Chapter 3

Role of the Formulation in the Efficacy and Dissipation of Agricultural Insecticides

Karina Buzzetti

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.72340

Abstract

Considering the implications the formulation may have on the effectiveness and residuality of an active ingredient, four trials were conducted comparing two commercial formulations of the diazinon insecticide, two of acetamiprid, two of lambda-cyhalothrin, and, finally, three formulations of imidacloprid. For diazinon and acetamiprid, the comparison parameters used correspond to efficacy against three key pests in apple trees: *Cydia pomonella*, *Diaspidiotus perniciosus*, and *Pseudococcus viburni*; for l-cyhalothrin, efficacy against *C. pomonella* was compared; and for imidacloprid, differences in control *P. viburni* were established. In all cases, their persistence was established in terms of initial and final residue levels in samples of fruits, at 1 and 25 days after application (DAA). Different formulations of the same insecticide correspond to a relevant factor in the general behavior that each product presents in field conditions, being able to affect parameters such as its persistence in the fruit and/or initial deposit of the active ingredient. This variation was demonstrated in the comparison performed on acetamiprid, imidacloprid, and diazinon, but it was not so in l-cyhalothrin. Efficacy was affected in all parameters evaluated for each group of insecticides, demonstrating that different formulations can deliver different biological activity in the control of various pests.

Keywords: pesticide formulations, efficacy, dissipation, residues, insecticide

1. Introduction

The use of multiple crop protection chemicals is a common practice in fruit production, given the requirements of different markets such as the search for plant health, organoleptic quality, and higher yields. In this context, pesticides are applied to agricultural systems for the purpose of protecting plants from damage due to weeds, insects, or diseases [1]. Then, the term pesticide or agrochemical is used to define a wide range of compounds including insecticides, fungicides, herbicides, rodenticides, molluscicides, nematicides, plant growth regulators, defoliant, and others [2].

The role of pesticides in global agriculture has been questioned by United States Environmental Protection Agency (EPA), the European Community, and institutions focused on the consequences of pesticides in human health and environmental subjects [3, 4]. The continuous revaluation of registered pesticides combined with major restrictions like lesser tolerance to residues of pesticides on food has led to an overall trend of reduced risk from pesticides using, for example, innovations in the development of new formulations [5]. It is understood by new formulation a new way of presenting the pesticide for sale, which generally includes, in addition to the active ingredien(s), different adjuvant(s), and/or other formulants combined to render the product useful and effective for the purpose claimed [6].

The supply of plant protection products is wide, although it varies from country to country according to its internal regulations and requirements. However, global development makes it possible to commercially find the same active ingredient formulated in various ways, which is expected to affect the final behavior of the pesticide, with consequences on the efficacy [7]. Some of the first pesticide formulations developed in the agricultural industry (like granules, aqueous solutions, dusts, powders, and mineral oil in water emulsions) was based on simple technologies. However, since the 1980s, the pesticide industry has made great strides for the development of new formulations, focusing in particular on the search for greater chemical stability, optimization of biological activity, differentiation, and greater safety in use [8]. In addition, the search for decreasing the dose required per hectare to reduce the amounts of pesticides distributed in the environment has focused on the development of new formulations [9, 10]. The main factors that determine the design of a formulation are the solubility characteristics of the active ingredient (AI), cost of manufacture, and the intended use, so interdisciplinary sciences are required in each new formulation development [11].

The efficacy of agrochemicals as crop protection agents is generally a function of the intrinsic properties of the active ingredients, such as their toxicity, plant movement, penetration capacity, and mechanism of action [12] but also can be influenced by the formulation and the mode of application of the commercial product and the participation of surfactants and adjuvants among other parameters [13]. Formulation is a key tool because different formulations can promote stability to photochemical degradation, or decrease the amount of active ingredient necessary to achieve pest control [14]. Different works propose that a formulation can improve handling safety and can play a crucial role in the duration of delivery of the active ingredient [15, 16]. The formulation may also be a key point in avoiding phytotoxicity [17] or incompatibility on mixes with other agrochemicals [18].

