$) are neonicotinoid insecticides that act as insect neurotoxins (Sharma and Singh, 2014). Methomyl (*S*-methyl *N*-(methylcarbamoyloxy) thioacetimidate; $C_5H_{10}N_2O_2S$) is an oxime carbamate insecticide used as a broad-spectrum insecticide since 1968 (Van Scoy *et al.,* 2013), which was banned few years ago but continues to be used illegally by qat farmers.

Therefore, the consumption of qat might be an important source of exposure to pesticides, especially because its leaves are consumed fresh, without any thermal treatments that can reduce pesticide residues (Daba *et al*., 2011). Qat chewing is similar to the smokeless tobacco chewing among workers in tea industry in India (Kausar *et al.,* 2014). Moreover, the failure of some local farmers to respect pesticide labels (dose, application method, and post-harvest interval) might lead to a high risk of qat contamination by pesticides (Date *et al*., 2004). Results obtained by Daba *et al.* (2011) showed high concentrations of the insecticides diazinon (751 µg kg^{-1}) and DDT (1,372 µg kg^{-1}) in qat collected from different farms in Ethiopia. In contrast, Hassan *et al.* (2013) reported the absence of pesticide residues in 120 qat samples collected from Jazan area, Saudi Arabia.

Information on the persistence of pesticides in qat is extremely scarce. The pres-

Table 1. Structure and key properties of imidacloprid, acetamiprid and methomyl (Gupta and Shanker, 2008; Gupta *et al.,* 2008; Tomasevic *et al.,* 2010; Van Scoy *et al.,* 2013).

Compound	M.W.	Solubility (mg L^{-1})	Log K_{ow}	p*Ka*	Structure
Imidacloprid CAS: 3380-34-5 Formula: 5-chloro-2-(2,4-dichlorophenoxy)-phenol	289.5	4.621	4.7	8.1	
Acetamiprid CAS: 101-20-2 Formula: 3,4,4′- trichlorocarbanilide	315.6	0.6479	4.9	n/a	
Methomyl CAS: 16752-77-5 Formula: S-methyl N-(methylcarbamoyloxy)thioacetimidate	162.2	57900	1.24	14	

ent study sought to determine the residue dissipation of the insecticides most used in the production of qat (imidacloprid, acetamiprid and methomyl) to control jassids, thrips and mites. To the best of our knowledge, this is the first work on the residues of these three insecticides in qat.

Materials and Methods

The commercial formula of selected insecticides were purchased from a local market in Jazan, KSA: imidacloprid (Imidor 200 g L^{-1}) (Astrachem, KSA), acetamiprid (Deltaride 20% sp) (Delta, KSA), and methomyl (Lanet 90 WP) (Du Pont, China).

Field trials were conducted at a private farm in the Fyfa Mountains area on the border zone between Yemen and Saudi Arabia (17° 15′ 3.76″ N, 43° 7′ 56.46″ E). Four separated plots of ten trees each, with a buffer zone of 10–15 m between plots were selected for this study. Consequently, the selected trees were labeled for each treatment. Trees were healthy, 10–12 years old, and were not treated with any pesticide for the last 4 years, as declared by the farm's owner. One plot was considered to be a control and treated only with tap water, while other plots were separately treated with the investigated insecticides at the recommended application rates. The applied concentrations of pesticides in the sprayed solutions were 1.25 ml L^{-1}, 0.5 g L^{-1}, and 0.5 g L^{-1} for imidacloprid, acetamiprid, and methomyl, respectively. The total sprayed solution was 10 L for each plot using a hand-operated sprayer (Mythos, Italy). All trees were treated until run-off.

For each treatment, leaves and buds were sampled from the four sides and top of each qat tree; an approximate total of 500 g of green qat leaves and buds were collected in a plastic bag from each plot at time 0 (1 h post-application) and 1, 3, 7, 12, 19, 26, and 37 days after application. At each of the specified times, collected samples (from treated and control plots) were placed in a field cooler at 4 °C and transferred to the laboratory. Accumulated precipitation during the experiment was 53.1 mm; the mean air temperature was 29.7 °C (Fig. 1).

