Chapter

Insecticide's Disappearance after Field Treatment and during Processing into Byproducts

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Abstract

Insecticide's disappearance after field treatments could be ascribed to different factors such as sunlight photodegradation, dilution effect due to fruit growth, co-distillation during fruit respiration and evaporation. Moreover, the epicuticular waxes could speed or slow down the degradation rate, and the cultivation in an open field or greenhouses could affect the residues dramatically. After harvest, the processing techniques to produce byproducts deeply influence insecticide residues. For example, fruit drying, winemaking, the industrial processing of tomatoes to produce purée, triple-concentrated paste, fine pulp, diced, olive processing to obtain table olive and olive oil, and other industrial applications on fruits affect residues and their half-life time. The scope of this chapter is to highlight the major factors responsible for the disappearance of insecticides after treatment. Moreover, the chapter intends to review the influence of the industrial processes on insecticide behaviour when the raw material is transformed into its byproducts.

Keywords: insecticide disappearance, photodegradation, fruit growth, food processing

1. Introduction

Insecticides are plant protection products, namely pesticides, intended to prevent, destroy, repel, or mitigate pests, regulated in the EU by Regulation (EC.) No 1107/2009 and Regulation (EC.) No 396/2005 [1, 2]. Their toxicological and legal limits on food (MRL), human and environmental risk assessment are defined, set and continuously revised.

Before an active substance can be used within a plant protection product, the European Commission must approve it. Active substances undergo an intensive evaluation process before a decision can be made on approval.

Insects represent the most abundant group of animals on the Earth; the number of species is more than any other group with an estimated number of living species of insects of 30 million and is the major competitors with humans for agriculture resources [3].

Insecticides act in different modes, disrupting the nervous system, impacting the development of the exoskeleton, or have a repelling activity. In addition, insecticides can be applied in various formulations such as sprays, dust, gels and baits, showing a different level of risk to non-target insects, people, pets and the environment [4].

In natural environments, insects live in a complex relationship with mutual limitations and constrictions, whereas in defined agroecosystems, the natural regulations are limited, and insect pest outbreaks can occur [5].

The factors influencing insecticide disappearance after treatment and during processing are primary to evaluate the possible dangerous effect of insecticides on human health and environmental safety.

2. Materials and methods

Photodegradation studies have been carried out under sunlight in field and in model systems; moreover, trials on model systems under artificial lights have been widely used. Sunlight experiments in the field have studied the disappearance rate of insecticides comparing open field treatments versus greenhouse treatments, and the degradation compounds in the greenhouse have been investigated simulating with petry dishes the effect of the covering glasses [6]. Other model systems built up trials with catalysator to investigate photocatalytic degradation with TiO_2 or oxidating compounds such as H_2O_2 and O_3 [7–14], and the different effects of soil thin layers or epicuticular waxes extracted from different commodities [15–17]. Model systems in laboratories trials employed different light sources, and the most common are represented by the xenon arc lamp and mercury lamps [12, 15, 18]. Trials were performed in water or methanol solutions in Pyrex (adsorb length < 290 nm) and quartz glass filter photochemical reactors.

Drying experiments have been conducted following traditional processes under sunlight exposure or the industrial process in an oven with controlled temperature and humidity [19–28].

The effect of fruit growing was assessed in field and greenhouses trials, correlating fruit growing with insecticide disappearance rate [29].

The effect of the technological process has been studied at industrial to avoid laboratory mystification of the results. Vinification, olive oil production and tomatoes processing have been carried out in real conditions allowing a real risk assessment [30–52].

Analytical measures of the insecticides and their metabolites have been made mainly using liquid chromatographic apparatus with UV–VIS or mass spectrometry detectors (MS).

3. Factors affecting insecticide's depletion

3.1 Photodegradation

Insecticides released in the environment are actively photodegraded by sunlight radiation, representing one of the most destructive pathways [5]; this is because most pesticides absorb UV–VIS bands at medium-short wavelengths. However, the sunlight reaching the Earth is mainly composed of UV-A and variable amounts of UV-B with only small amounts of short wavelengths of UV radiation; therefore, the effect on pesticides should be only of limited importance [7].