The production of fruit in Chile corresponds to an industry focused on the export of fresh fruit [19], so it is subject to different phytosanitary requirements [20]. Within them, pest management is a relevant item, where the main management is carried out based on the chemical synthesis insecticides [21]. Due to the high rate of use of these products in developing countries like Chile [22], the chemical industry has found an attractive market, generating a wide range of insecticides, with several formulations of the same active ingredient. The above occurs, for example, with neonicotinoid insecticides acetamiprid and imidacloprid [23]; with the organophosphate insecticides diazinon [24], chlorpyrifos [25]; and with the pyrethroid insecticide lambda-cyhalothrin [26], among others. All these insecticides are commonly used in apple orchards in Chile.

Acetamiprid and imidacloprid are widely used to control obscure mealybug (*Pseudococcus viburni*) (Hemiptera: Pseudococcidae), San Jose scale (*Diaspidiotus perniciosus*) (Hemiptera: Diaspididae), wooly apple aphid (*Eriosoma lanigerum*) (Hemiptera: Aphididae) [27] and also, in the case of acetamiprid, is used to control codling moth (*Cydia pomonella*) (Lepidoptera: Tortricidae) on apple orchards [28, 29]. Diazinon is mainly used in the control of wooly apple aphid [30] and mealybugs [31] until the first stages of fruit development, while l-cyhalothrin is used up to the preharvest period to control codling moth [32]. The use of these pesticides is suggested based on their control objective, respecting a preharvest interval estimated to comply with the maximum residue limits. These intervals are currently estimated for the active ingredient independent of the formulation used [33], even when different works propose that formulations can affect dissipation of residues [34] and residue amount [35]. Likewise, formulation can affect efficacy of the application, generating a direct impact on the number of applications required to achieve adequate control [36, 37]. Also, formulation type might impact on the proportionality of residues, especially when changes in rate (kg active ingredient ha^{-1}) are accomplished by changing the spray concentration, because depending on the type of formulation, increasing spray rate will also increase surfactant and other adjuvant concentrations in the spray solution which can help the crop to retain for a longer period the residue [38]. About the influence on the efficacy, for example, a comparison performed between two formulations of imidacloprid and carbofuran found an increase in the control period of aphid and leafhopper in potato, when using encapsulated formulations of those insecticides compared with commercial formulations WP and G, respectively, but not in the dissipation of its residues [39].

The aim of this chapter is to evaluate effectiveness and residuality of two commercial formulations of the diazinon insecticide; two commercial formulations of acetamiprid, two commercial formulations of active ingredient lambda-cyhalothrin, and finally, three commercial formulations of imidacloprid insecticide. For diazinon and acetamiprid formulations, the comparison parameters used correspond to the efficacy in the simultaneous control of three primary importance pests in apple trees: *C. pomonella*, *D. perniciosus*, and *P. viburni*; for l-cyhalothrin formulations, efficacy against *C. pomonella* was compared; and for imidacloprid formulations, differences in control *P. viburni* were stablished.

2. Methodology

2.1. Insecticides

Assays were conducted using commercial formulations of insecticides. Then, diazinon 50% p/v emulsion in water (EW) emulsion (Diazol® 50 EW; Adama Makhteshim Ltd.) and diazinon 40% p/p wettable powder (WP) (Diazinon® 40 WP; Anasac Chile S.A.) were compared. Also was performed the comparison between acetamiprid 70% wettable powder (Hurricane® 70 WP; Anasac Chile S.A.) and 20% soluble powder (Mospilan® 20 SP; Nippon Soda Co., Ltd.). For lambda-cyhalothrin, 5% p/v microcapsule suspension (Karate Zeon® 050 CS; Syngenta S.A.) and 5% emulsifiable concentrate (EC) (Zero® 5 EC; Anasac Chile S.A.) formulations were compared, and finally, for imidacloprid insecticide, 20% p/p soluble liquid (SL) (Confidor® Forte 200 SL; Bayer CropScience AG), 35% p/v suspension concentrate (Confidor® 350 SC; Bayer CropScience AG), and 70% p/p wettable powder (Punto® 70 WP; Anasac Chile S.A.) were used.

2.2. Efficacy evaluations

During the spring of 2016, an apple orchard, cultivar *Royal Gala* located in the main pome fruit-growing area of Chile (34°46′45.9″S 71°02′50.0″W), was selected for this study. This orchard was naturally infested with the San Jose scale (*D. perniciosus*) and obscure mealybug (*P. viburni*). Prespraying evaluation was performed, determining that the appropriate statistical design was completely randomized with four replicates (each one with 50 plants, equivalents to 0.125 hectares).