Upon arrival to the laboratory, each sample was chopped separately using a domes-

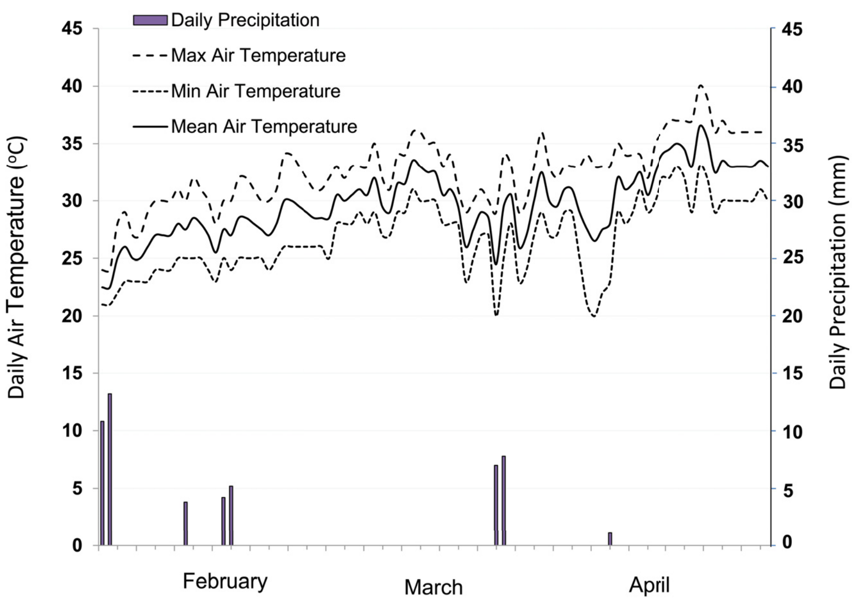


Figure 1. Weather parameters at the research farm of qat during the period of the insectiside residue field experiment.

tic glass blender 1.8 L (Moulinex, France). For each sample, three homogenized subsamples of 150 g were transferred into a 250 mL amber glass bottle with cap and stored at -20 °C until analysis by the end of field experiments. In order to determine the pesticide residues, frozen samples were placed inside a field cooler and shipped frozen to an accredited lab (Australian Laboratory Services, Dammam, Saudi Arabia). The pesticide residues were extracted from a homogenized sample with 1% acetic acid in acetonitrile (QuEChERS procedure) according to the method described by Anastassiades et al. (2003). The extract was analyzed by liquid chromatography with mass detection (LC-MS/MS) as described by Anastassiades et al. (2003) and EC (2007). The calibrated range of the method was 0.01-0.2 μg ml^{-1}, which equates to 0.01–0.2 mg kg^{-1} in the sample (0.02–0.4 mg kg^{-1} in the dry samples). The retention times were 2.68, 3.46 and 3.85 minutes for methomyl, imidacloprid and acetamiprid, respectively (Fig. 2). A recovery test for the extraction method of insecticides was made separately in 3 samples of untreated qat leaves (collected from the control plot trees) spiked with a known amount of each insecticide. A blank of untreated qat leaves was extracted at the same time as control. The recovery rate was acceptable with values of 101.2±3.1%, 98.3±2.7% and 94.6±1.2% of the initial amount for imidacloprid, acetamiprid and methomyl, respectively. None of the investigated pesticides were detected in the samples collected from the control plot.

Data analysis was conducted using Microsoft Excel 2002 (Microsoft Canada, Toronto, ON). Dissipation curves were plotted using SigmaPlot (Version 10, Systat Software Inc., Chicago, IL). The half-life of each insecticide was calculated separately using the equation of first-order rate, as described by Gupta *et al.* (2008).

Results and Discussion

The initial concentration of imidacloprid residues in qat leaves was 6.2 mg kg^{-1}. Its degradation then approximated first order (r^2 = 0.95); 37 days after treatment 10.65% of initial residues remained in the qat leaves (Tables 2 and 3). The wash of insecticide with rain was negligible because of the low precipitation after its application (Fig. 1). Itoiz *et al.* (2012) reported similar initial residue concentrations of imidacloprid in lettuce leaves of 5.97 mg kg^{-1}, which then declined to 0.69 mg kg^{-1} 14 days after application. Persistence

