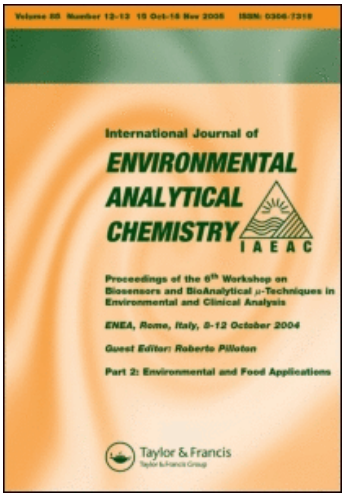

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Dissipation of insect growth regulators in fresh and canned fruits

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The objective of the study was to determine the dissipation of insect growth regulators in fresh and canned mandarin and apricot to determine the exposure to them. Field studies were carried out in the preharvest period with good agricultural practices (GAP) and in critical agricultural practices. The processing studies were carried out in each relevant step in a pilot plant. A validated methodology was developed (limit of quantification of 0.05 mg kg^{-1} for apricots, 0.10 mg kg^{-1} for mandarin) including acetone–dichloromethane extraction, cleanup, and liquid chromatography-diode array detection. The pesticides complied with the maximum residue limits (MRLs) except pyriproxyfen, which has not been authorized in apricots, and it did not comply with its MRL for peaches. The dissipation rates ($t_{1/2}$) with GAP were fenoxycarb-apricot > pyriproxyfen-apricot > fenoxycarb-mandarin > pyriproxyfen-mandarin. In the processing studies, there was only residue transference in the canning of apricots. All final cans contained residues much lower than the MRLs.

Keywords: Dissipation; Insect growth regulators; Mandarin; Apricot; Field studies; Processing studies

1. Introduction

Insect growth regulators (IGRs) started to be used over the last decade as pesticides similar to biological compounds of insects and acarus. At present, some of them are increasingly applied in different plant products [1]. They are classified in different chemical groups according to their mechanism of action: hormonal action—*regulators*; or structural action—*inhibitors* [2, 3].

Fenoxycarb [ethyl 2-(4-phenoxyphenoxy)ethylcarbamate mimics the juvenile hormone and inhibits the specific esterases. It inhibits metamorphosis to the adult stage and interferes with the moulting of early instar larvae. Fenoxycarb is active by contact and ingestion.

Flufenoxuron [1-[4-(2-chloro-α,α,α-trifluoro-*p*-tolyloxy)-2-fluorophenyl]-3-(2,6-difluoroben-zoyl)urea] is an inhibitor of chitin synthesis in insects and acarus.

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The larvae do not molt correctly, and adults do not produce viable lays. Flufenoxuron is active through contact or ingestion.

Lufenuron [(*RS*)-1-[2,5-dichloro-4-(1,1,2,3,3,3-hexafluoro-propoxy)phenyl]-3-(2,6-difluorobenzoyl)urea] is an inhibitor of chitin synthesis in insects and acarus, is highly active when ingested, and is widely used in vegetables and fruits.

Pyriproxyfen [4-phenoxyphenyl(*RS*)-2-(2-pyridyloxy)propyl ether] is an insect growth regulator because it imitates the juvenile hormone, suppresses embryogenesis, and inhibits metamorphose and reproduction. It is widely used to combat various types of insects.

Fenoxycarb is authorized as a phytosanitary in apricots and mandarins, but pyriproxyfen is not allowed for apricots. Flufenoxuron and lufenuron are authorized for mandarin [4].

According to recent statistics from the Food and Agriculture Organization of the United Nations (FAO), fruits, vegetables, and roots were the third commodity consumed for the years 2001–2003. Developed countries consumed 308 kcal/caput/d, and developing countries 295 kcal/caput/d from fruits, vegetables, and roots for this period [5].

Figures from the FAO indicate that the major producers of fruits and vegetables in 2004 were China (36.62%), India (9.22%), and USA (5.01%) related to total world production [6]. According to European Union (EU) statistics, European countries produced 16% of fruits and vegetables in 2004 related to total agricultural production by the 25 member countries [7].

However, in the case of apricots and mandarins, a high amount of production is consumed as processed fruits. In the USA in 2004, the total per capita consumption for apricots (fresh weight equivalent) was 0.4 kg, but only 0.04 kg was consumed as fresh apricot. For mandarin and tangelos in the USA in 2004, the total per capita consumption was 1.76 kg, 1.27 kg was consumed as fresh fruit, and 0.49 kg was consumed as processed fruit [8].