The climatic conditions at the study period were as follows: average air temperature of 18.5°C (8.8–28.1°C) and relative humidity of 65.4% (33.2–97.6%). The first 22 days were free of precipitation, and then a total of 4 mm were recorded between days 23 and 25 post application. The phenological status at the beginning and the end of the study was 16 and 25 mm of diameter of fruits, respectively.

For *C. pomonella* evaluations, artificial infestations with neonate larvae (L_1) were performed on laboratory over 100 uninfested fruits collected per experimental unit. Neonate larvae were obtained from previous breeding in the laboratory, with insects coming from orchards not previously treated with insecticides. The fruits were collected from the experimental units at 3, 7, 10, 14, 21, and 25 days after application (DAA); collecting them from the pedicel to avoid the excessive manipulation of the residue of insecticides or removal. One larva was used per fruit, and mortality was recorded under microscope at 24 h post each infestation. Between infestation and evaluation, the fruits were maintained in breeding chamber at light conditions: darkness 16: 8 h, with 16 ± 2°C.

For *D. perniciosus* and *P. viburni* evaluations, the number of infested fruits and the number of live scales and live mealybugs were counted under microscope on 100 fruits collected per experimental unit, reaping 2 apples randomly per tree from each repetition at 3, 7, 10, 14, 21, and 25 DAA. In all cases to score insects as dead, failure of the insect to respond when probed with a dissecting needle, shriveling, and color variation was considered.

Mortality of codling moth larvae percentage was calculated for each insecticide and corrected using the Abbott's formula [40]. The data of efficacy on San Jose scale and obscure mealybug obtained from the experiment described above separately by active ingredient were subjected to analysis of variance (ANOVA) by taking appropriate transformations. Mean comparisons in significant ANOVAs were performed with a Tukey's test ($p \geq 0.05$). Statistical analyses were conducted using the software Minitab®16.1.0 (Minitab Inc.).

2.3. Treatments

A control treatment without insecticide applications was considered. In order to represent the use of insecticides under equal conditions, a single dose was used per active ingredient

(A.I.), given a total of 10 treatments and control included. Then, two treatments contained 50 g of diazinon/100 l of water; two treatments contained 8.4 g of acetamiprid/100 l; two treatments contained 1 cc of lambda-cyhalothrin/100 l; and three treatments contained 21 g of imidacloprid/100 l.

All applications were performed just once on the season, on November 2, with a conventional hydraulic sprayer (Line Ecofrut 2000, Parada S.A) dosing each treatment for 2000 l of water per hectare. Between treatments were left at least 30 m free of evaluations to avoid interference in the measurements.

2.4. Residue estimation of insecticides

Four apple samples (4 kg per experimental unit) for determination of each insecticide residues were taken at 1–25 DAA from all treatments [41]. Apple samples from each replicate of each treatment were chopped into small pieces and mixed, and subsample (100 g) was used for extraction.

Determination of acetamiprid and imidacloprid residues was done using P-002 Luke, method based on gas chromatography with mass detector (GC-MS) and high-performance liquid chromatography (HPLC) with triple quadrupole detector (MS/MS) [42, 43]. Determination of diazinon and l-cyhalothrin residues was done using gas chromatography (GC) with triple quadrupole detector (MS/MS) [44]. Finally, the data obtained on the initial and final deposits of different formulations of each active ingredient were subjected to ANOVA. For imidacloprid, mean comparisons were performed using ANOVA and Tukey's test ($p \geq 0.05$).

3. Results and discussion

3.1. Efficacy of diazinon formulations

Major knockdown effect and longer residual period to control *D. perniciosus* (**Figure 1**, **Table 1**) and *P. viburni* (**Figure 2**, **Table 2**) was achieved by using emulsion in water (EW) than wettable powder (WP). In addition, higher levels of mortality of both pests were achieved with the use of EW formulation. One work performed with diazinon against the attack of San Jose scale crawlers showed that diazinon provided 12–13 days of protection [45], which can be considered similar to results obtained on this chapter for WP formulation, but apparently it is underestimated for EW formulation. On both parameters (mean of infested fruits by scales or mealybugs and mean of living scales or mealybugs on fruits), EW seems to be effective even until the last evaluation carried out at 25 DAA.