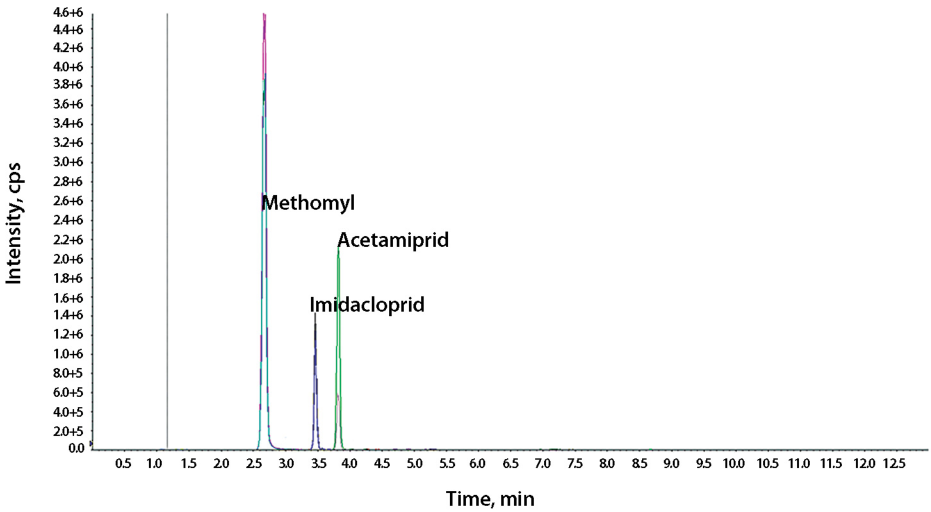


Figure 2. Representative LC-MS/MS chromatogram for standards mixture of imidacloprid, acetamiprid and methomyl.

Table 2. Residues (mg kg^{-1}) of imidacloprid, acetamiprid and methomyl, and the percentage of remaining residues (%) in leaves of qat at different time intervals after application.

Time (days)	Imidacloprid		Acetamiprid		Methomyl	
	Residues	%	Residues	%	Residues	%
0 (1h)	6.2 ± 0.41	100	3.0 ± 0.28	100	12.0 ± 0.63	100
1	5.2 ± 0.33	83.87	2.6 ± 0.30	86.67	2.6 ± 0.43	21.67
3	3.9 ± 0.19	62.90	2.1 ± 0.24	70.00	2.3 ± 0.39	19.17
7	3.1 ± 0.22	50.00	2.0 ± 0.11	66.67	1.1 ± 0.22	9.17
12	1.8 ± 0.12	29.03	1.3 ± 0.08	43.33	0.54 ± 0.18	4.50
19	1.8 ± 0.16	29.03	1.0 ± 0.09	33.33	0.31 ± 0.04	2.58
26	1.1 ± 0.09	17.74	0.89 ± 0.10	29.67	0.17 ± 0.06	1.42
37	0.66 ± 0.07	10.65	0.25 ± 0.05	8.33	0.03 ± 0.01	0.25

Table 3. Dissipation rate parameters for the fit of imidacloprid, acetamiprid and methomyl in qat leaves, to a first order kinetic model.

Pesticide	r^2	K (day^{-1})	C_0 (mg kg^{-1})	Std. error	$t_{1/2}$ (days)
Imidacloprid	0.9542	0.057a	6.2	0.0021	12.2
Acetamiprid	0.9482	0.059a	3.0	0.0017	11.7
Methomyl	0.9290	0.135b	12	0.0009	5.1

r^2: determination coefficient; K: rate constant; C_0: initial concentration of residue; Std. error: Standard error; $t_{1/2}$: half-life; ^{a,b}: significant difference between treatment using a Student T test.

of pesticides in plants, which is longer in the dry season than in the wet season, is influenced by different factors, such as the targeted plants, the physico-chemical properties of the pesticide, and its application methods (Itoiz *et al*., 2012; Gupta *et al.,* 2008; Fujita *et al*., 2014). However, a variety of similar studies have been realized to determine the dissipation of imidacloprid using different application techniques on different plants. The half-life of imidacloprid residues in qat leaves was relatively long at 12.2 days (Table 3), which is consistent with another study showing that the half-lives of imidacloprid in sugarcane leaves were 8.1–9.7 days in two different application doses (Sharma and Singh, 2014). In contrast, imidacloprid was reported to dissipate more rapidly in other plants, such as tea shoots, with a half-life of 1.09–1.25 days (Gupta *et al.,* 2008), 4.4 days in lettuce leaves (Itoiz *et al.,* 2012), and 1.7–2.3 days in chickpea pods and leaves (Chahil *et al.,* 2014).