Photodegradation of insecticides could lead to non-toxic metabolites or more toxic compounds, such as systemic insecticides that are converted into more water-soluble compounds. For example, 95% of the nicotinoid imidacloprid is degraded into olefine, and 4-5-dihydroxy when applied as a drench or granule. These two metabolites are active against insect pests such as aphids. Thiamethoxam is converted to clothianidin, whereas acetamiprid is converted into five active metabolites [53].

The possible toxic effect of insecticides metabolites has led to the development of environmental monitoring studies to evaluate the presence of the parent compound and its metabolite in water and soil.

The mechanisms involved in the photodegradation process could be direct photodegradation, photosensitized degradation, photocatalytic degradation and degradation mediated by hydroxyl radicals [54].

When dealing with food and the environment, UV radiation comes from the sunlight, and direct photodegradation represents the primary mechanism, while other mechanisms are involved when remediation studies occur [7].

Plant surfaces, especially leaf surfaces, are the first reaction environment for a pesticide molecule after application, and spray drift would indirectly present a similar situation. Photolysis on soil surfaces becomes essential when a pesticide is directly applied to soil or not significantly intercepted by plants, providing that the leaf cover does not shade the ground from sunlight. Because the foliar interception of pesticides depends on plant species and usually increases with their growth stage [55], the importance of soil photolysis is considered to be lessened when plants become mature. Spray drift after pesticide application or wash off from plants by rain is the indirect route by which a pesticide reaches the soil [5].

Photodegradation of insecticides in typical environmental conditions did not lead to individual responses (homolysis, heterolysis, or photoionization). Therefore, trials in model systems have been carried out to define the effect of direct irradiation [56, 57]. These trials investigate photodegradation in water solutions in the presence of catalysts or OH donators.

Photodegradation experiments showed a higher rate in aqueous solution than in dry film; therefore, the results of model systems should be correct accordingly when dealing with fruit and vegetables in the field.

Amidinohydrazone insecticides led to three products in an aqueous medium within 10 hours and were only slightly affected by pH [9]; on the other hand, carbaryl and propoxur photodegradation increased with the pH, and the main photochemical products were derived from the ester bond cleavage [54].

Carbamate insecticide photodegradation has been widely studied, and different UV irradiation lengths and mediums have been used in model systems to reproduce the natural condition. Apolar solvent (hexane, cyclohexane, isopropanol) was used to simulate plant surface, and water at different pH was used to evaluate the influence of acidity; in addition, additional studies added O_3 or other oxidants (H_2O_2, TiO_2) to verify the enhanced oxidant effect of UV irradiation at selected wavelengths [7, 9–14]. Dry film photodegradation trials in the presence of epicuticular waxes extracted from fruits and vegetable commodities or soil with humic substances led to different results in the half-life time of insecticides [12, 13].

The epicuticular waxes from different vegetables and fruits did not show univocal results, decreasing or enhancing photodegradation (**Table 1**) [15].

The photochemical degradation of carbaryl and carbofuran under sunlight and UV (λ 290 nm) exposure in the natural waters of Northern Greece has been investigated. The major photoproducts observed were carbofuran–phenol from carbofuran and naphthol from carbaryl [54].

The analysis of the degradation pathways of aldicarb and carbaryl in water showed as major photodegradation products aldicarb sulfoxide and 1-naphthol, respectively. In addition, the study highlighted the influence of the UV source on the rate of photodegradation [28].

Organophosphorus insecticides in water solutions showed first-grade rate constants with an observed half-life in the range of hours [58, 59].

Neonicotinoid pesticides have shown a high degree rate of photodegradation on tomato leaves after treatment in water solutions [60, 61].

		$K_{obs} \times 10^{-5}$ s^{-1}		T ½ (min)		
Compound	K^w/K^b	$Wax^a \pm SD$	Blank ± SD	Wax^a	Blank	r^2
Methiocarb	1.0	2.5 (0.06)	2.5 (0.08)	436	438	0.9976
Methiocarb sulfone	0.9	0.35 (0.08)	0.39 (0.11)	3351	2964	0.9955
Fenthion	2.9	5.6 (0.4)	1.9 (0.5)	204	593	0.9889
Aminocarb	0.3	5.2 (0.2)	19.2 (1.8)	222	60	0.9921
Pirimicarb	3.0	19.4 (1.2)	6.4 (1.5)	59	181	0.9959