On the other hand, about *C. pomonella* control (**Figure 3**), both formulations showed and optimal and similar control until 10 DAA, and then, better results—but not optimal—were obtained with EW formulation. One work conducted in 1965 proposed that for diazinon, optimal insecticide activity against *C. pomonella* would have an approximate duration of 6 days [46]; in the present work, demanding for 90% minimum of larvae mortality, both formulations deliver 10 days of control. On 14 DAA evaluations, EW formulation showed a mortality level close to 80%, which is considered insufficient from the economic point of view for the

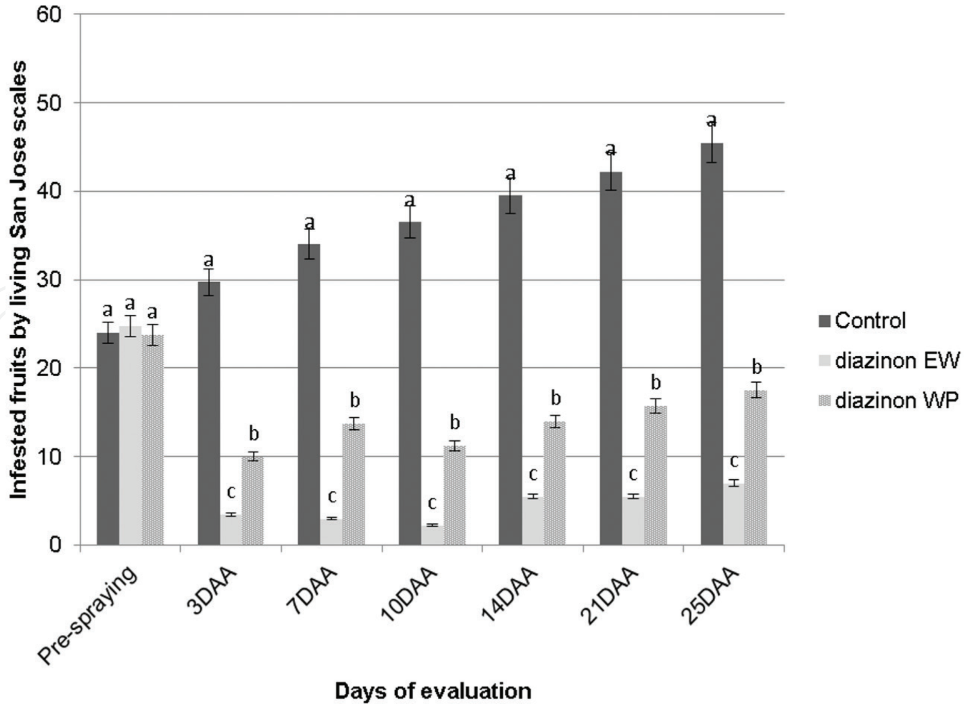

Figure 1. Mean of infested fruit by living San Jose scale according to the treatment of diazinon formulations. Values followed by different letters indicate significant differences with $p < 0.05$ (ANOVA, Tukey's test).

farmer. Therefore, although both formulations show significant differences in the control of *C. pomonella*, commercially (demanding a mortality of at least 85%), both only control efficiently for up to 10 days.

3.2. Residues of diazinon formulations

Emulsion in water generates higher initial and final diazinon residues than wettable powder (**Figure 4**). These results are probably due to differences between formulations that affect

Mean of living scales (*D. perniciosus*) on fruits according to diazinon formulation by evaluation moment (DAA)							
Treatment	**Prespraying**	**3DAA**	**7DAA**	**10DAA**	**14DAA**	**21DAA**	**25DAA**
Control	31.00a	36.00a	39.25a	40.00a	43.75a	47.75a	51.75a
Emulsion in water	29.25a	7.25c	4.75c	3.25c	6.75c	7.75c	8.25c
Wettable powder	27.50a	11.75b	14.75b	12.75b	12.00b	17.50b	19.25b
F	**1.08**	**200.45**	**78.63**	**72.98**	**172.79**	**155.83**	**137.18**
***p* value**	**0.379**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**

Means followed by different letters indicate significant differences with $p < 0.05$ (ANOVA, Tukey's test).