Until these days, there is no legislation in the qat production countries for the recommended minimum pre-harvest intervals (PHIs) or for the maximum residue limits MRLs of pesticides in qat despite its high consumption by about 10 million people of different countries. Consequently, no value has yet been established with respect to the maximum permissible intake of imidacloprid, acetamiprid and methomyl in qat. Due to the lack of some scientific information on the persistence of pesticides in qat and the absence of MRL values in its leaves in the major guidance documents i.e. Codex (2015) and EU (2005), we used the MRL values already established for lettuce leaves to compare the preharvest intervals of investigated insecticides because both lettuce and qat leaves are chewed fresh and uncooked among the qat consumers and approximately at the same quantity weekly. The MRL for imidacloprid in lettuce is 3.5 mg kg^{-1} and the recommended PHI is 7 days (Global MRL Database, 2015). In our study, the residue concentrations of imidacloprid were below the MRL at 3.1 mg kg^{-1} (Table 2) 7 days after treatment. In contrast, Chahil *et al.* (2014) reported that the residue concentrations of imidacloprid were below the MRL directly after application (2 h) in chickpea pods and leaves. This difference might be due to the very low initial concentration of imidacloprid (0.29–0.49 mg kg^{-1}) in chickpea pods and leaves. Moreover, imidacloprid residue concentrations ranging from 0.01 to 0.76 mg kg^{-1} were detected in some fruit and vegetable samples collected from the Aegean region in Turkey (Bakirci *et al.,* 2014).

The dissipation kinetics of acetamiprid in qat leaves was similar to that of the other investigated neonicotinoid insecticide, imidacloprid, although the initial concentration of acetamiprid residues in qat leaves was 3.0 mg kg^{-1}, which is 52% less than that of imidacloprid. Therefore, its degradation approximated first order (r^2 = 0.95); 37 days after treatment 8.33% of initial residues remained in the qat leaves (Tables 2 and 3). The initial residue concentrations of acetamiprid obtained in this study (3.0 mg kg^{-1}) were much higher than the concentrations reported in chillies (0.02–0.1 mg kg^{-1}) after treatment at the recommended and double-the-recommended doses (Sanyal *et al*., 2008). A possible explanation for this discrepancy could lie in the fact that qat leaves received a higher amount of pesticide than the chilli peppers due to their larger surface; consequently, the concentrations of the chemical in leaves were found to be higher than those in fruits.

Dissipation of acetamiprid in different plants has been reported in many recent studies; however, the literature contains no information about the dissipation of acetamiprid in qat leaves. In our study, the dissipation rate of acetamiprid in qat was relatively slow (half-life = 11.7 days) compared to that of other plants, such as 1–1.6 days for the mustard plant (Pramanik *et al*., 2006), 1.8–2.3 days for green-tea shoots (Gupta and Shanker, 2008), 2.2–4.8 days in chillies (Sanyal *et al.,* 2008), and 1.9 and 2.5 days in zucchini and zucchini leaves, respectively (Park *et al.,* 2010). Similar to the case of imidacloprid, no MRL value has yet been established for acetamiprid in qat, thus, we used its value in lettuce leaves to compare the preharvest intervals (PHIs). For acetamiprid in lettuce, the MRL = 3 mg kg^{-1}, and the recommended PHI is 7 days (Global MRL Database, 2015). In the present study, the residue concentrations of acetamiprid were below the MRL at 2.6 mg kg^{-1} 1 day after treatment (Table 2). However, a PHI of 1 day after application is recommended for tea shoots to ensure safe consumption (Gupta and Shanker, 2008); the PHI of 1 day could be recommended for acetamiprid in qat leaves. Acetmiprid residues were detected in some fruit and vegetable samples collected from the Aegean region in Turkey, but they ranged from 0.01 to 0.06 mg kg^{-1} and were therefore below the MRL value of 3 mg kg^{-1} (Bakirci *et al.,* 2014).