[a] *70ug cm^{-2}*
[b] *blank*
[w] *waxes*

Table 1.
Photolysis rates of some insecticides in the presence of epicuticular waxes of Persica laevis *[15].*

3.2 Fruit and vegetable growing and shape

Insecticide amount on fruit and vegetable is related to the moment of treatment, the shape and cultivar. Fruits and vegetable sizes increase during development depending on the species and the agricultural practice adopted, modifying the rate surface/weight (s/w) and influencing the residue amount profoundly. The maximum residue limit (MRL) is the highest level of pesticide residue acceptable in food or feed when pesticides are applied following Good Agricultural Practice (GAP) [62] and is expressed as mg/Kg or mg/L of active ingredients (a.is.); therefore, the rate surface/weight (s/w) represents the discriminant leading to the residue amount.

The first treatment is made after the fruit set; when no other factors are involved in the residue decrease, the amount of the insecticides in the harvested commodities at commercial ripening is reduced by the growth factor and the residues are lower when the treatment is done much in advance of the harvest.

Therefore, when insecticides are applied to fruit and vegetable before harvest when the development is concluded, the growth dilution could not more influence the residue amount.

On the other hand, the shape and final size of the commodities have great importance. For example, tomatoes have different dimensions and shapes depending on the cultivar ranging from 12 to 200 g from cherry to beef heart. The surface/weight ratio for 1 Kg is notably higher for cherry; therefore, the same treatment applied on the cultivar would lead to entirely different results with higher residue expressed in mg/Kg in the cherry tomatoes. The cultivar (CV) Koreniki has small olives (1–2 g), whereas Yacouti has big olives (5–6 g), accounting for a lower s/w ratio and minor final residues (**Table 2**).

In iceberg and romana lettuce CV, the edible parts have different shapes: an open calyx in romana and ball-shaped in the iceberg; similar consideration can be made for artichoke when comparing meda or masedu cv (calyx shape) to spinoso sardo and romanesco cv (close shape). The calyx shape allows the deposition of treatment solution among the fruit leaf, with prolonged contact and final higher residue concentration, whereas the ball and close shape let the solution slide down, allowing only a short contact (**Figure 1**). Moreover, the outer leaves in both cases are removed before eating [29].

3.3 Drying

Drying is one of the oldest and most common preservation methods; water removal minimizes many moisture-driven deterioration reactions. However, drying fruit to obtain raisins, prunes and apricots could increase insecticide levels in the

Commodities	Cultivar	s/w ratio	
Olive	Yacouti	0.7	
	Koroneiki	1.3	
Tomatoes	Shiren	1.8	
	Caramba	0.8	
		Weight (diluting factor/day)	
Peaches	Flavorcrest	45 (1.07/1)	135 (3.21/15)

Table 2.
Surface/weight ratio of different cultivars and after development.

Figure 1.
Different shapes of lettuce and artichoke cultivars.

final product due to the concentration factor (4, 3 and 6, respectively) [19]. In addition, sunlight or oven drying processes lead to different results [20].

In raisins, insecticides decrease has been ascribed to the temperature of oven drying and lesser effect to sunlight, correlating the decrease to the degradation of the pesticides [21]. However, trials in model systems evaluating the process of disappearance during oven drying showed that insecticide co-distillation with water could be as important as heat degradation [22, 23].

Apricots, plums and prunes showed lower residues in the dried product; however, results were not the same for the different pesticides; moreover, the effect of sunlight in apricot was more efficacious (**Table 3**) [24–26].

Chilli pepper subjected to oven drying showed a concentration factor of almost 5, and the insecticides tested had different behaviour some were more concentrated in the final product while other decreased [27]. A similar experiment on orange slices showed a general decrease in the pesticide investigated even if the mechanism was not explained [28].