In previous years, the residues of these IGRs have been monitored in fresh products like mandarin and apricots in order to report the compliance of maximum residue limits (MRLs), as US Food and Drug Administration residue monitoring and EU residue monitoring show in their pesticide programme [9–12].

Nevertheless, there is an increasing need to study the pesticide dissipation rates to know exactly the degradation to which they are subjected and the residues they produce in food when they are used [13–15]. It is necessary to determine the exposure to these pesticides up to the point at which the foodstuffs reach consumers.

Dissipation studies are conducted to provide a more realistic picture of what happens to the parent compound and breakdown products in the environment. Under field conditions, pesticides are exposed to several dissipation processes at the same time. The results of field studies and laboratory data are integrated to characterize the persistence and transport of a pesticide and its breakdown products. From these data, a quantitative environmental fate profile or assessment and model estimates of exposure to the pesticide in fresh commodities can be obtained [16–20].

Processing studies are focused on the residues of pesticides in food influenced by the storage, handling, and processing that occur between harvesting of raw agricultural commodities and consumption of prepared foodstuffs. A review of the extensive literature showed that in most cases, these steps lead to large reductions in residue levels in the prepared food, particularly through trimming, washing, blanching, peeling, and general cooking operations [21–23].

The analytical methodology published for insect growth regulators has consisted of several techniques including cleanup in the extraction. LC with DAD or MS has been used for benzoylphenylureas such as flufenoxuron and lufenuron in apricots and citrus fruits, as Gamón *et al*. (1998) and Valenzuela *et al*. (2000) reported [24, 25]. Štepán *et al*. (2004) reported residue analysis by GC with NPD for fenoxycarb [26]. LC methods have been published for fenoxycarb and pyriproxyfen, as Bicchi *et al*. (1990), Wang *et al*. (2000) and Soler *et al*. (2004) reported [27–29].

The objective of this work was to determine the dissipation rates of two kinds of IGRs in fresh and canned satsuma mandarin (*Citrus reticulata*) and bulida apricot (*Prunus armeniaca*) in order to determine the exposure to these pesticides. The dissipation studies were carried out in crops in the preharvest period with good agricultural practices (GAP) and in a situation of critical agricultural practices (CAP). The processing studies were carried out with fruits from both these situations in each relevant step of the process in an industrial pilot plant. A unique methodology was developed for the residue analysis of the IGRs in apricots and mandarins (limit of quantification of 0.05 mg kg^{-1} for apricots and 0.10 mg kg^{-1} for mandarin) according to the European ISO 17025 norm and SANCO recommendations [30, 31].

2. Experimental

2.1 *Products studied*

All the analytical standards of the pesticides were 99% or more pure and were provided by the Dr Ehrenstorfer firm (Ausgburg, Germany). They were used to prepare solutions in acetonitrile : water 50 : 50 (v : v), at concentrations from 0.05 to 10 mg L^{-1}, preserved in a cold chamber. The commercial formulates were Insegar (fenoxycarb 25% [WG] p/p) from Syngenta Crop Protection AG (Basel, Switzerland), Atominal 10 EC (pyriproxyfen 10% [EC] P/V) from Comercial Química Massó. S.A. (Barcelona); Cascade (flufenoxuron 10% [DC] p/v) from Basf Agro BV (Wädenswil/Au, Switzerland) and Match 5 EC (lufenuron 5% [EC] p/v) from Syngenta Crop Protection AG (Basel, Switzerland).

2.2 *Reagents and solvents*

These were as follows: HPLC-quality acetonitrile, Scharlau (Barcelona); milliQ water, Millipore Purification Pak (Billerica, MA); acetone for residue analysis, Panreac (Barcelona); dichloromethane for residue analysis, Panreac (Barcelona); petroleum ether 40–60°C for residue analysis, Merck (Whitehouse Station, NJ); dimethyltercbuthylether, Merck (Whitehouse Station, NJ); cartridges Sep-Pack megabondelut-NH_2, Varian (Harbor City, CA).