Table 1. Mean of living San Jose scale on fruits according to the treatment of diazinon formulations.

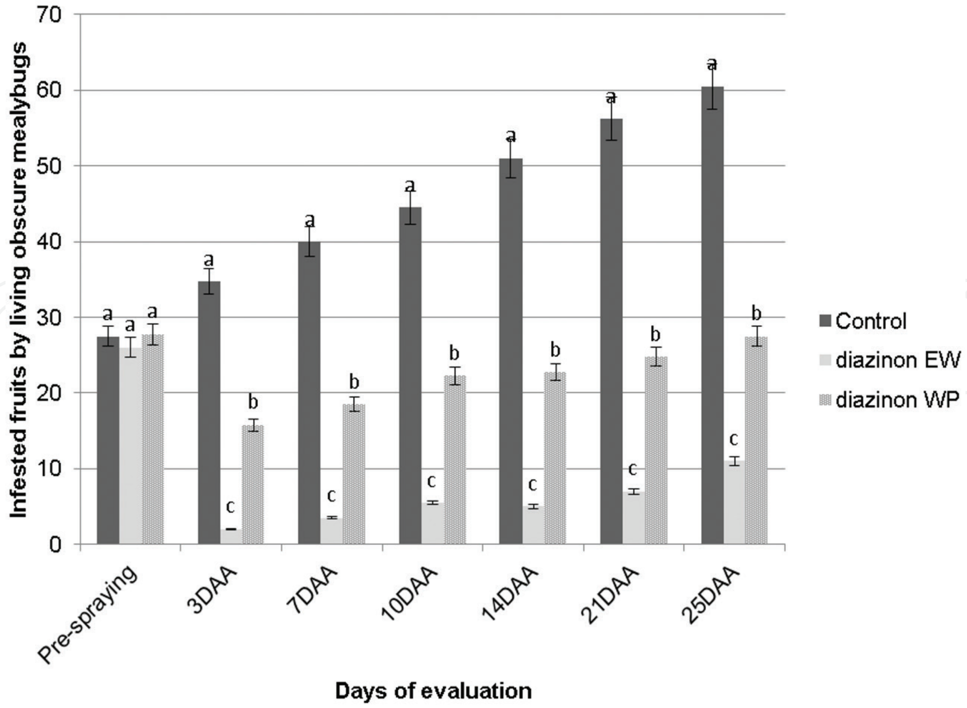

Figure 2. Mean of infested fruit by living obscure mealybugs according to the treatment of diazinon formulations. Values followed by different letters indicate significant differences with $p < 0.05$ (ANOVA, Tukey's test).

the surface tension of the solution and hence droplet formation and deposition of diazinon residue. Diazinon is a water-soluble insecticide with high affinity for lipids [47]; then, solvent and emulsifier used on emulsion in water formulations can play a crucial role on the deposition pattern. Emulsion in water dissolved in water forms an emulsion, which does not need constant agitation to maintain it; instead, the wettable powder formulation forms a suspension, which requires constant agitation to keep its fine particles suspended in the water. These differences in the physical-chemical behavior of both formulations were reflected in differences in their initial deposition and persistence of its residues, but this does not seem to be a constant to all types of formulations and insecticides. One work comparing residue levels generated by three formulations of chlorpyrifos (emulsifiable concentrate (EC), wettable granules (WG),

Mean of living obscure mealybugs on fruits according to diazinon formulation by evaluation moment (DAA)							
Treatment	**Prespraying**	**3DAA**	**7DAA**	**10DAA**	**14DAA**	**21DAA**	**25DAA**
Control	33.50a	42.75a	48.00a	55.00a	57.00a	61.50a	62.25a
Emulsion in water	31.25a	3.00c	6.00c	5.75c	5.50c	7.25c	12.50c
Wettable powder	32.75a	18.75b	21.25b	24.75b	24.50b	26.50b	32.25b
F	**0.55**	**80.36**	**175.45**	**279.37**	**129.88**	**178.28**	**142.53**
***p* value**	**0.597**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**

Means followed by different letters indicate significant differences with $p < 0.05$ (ANOVA, Tukey's test).

Table 2. Mean of living obscure mealybugs on fruits according to the treatment of diazinon formulations.