Despite the relatively high initial residue concentration of methomyl in qat leaves (12 mg kg^{-1}), its dissipation, with a half-life of 5.1 days, was significantly more rapid than that of imidacloprid and acetamiprid (Tables 2 and 3). The decline of methomyl residues was very fast after application: About 78.3% of the residues had dissipated 1 day after treatment; its degradation then approximated first order (r^2 = 0.93), and the residue concentrations at the end of the experimentation, 37 days after treatment, were 0.03 mg kg^{-1}. Similar to the case of imidacloprid and acetamiprid, no value has yet been established with respect to the maximum permissible intake of methomyl in qat. Therefore, we used its value in lettuce leaves to compare the preharvest intervals (PHIs). The MRL value of methomyl residues in lettuce is suggested to be 5 mg kg^{-1} (Global MRL Database 2015). In the present study, the residue concentrations of methomyl, at 2.6 mg kg^{-1}, were below the MRL 1 day after treatment (Table 2); at 5.1 days, its half-life is in agreement with results obtained by Reeve *et al.* (1992), which showed that variable half-lives of methomyl in grape foliage in 36 U.S. fields ranged from 1 to 7.7 days. In contrast, the half-life of methomyl in qat leaves, as demonstrated in our study, is longer than the reported half-lives in other studies of other plants e.g., 0.9-1.34 days for tomatoes (Gambacorta *et al.,* 2005; Malhat *et al*., 2015) and 0.88–0.94 days for okra fruits (Aktar *et al.,* 2008). The half-life of methomyl in plants increases significantly with the progression of the summer months (Reeve *et al.,* 1992) due to the slow growth of plants and, consequently, less efficiency in the degradation of the pesticides. The initial residual concentration in qat leaves was higher than results reported in tomatoes (1.54 mg kg^{-1}) (Gambacorta *et al.,* 2005) and 5.61–8.42 mg kg^{-1} in okra fruits treated at the recommended and double-the-recommended doses, respectively (Aktar *et al.,* 2008). Methomyl residue concentrations ranging from 0.01 to 1.42 mg kg^{-1} were detected in grape samples collected from the Aegean region in Turkey and in some vegetables (arugula, eggplant, bean, cucumber, leek, mushroom, onion, and pepper); at concentrations ranging from 0.01 to 2.13 mg kg^{-1}; the residues in all samples were below the MRL of 5 mg kg^{-1} (Bakirci *et al.,* 2014). The rapid dissipation of methomyl and its relatively short half-life led to decrease the residues below the MRL value within only 1 day after application.

Conclusions

The present study demonstrates that the neonicotinoid insecticides imidacloprid and acetamiprid have similar dissipation pathways in qat leaves; their persistence was significantly higher than the carbamate insecticide methomyl. Half-life values for imidacloprid, acetamiprid and methomyl, when applied at recommended dosages on qat trees, were 12.2, 11.7 and 5.1 days, respectively. Our results showed that the residues of the investigated pesticides were below the MRL for lettuce 7 days post-application for imidacloprid and 1 day post-application for acetamiprid and methomyl. In view of the increased consumption of qat and the scarce information about the dissipation of pesticides in this plant, more studies are required to assess the risk of human exposure to pesticides by chewing qat leaves.

AJ Al-Rajab designed the experiments, data interpretation, manuscript writing, and submission corresponding. AM Alhababy contributed in experiments design, treatments, samples preparation, data collection and interpretation. T. AlFaifi contributed in pesticides' treatment, sampling, lab preparation and data collection.

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Υπολειμματικότητα imidacloprid, acetamiprid και methomyl σε φύλλα του φυτού *Catha edulis*

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Περίληψη Η μάσηση των φύλλων του φυτού *Catha edulis* αποτελεί συνήθεια σε καθημερινή βάση περίπου 10 εκατομμύριων ανθρώπων σε διάφορες χώρες. Στην παρούσα μελέτη διερευνήθηκε η υπολειμματικότητα των πλέον χρησιμοποιούμενων εντομοκτόνων σκευασμάτων στην καλλιέργεια του φυτού (δραστικές ουσίες imidacloprid, acetamiprid και methomyl). Τα εντομοκτόνα εφαρμόστηκαν ξεχωριστά σε πειραματικά τεμάχια των δέκα φυτών στις συνιστώμενες δόσεις εφαρμογής. Συλλέχθηκαν δείγματα φύλλων 1 ώρα μετά την εφαρμογή και 1, 3, 7, 12, 19, 26 και 37 ημέρες μετά την εφαρμογή. Ο προσδιορισμός των υπολειμμάτων πραγματοποιήθηκε με τη χρήση υγρής χρωματογραφίας σε συνδυασμό με φασματομετρία μάζας τριπλού τετραπόλου (LC -MS/MS). Οι χρόνοι ημίσειας ζωής των imidacloprid, acetamiprid και methomyl ήταν 12.2, 11.7 και 5.1 ημέρες, αντίστοιχα. Συνολικά, τα αποτελέσματα έδειξαν ότι οι ουσίες imidacloprid και acetamiprid παρουσίασαν μεγαλύτερη υπολειμματική διάρκεια σε σύγκριση με το methomyl στα φύλλα του φυτού. Λαμβάνοντας υπόψη τα ανώτατα όρια υπολειμμάτων (MRL) στο μαρούλι, λόγω απουσίας MRL σε φύλλα του ιδίου φυτού, οι συγκεντρώσεις υπολειμμάτων ήταν κάτω από τα MRL για το imidacloprid, 7 ημέρες μετά την εφαρμογή, και 1 ημέρα μετά την εφαρμογή για το acetamiprid και το methomyl.

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