2.3 *Instruments*

These were as follows: *Maruyama MS073D* backpack for application of phytosanitary products (Auburn, WA); HPLC chromatograph series 1100 Hewlett-Packard

(Palo Alto, CA), with quaternary pump, autoinjector, thermostat compartment for the column, and a diode array detector, coupled to an HPChemstation revision A.10.02, equipped with a C_8 Zorbax XDB Eclipse column in reverse phase, 4.6×150 mm, 5 μm, Agilent (Palo Alto, CA); Polytron high-speed homogenizer, Kinematica AG (Luzern, Luzern); rotary evaporator Büchi (Flawil, State of St. Gallen, Switzerland) with Univeba-400 bath from P-Selecta (Barcelona) and V-500 vacuum pump from Büchi; phase separator article of 150 mm diameter, Filtros Anoia (Barcelona); centrifuge Heraeus Christ (Osterode, Germany).

2.4 *Crop studies*

Experimental fields were located on producer farms in the Region of Murcia (south-east Spain). These were chosen as being representative and protected from pollution, and were separated into a control area and an area of application [32]. The control plots were located close enough to the treated plots to secure identical growing and climatic conditions. However, the control plots were sufficiently separated to exclude any contamination from the treated plots.

The field containing satsuma mandarin (*C. reticulata*) crop was located in the Region of Murcia. The GPS numbers were: 38.0349° N; 1.11534° W; height, 72 m. The field was 9 m long and 3 m wide, and contained seven satsuma trees. The total production was 350 kg. The field containing Bulida apricot (*P. armeniaca*) crop was located in the Region of Murcia. The GPS numbers were: 38.06006° N; 1.52930° W; height, 420 m. The field was 7 m long and 6 m wide, and contained four apricot trees. The total production was 300 kg.

The phytosanitary products were applied as they are authorized by European legislation for each crop except pyriproxyfen. It is authorized in mandarin but not in apricot. In order to study the behaviour of pyriproxyfen in apricot, it was applied in this fruit at the level authorised in peach. Flufenoxuron, lufenuron, fenoxycarb, and pyriproxyfen were studied in mandarin. Fenoxycarb and pyriproxyfen were studied in apricot.

A backpack with double-fan nozzle for mandarin trees and with a pocket pistol for apricot trees was used to apply the formulations. These were Insegar® (fenoxycarb 25% [WG] p/p), Atominal 10 EC® (pyriproxyfen 10% [EC] p/v), Cascade® (flufenoxuron 10% [DC] p/v) and Match 5 EC® (lufenuron 5% [EC] p/v).

A treatment under GAP and another under CAP were carried out for each crop with controlled conditions of temperature and relative humidity. In all cases, the pesticides were applied at the same time. The amount sampled was that recommended by FAO, and the parts indicated in annex I of the RD 280/1994 were crushed for analysis of pesticide residues [33].

2.4.1 Pesticide treatment under GAP conditions. The GAP code, security times, and registered doses were maintained [34, 35]. The doses applied for fenoxycarb, pyriproxyfen, flufenoxuron, and lufenuron in mandarin were 0.04, 0.05, 0.05, and 0.15%, respectively. A volume of 25.6 L and dose of 1306.20 L ha^{-1} were applied. The temperature was 21°C and the relative humidity 80%. In apricot, the doses were 0.03 and 0.04% for fenoxycarb and pyriproxyfen, respectively. A volume of 22 L and dose of 1309.50 L ha^{-1} were applied. The temperature was 20°C and the relative humidity 50%.

To determine residues up to harvesting, representative and periodic samples were taken from the treated and control fields. Samples were taken 2 h after the application of the products (the drying time) and at 3, 7, 14, and 21 days for apricot and at 3, 7, 14, 21, 28, 30, and 45 days for mandarin. The last sample corresponded to the expiry date for the relevant security time. In the samples at the security time, another 10 kg was collected for industrial processing.

2.4.2 Pesticide treatment under CAP conditions. At the security times, the same aforementioned doses were applied again. In mandarin, the temperature was 22°C and the relative humidity 50%. In apricot, the temperature was 28°C and the relative humidity 61%. After 2 h, a sample was taken for the residue analysis and for the processing studies (10 kg). The CAP conditions allowed to study the exposure to pesticides when they were used dangerously.

2.5 *Processing studies*

The fruits were transformed into canned products in an industrial experimental plant located in the Technological National Centre of Canning Industry from the Region of Murcia. Apricots and mandarins were transformed into canned products. The samples of the fruits collected at the end of the security time and 2 h after the second treatment were subjected to the same technological processes as are currently used in the food industry. Representative samples of 1 kg were taken after each relevant step of the process in order to study their effect on the dissipation of the residues.