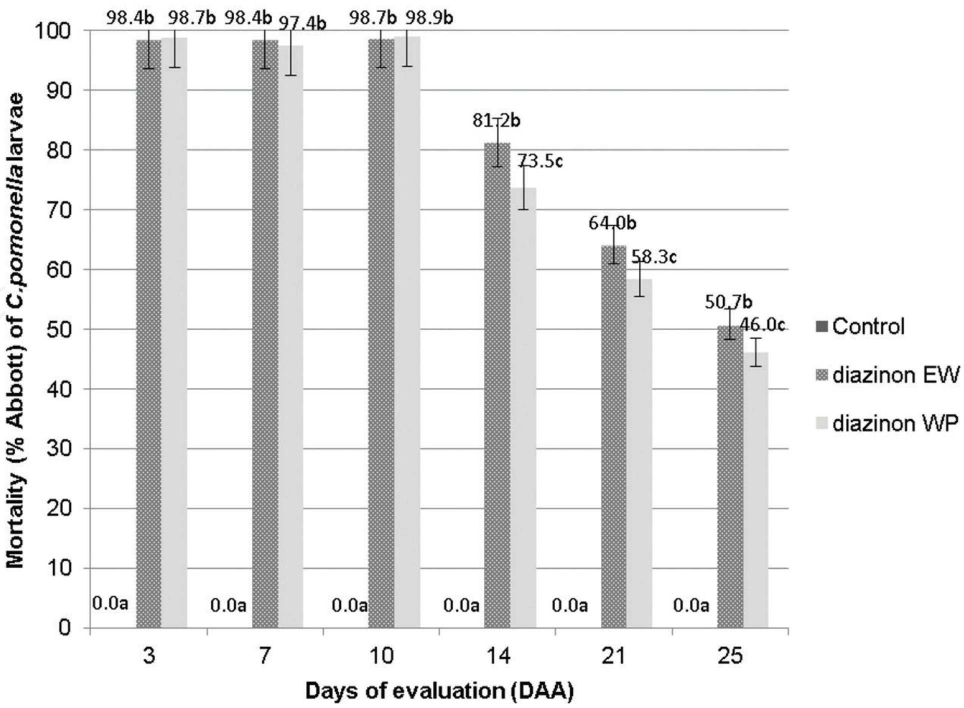

Figure 3. Mortality (% Abbott) of *C. pomonella* larvae according to the treatment of diazinon formulations. Values followed by different letters indicate significant differences with $p < 0.05$ (ANOVA, Tukey's test).

and microencapsulates (ME)) applied to oranges shows that the decline curve and the residue levels in fruits, leaves, and soil could change remarkably if the same active ingredient is used in different formulations [48]; on contrary, the study performed with fenitrothion applied to oranges and clementines with emulsifiable concentrate and microencapsulate formulations did not find differences on rate of decline residue of the active ingredient for both kinds of commercial formulations [49]. For the insecticide azadirachtin, EC formulations compared