3.4 Technological processes

3.4.1 Wine, beer and byproducts

The fate of insecticides residues on grapes during winemaking has been widely studied [30–37]. Depending on the technology adopted, two categories of wine

Commodities	Insecticides	Fruit weight (g)	mg/kg ± SD	Conc. factor	Reference
Apricots					[25]
Diazinon	Fresh fruit	43.3 ± 3.3	0.50 ± 0.13		
	Dried fruit	6.6 ± 0.6	0.63 ± 0.20	6.56	
Phosalone	Fresh fruit	42.5 ± 2.0	0.48 ± 0.14		
	Dried fruit	7.6 ± 1.1	1.56 ± 0.37	5.59	
Prunes					[24]
Phosalone	Fresh fruit	38.7 ± 1.3	0.21 ± 0.06		
	Dried fruit	12.5 ± 1.2	0.62 ± 0.16	3.09	

Table 3.
Insecticides level after drying process.

are obtained, white wines and red wines. The former are wines produced in the absence of skins, whereas red wines are produced with maceration in the presence of the skins. During fermentation, two main waste products are generated, lees and grapes. These fractions adsorb insecticides due to the affinities for the solid residues during alcoholic fermentation and, therefore, sequestered them from the must, which results free from residues or with reduced amounts with respect to the grapes. Moreover, active degradation by the yeast could be encountered, and these results were also confirmed during beer preparation [31, 32]. In the second stage, the malolactic fermentation by bacteria can actively decrease pesticide levels, which would encounter an added decrease with the clarification step using fining agents such as activated carbon, bentonite, polyvinylpolypyrrolidone (PVPP), gelatin, egg albumin, isinglass-fish glue, and casein [31, 38–41].

The spirit drink industry can use grapes and lees to produce alcohol, and distilled beverage spirits and insecticides could concentrate in the distillate of a factor between one (cake) and six hundred (lees) (Garoglio 1973). When wines are used to produce distillate, the concentration factor would be 10 times.

Literature data showed that only small amounts of fenthion (2%) and quinalphos (1%), and other organophosphate insecticides passed during the distillation process from artificially contaminated lees [42–44], indicating that insecticides hardly migrate to the distilled spirits.

3.4.2 Olive oil

The transfer to virgin olive oil is related to the active ingredients' octanol/water partition coefficient during the production step. Since no MRL is set in olive oil, the values for olive are adapted to the oil relating to the partition coefficient. In 2015, EU differentiated between fat-soluble and fat insoluble compounds, setting processing factors of 5 and 1, respectively [45]. On the other hand, highly polar insecticides showed negligible transfer rates in the oil being concentrated in the aqueous phase [46].

Insecticides with Kow > 0 increase their concentration in the oil while decreasing their polarity. For example, organophosphorus insecticides concentrate 7 times in the oil following the concentration factor from olive to oil (7 kg olives for 1 l of oil) [47]. Although, on the other hand, triazoles and neonicotinoids displayed different behaviour, so that an increase of hydrophobicity did not cause such an increase of pesticide transfer efficiency for these two classes, water addition during the extraction step caused a decrease of the insecticides with lower Kow [46–48].

3.4.3 Tomatoes processing

Europe is the most important producer of tomatoes, and integrated pest management strategies (IPM) are applied widely. For example, insecticides applied in the field could be transferred and concentrate into processing products such as purée, triple concentrated paste, fine pulp, and diced tomatoes [49].

Washing and peeling led to a decrease in insecticide residues, even if washing affected only the pesticide adsorbed on the dust adhering to the surface [50, 51].

Different batches of tomatoes from different fields subjected to different agriculture procedures and pesticide treatments are processed jointly during the industrial process. Therefore, a dilution effect would occur during the various production steps. The main effect related to the decrease of insecticides during tomatoes processing are represented by peeling and the dilution effect [52].

4. Conclusions

The disappearance of insecticides after treatment could be related to many different paths. The main effects in the field are related to sunlight photodegradation and the development of the fruits during fruit growing leading to a decrease of the residues below the legal limit and sometimes the analytical detectable levels. Run-off and washing could affect only the residues adsorbed in the adhering dust on fruits and vegetable surfaces not influencing the residues adsorbed in the epicuticular waxes. Drying causes a reduction in weight, theoretically the residue could increase giving a value that is a function of the concentration factor, however the results showed a decrease in insecticide residues in foodstuffs. The different processing steps affect insecticides residues involving partition, microbiological and chemical degradation, and adsorption on the waste such as lees, marc, vegetation water and pomace.

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Conflict of interest

The authors declare no conflict of interest.

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