2.5.1 Mandarin canning study. For canned mandarins, the manufacturing process was: peeling; segmenting; washing with osmotic water for 2–3 min; washing with a solution of HCl 0.2% at 30°C for 35–40 min; three new washings with osmotic water for 2–3 min; washing with a solution of 0.2% NaOH at 34°C for 15 min; four new washings with osmotic water for 2–3 min; canning the segments of satsuma mandarin (290 g) with syrup at 26° Brixs and sterilization at 87°C for 10 min (see figure 1).

2.5.2 Apricot canning study. The manufacturing process for canned apricots was as follows: washing with water for 2 min; cutting in half and removal of the stone; canning the parts (240–250 g) with syrup at 95°C, 14° Brixs and 0.01% citric acid; sterilization at 98°C for 8 min and cooling down at 35°C in 10 min (see figure 2).

2.6 *Methodology for residue analysis*

The residue analyses were carried out with samples from the preharvest period and harvesting of the GAP treatment, after the CAP treatment and from the steps of the industrial transformation. The samples were crushed and analysed the same day they were collected. The field samples were analysed unpeeled as the MRL legislation says. The analytical method was based on Gamón *et al.* [24]. It included an extraction from

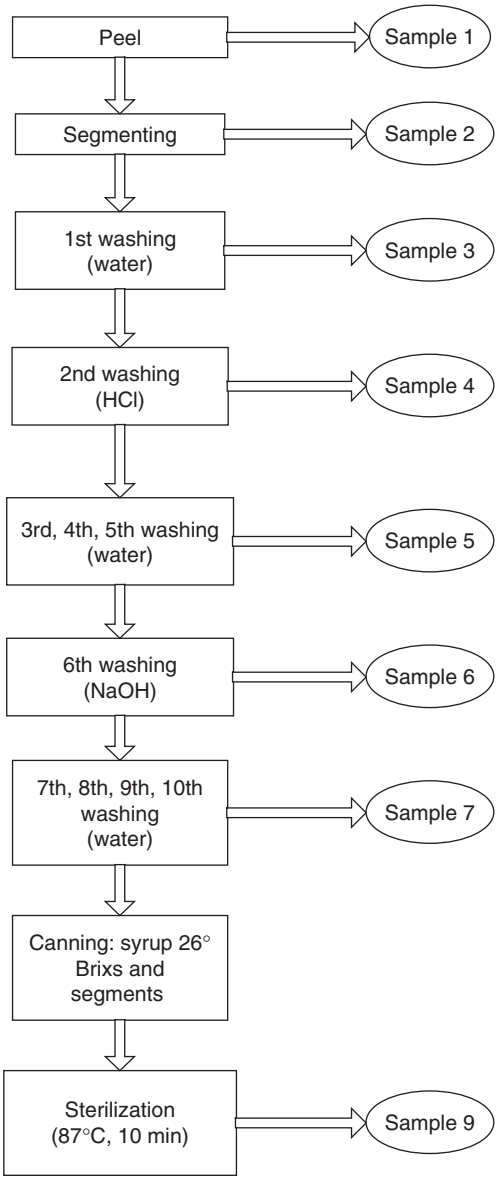

Figure 1. Mandarin canning study.

15 g of crushed sample with 30 mL of acetone (homogeneization 30 s) and with 60 mL of dichloromethane : petroleum ether 50 : 50 v : v (homogeneization 60 s).

A cleanup with aminopropyl cartridges was carried out. First, the cartridge was eluted with 15 mL of hexane. Then, 25 mL of the extract was evaporated until dryness (25°C), dissolved in 2 mL of hexane, and purified by the cartridge. A first elution was done with 9 mL of hexane and 8 mL of hexane : dimethiltercbuthylether 80 : 20 (v : v). The second elution was done with 5 mL of acetonitrile : water 50 : 50 (v : v).