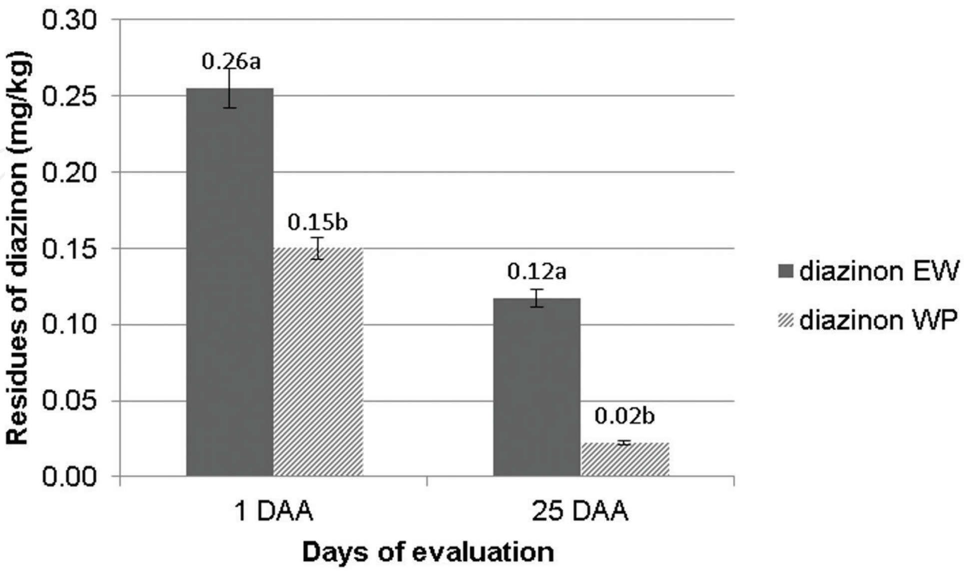

Figure 4. Initial and final residues of diazinon quantified for each formulation. Values followed by different letters indicate significant differences with $p < 0.05$ (ANOVA).

with WP formulation showed differences in the droplet-size spectra and deposit levels, attributed to the influence of additives present in different formulations [50].

3.3. Efficacy of acetamiprid formulations

Differences on efficacy only after 21 DAA were observed with acetamiprid formulations on codling moth (**Figure 5**). Major knockdown effects on San Jose scale (**Figure 6**; **Table 3**) and obscure mealybug (**Figure 7**; **Table 4**) were obtained using wettable powder (WP); nevertheless a longer protection period was obtained using soluble powder (SP). On *C. pomonella*, both treatments showed appropriate control until 21 DAA, and then, only soluble powder maintained a percentage of control with over 85% larvae mortality until 25 DAA.

Acetamiprid has shown good control activity against *C. pomonella* [51]. It is systemic and intended to control sucking insects like aphids, mealybugs [52], and San Jose scale [53]. In this study, differences on the behavior on control could be explained by differences on chemical-physical property between both formulations. Although they have many similarities, when mixed on water, WP generates a suspension, and when applied, formulation particles remain on the treated surface [54]; instead, SP generates a homogenous solution which is easily incorporated by the plant. In addition, between both formulations, the concentration of active ingredient and the proportion and type of coformulants vary. Then, it is possible that these differences are reflected in different rates of absorption by the plant and/or insects [55]. There is some consensus that biological performance of a pesticide is frequently affected by the choice of formulation type [56, 57], for example, a formulation which delivers the chemical in

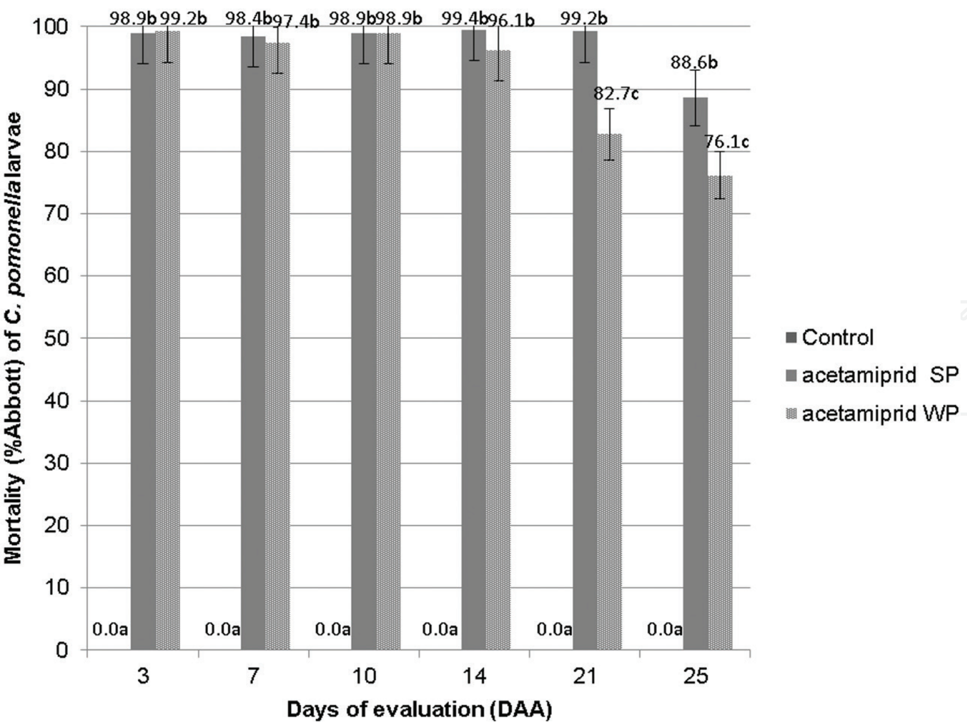

Figure 5. Mortality (% Abbott) of *C. pomonella* larvae according to the treatment of acetamiprid formulations. Values followed by different letters indicate significant differences with $p < 0.05$ (ANOVA, Tukey's test).