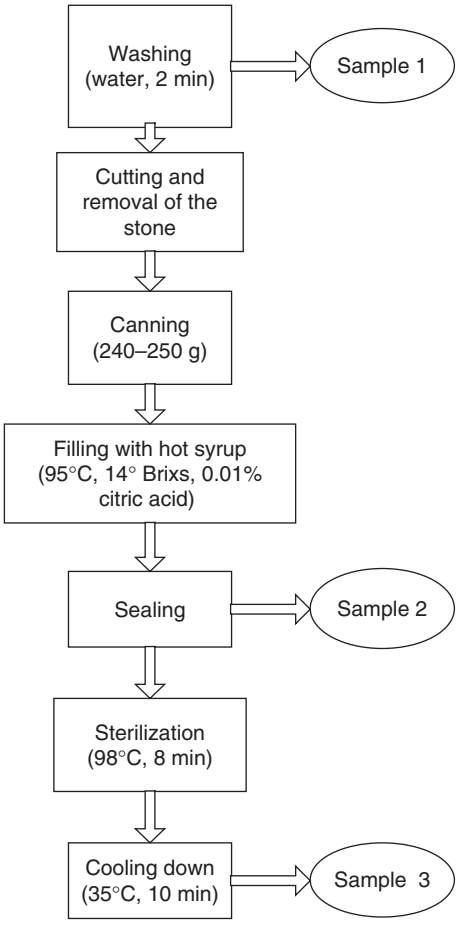

Figure 2. Apricot canning study.

Pyriproxyfen appeared in the first eluate and fenoxycarb, lufenuron, and flufenoxuron in the second eluate. The amount of matrix in the final extracts was $1\,g\,mL^{-1}$.

High-performance liquid chromatography-diode array detection analysis at 230 nm was carried out with an acetonitrile : water gradient (from 50 : 50 to 70 : 30 in 7 min and 70 : 30 for 8 min, v : v) and flow rate of $1\,mL\,min^{-1}$, and using a reverse-phase C8 column.

This methodology was validated according to ISO 17025 norm and SANCO Guide recommendations. A quality-control sequence was always introduced in the residue analyses to ensure the compliance of the validation values.

2.7 *Statistics*

The Minitab version 14.0 statistics program was used to obtain the descriptive statistical parameters and the linear regression of the data.

3. Results and discussion

For the validation of the analytical methodology for both standards and fruit matrices, the limit of quantification (LOQ) was 0.05 mg kg^{-1} in apricot and 0.10 mg kg^{-1} in mandarin; the linear interval was from the LOQ to 1.00 mg L^{-1} in apricot or to 2.00 mg L^{-1} in mandarin, with a linear regression coefficient (r^2) higher than 0.9; as regards repeatability, accuracy, and intra-laboratory reproducibility, a coefficient of variation (CV) of less than 20% was obtained with seven samples in standards and five samples in matrices, and the recovery percentages were always 70–110%. The precision and accuracy were studied at the LOQ and upper level of the linear interval (see table 1).

The residues and dissipation curves of the IGRs in apricots and mandarin when the phytosanitaries were applied in the field under GAP and CAP conditions are shown in figures 3 and 4 and table 2. The residues of flufenoxuron and lufenuron in mandarin were not detectable in GAP conditions when the citrus fruit was entirely crushed as the legislation obligates. However, they were detectable when CAP conditions were used. The dissipation rates of fenoxycarb and pyriproxyfen in mandarin and apricot in the crop dissipation study under GAP conditions are shown in table 3.

The dissipation rates found in the processing studies are shown in figures 5 and 6. In mandarin, all the IGRs presented residues only in the peel; in the other steps, the residues were not detectable. There was a residue transference in the canning of apricots for pyriproxyfen under GAP and CAP conditions and fenoxycarb under CAP conditions. The fenoxycarb residues in apricot for GAP conditions were below the LOQ (0.05 mg kg^{-1}).

All controls in the field were negative in terms of compound presence. A quality-control sequence was applied in each series of analyses to verify the compliance of the methodology validation parameters. Blanks of samples, reagents, and solvents, standards, and spiked samples at the lower and upper value of the interval were used. All blanks were negative in terms of compound presence. The recovery and r^2 values met the validation criteria (see table 4).

Table 1. Validation results of the standards and matrices.

	IGR	r^{2a}	Repeatability[b] (%)	Reproducibility[b] (%)	Recoveries[c] (%)
Standard I[d]	Fenoxycarb	1.00	1.84–0.50	1.27–0.71	
	Lufenuron	1.00	1.47–0.10	2.54–0.35	
	Pyriproxyfen	1.00	0.82–0.19	1.28–0.34	
	Flufenoxuron	1.00	1.80–0.26	1.89–0.46	
Mandarin	Fenoxycarb		8.19–4.27	12.44–4.78	97.59–73.44
	Lufenuron		16.07–3.49	7.66–1.85	79.28–71.72
	Pyriproxyfen		6.02–2.62	9.50–2.20	106.42–79.26
	Flufenoxuron		16.72–4.42	6.23–3.57	85.68–71.72
Standard II[e]	Fenoxycarb	0.999	12.33–0.75	9.48–0.87	
	Pyriproxyfen	1.00	6.06–0.16	7.27–0.57	
Apricot	Fenoxycarb		13.96–6.20	11.27–0.43	94.84–81.96
	Pyriproxyfen		14.85–8.19	16.78–3.96	93.02–78.14

[a]Linear interval, 0.10–2 mg L^{-1} in mandarin, 0.05–1 mg L^{-1} in apricot.
[b]Repeatability and intra-laboratory reproducibility determined by RSD (%) in the lower and upper level of the interval with $n = 7$ for standard and $n = 5$ for matrices.
[c]Recoveries in the lower and upper level of the interval with $n = 5$.
[d]Standard for mandarin.
[e]Standard for apricot.

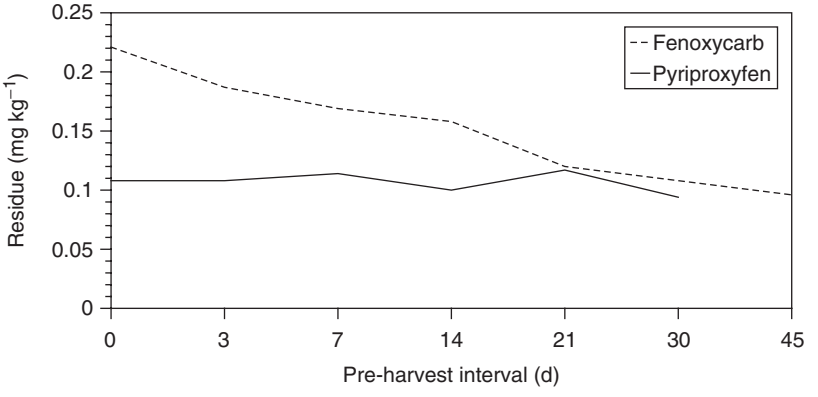

Figure 3. Dissipation rates of fenoxycarb and pyriproxyfen in satsuma mandarin under GAP treatment.

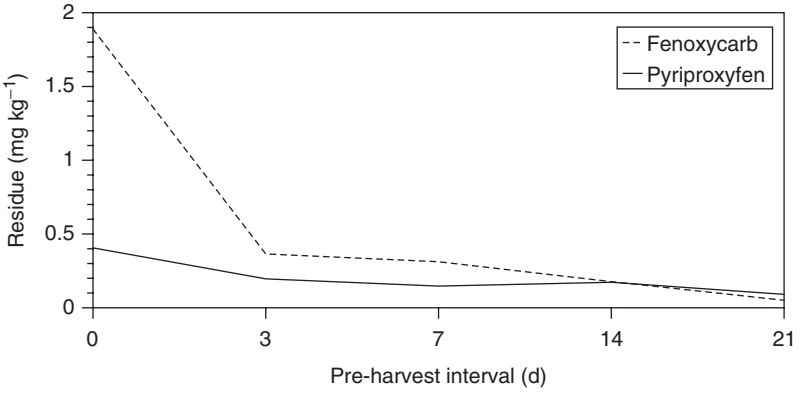

Figure 4. Dissipation rates of fenoxycarb and pyriproxyfen in bulida apricot under GAP treatment.

Table 2. IGR residues in the crop study under CAP conditions.

C (mg kg^{-1})	Mandarin	Apricot
Fenoxycarb	0.237	1.244
Flufenoxuron	0.099	
Lufenuron	0.186	
Pyriproxyfen	0.176	0.569

Table 3. Dissipation rates of IGRs in satsuma mandarin and bulida apricot.

	FEN–MND[a]	PYR–MND	FEN–APR	PYR–APR
Equation	$\ln C = -1.55 - 0.0258t$	$\ln C = -2.20 - 0.00329t$	$\ln C = 0.046 - 0.144t$	$\ln C = -1.23 - 0.0545t$
r^2	0.944	0.213	0.878	0.732
$T_{1/2}$ (d)	26	212	5	13

[a]FEN: fenoxycarb; MND: mandarin; PYR: pyriproxyfen; APR: apricot.

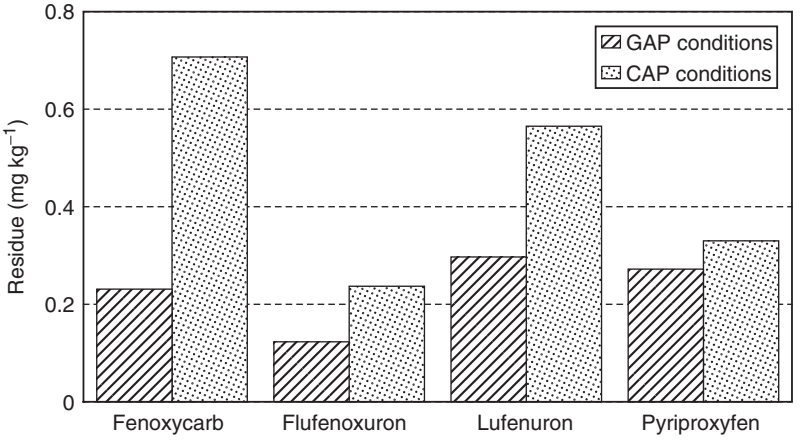

Figure 5. Residues found in the peel of mandarin in the canning studies.

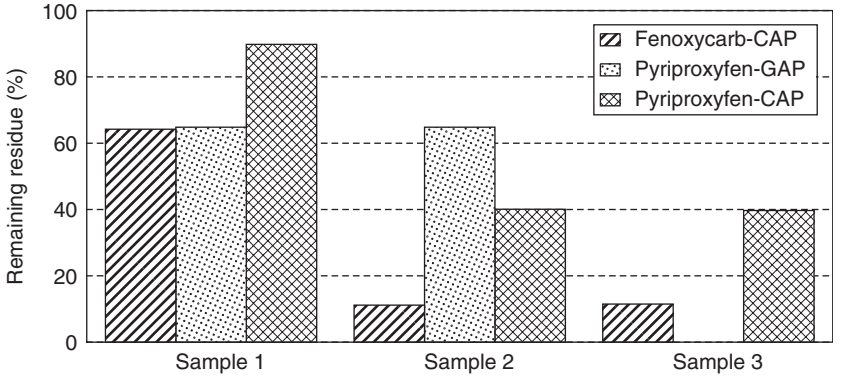

Figure 6. Dissipation rates of fenoxycarb and pyriproxyfen in the apricot canning studies.

In the crop dissipation study for mandarin under GAP conditions, only residues for fenoxycarb and pyriproxyfen appeared in the fruit. The two benzoylphenylureas, flufenoxuron and lufenuron, did not show any residues. Fenoxycarb started with 11% of its MRL (2 mg kg^{-1}) and reached 4.8% at the security time (45 days). Pyriproxyfen started with 21.6% of its MRL (0.50 mg kg^{-1}) and reached 18.8% at the security time (30 days). The dissipation curve of fenoxycarb followed an exponential regression model ($r^2 = 0.944$ in the logarithmic regression equation). However, pyriproxyfen did not follow this ($r^2 = 0.213$), showing a persistent tendency. Their half-lives were 26 and 212 days for fenoxycarb and pyriproxyfen in mandarin, respectively.

In the crop study for mandarin under CAP conditions, flufenoxuron showed a residue level of 33% and lufenuron 62% compared with their MRLs (0.30 mg kg^{-1}). Fenoxycarb reached 11.8% and pyriproxyfen 35.2% compared with their MRLs. Therefore, their residue levels were similar to that of the sample on the first day of application with GAP.

In the mandarin canning studies, all residues were found only in the peel of the fruit. In the processing study with samples of the application with GAP, fenoxycarb and

Table 4. Quality-control sequence values in the residue analyses.

	r^{2a}	Recovery LOQ (%)	Recovery UL[b] (%)
Fenoxycarb–mandarin	1.00	71.3	67.0
Lufenuron–mandarin	1.00	87.3	75.1
Flufenoxuron–mandarin	0.999	93.9	70.4
Pyriproxyfen–mandarin	0.995	99.2	80.7
Fenoxycarb–apricot	0.946	88.5	87.2
Pyriproxyfen–apricot	0.948	70.2	80.3

[a]Linear interval, 0.10–2 mg L^{-1} in mandarin, 0.05–1 mg L^{-1} in apricot.
[b]UL: upper limit of the interval.

pyriproxyfen residues were concentrated 2.4 and 2.8 times in the peel of satsuma mandarin, respectively. When CAP conditions were used, concentrations of 2.9- and 1.8-fold were found for fenoxycarb and pyriproxyfen, respectively. The residue levels for flufenoxuron and lufenuron in the peel of satsuma mandarin were 0.297 and 0.123 mg kg^{-1} in GAP conditions. In CAP conditions, flufenoxuron and lufenuron showed concentrations of 2.3 and 3 times, respectively.

In the crop dissipation study for apricot under GAP conditions, fenoxycarb started with a residue level (1.889 mg kg^{-1}) above the MRL (1 mg kg^{-1}) and reached 5.1% compared with it of this level at the security time (21 days). Pyriproxyfen started with a residue level (0.406 mg kg^{-1}) above the MRL (0.05 mg kg^{-1}) and was still above the MRL (0.091 mg kg^{-1}) at the proposed security time (21 days). The dissipation curve of fenoxycarb followed an exponential regression model ($r^2 = 0.878$ in the logarithmic regression equation). Pyriproxyfen followed an exponential regression model ($r^2 = 0.732$ in the logarithmic regression equation), too. Their half-lives were 5 and 13 days for fenoxycarb and pyriproxyfen, respectively.

In the crop study for apricot under CAP conditions, residue levels of 0.65 and 1.4 times were found compared with the initial levels of the application with GAP for fenoxycarb and pyriproxyfen, respectively. Thus, their residue levels were similar to the sample of the first day of the application with GAP.

In the apricot canning study for the application with GAP, no residues of fenoxycarb were detectable from the beginning of the process. For pyriproxyfen, the level of residues was 64.2% after washing; it had the same value after sealing, and the level decreased down to values below the LOQ in the can, compared with the residue level at the security time from which the fruit began the processing. Thus, the steps that contributed most in the decrease were the final sterilization and cooling down. In CAP conditions, there was an initial decrease to 64.2 and 89.8% after washing, and the remaining residues decreased further to 11.1 and 40% after the intermediate steps (cutting the fruit in half and removal of the stone, canning, filling the can with hot syrup, and sealing) and the levels in the final can were 11.4 and 39.7%, for fenoxycarb and pyriproxyfen, respectively. Thus, the steps that contributed most in the decrease were the intermediate steps.

All the treated samples of satsuma mandarin had lower residue levels than the official MRLs during the preharvest period in a treatment with GAP. In a critical second treatment, approximate levels to the initials ones in the GAP treatment were obtained, but all the residue levels were equal to or lower than the MRLs. In the industrial process to obtain canned products, peeling the fruit eliminated the IGR residues in both cases.

When the apricot crop was treated with fenoxycarb, the authorized MRL was respected. In contrast, when it was treated with pyriproxyfen, the MRL was exceeded. In critical phytosanitary applications, both residues were similar to those in the application with GAP. After the first step or washing in the industrial transformation, the fenoxycarb residues were not detected for the correct application, since they were already low in the harvested sample at the security time. For the critical application, the process initially started with higher residues and managed to reduce them significantly after the first step, which included an important change in temperature (filling with hot syrup at 95°C). For pyriproxyfen, the residues were observed after the washing and sealing for GAP but not in the final cans, and the second step which included an important change in temperature (sterilization and cooling down) decreased the residues down to values below the LOQ ($0.05\,mg\,kg^{-1}$). In the processing study for CAP conditions, the residues of pyriproxyfen were present from the beginning to the end of the process, but they decreased more in the filling with hot syrup.

Using CAP, the field dissipation rates of fenoxycarb in apricot were higher than pyriproxyfen in apricot, which was higher than fenoxycarb in mandarin and this was higher than pyriproxyfen. This is because of the different characteristics of the fruits and the chemical nature of the pesticides. The particular structure and composition of the peel of citrus fruits are known to retain pesticides, due to numerous oil sacs or glands filled with aromatic essential oils. Also, it is known that pyriproxyfen is a relatively stable aromatic compound, and fenoxycarb is expected to break down relatively quickly in plants.

In the processing studies, the peeling of the citrus fruit and the apricot canning steps including a rise in temperature were effective in reducing the pesticides levels. The elimination of the mandarin peel with its lipofilic components and the changes produced in the pesticides stability in the apricot canning reduced the pesticide concentrations.

Finally, these pesticides complied with the official MRLs in apricot and mandarine. Pyriproxyfen, which has not yet been authorized in apricots, did not comply with its MRL in peaches when the legal parameters for peaches were used. The dissipation under field conditions was higher in apricot than in mandarin and also higher in fenoxycarb than in pyriproxyfen. In the processing studies, there was only residue transference in the canning of apricots, but in all cases there was dissipation of pesticides. All final cans contained residues much lower than the MRLs.

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