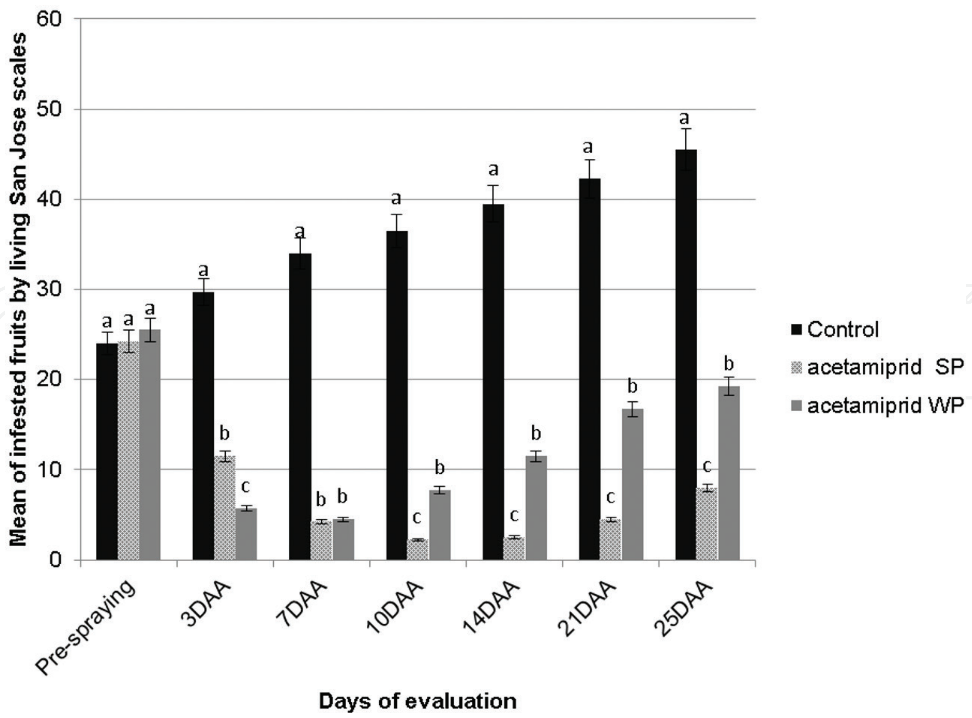

Figure 6. Mean of infested fruit by living San Jose scale according to the treatment of acetamiprid formulations. Values followed by different letters indicate significant differences with $p < 0.05$ (ANOVA, Tukey's test).

a solution, as in SL, EC, or SP formulations, is commonly considered more biologically active than WP or SC formulations, but also, it has a greater risk of being phytotoxic [58].

3.4. Residues of acetamiprid formulations

Wettable powder formulation generated higher initial deposition of acetamiprid than observed for the soluble powder formulation (**Figure 8**). These results contradict what was proposed for a comparison between decline curves of acetamiprid on apple (cv. Pink Lady) performed with SL and WP formulations. In that work, no significant differences were found on the initial and final depositions of acetamiprid between both formulations, applied on

Mean of living scales (*D. perniciosus*) on fruits according to acetamiprid formulation by evaluation moment (DAA)

Treatment	Prespraying	3DAA	7DAA	10DAA	14DAA	21DAA	25DAA
Control	31.00a	36.00a	39.25a	40.00a	43.75a	47.75a	51.75a
Soluble powder	28.25a	11.50b	6.50c	2.25c	4.50c	6.00c	9.25c
Wettable powder	30.25a	6.00c	13.50b	8.25b	12.50b	24.25b	27.75b
F	**1.22**	**204.07**	**79.46**	**169.31**	**178.52**	**127.69**	**102.01**
***p* value**	**0.34**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**

Means followed by different letters indicate significant differences with $p < 0.05$ (ANOVA, Tukey's test).

Table 3. Mean of living San Jose scale on fruits according to the treatment of acetamiprid formulations.

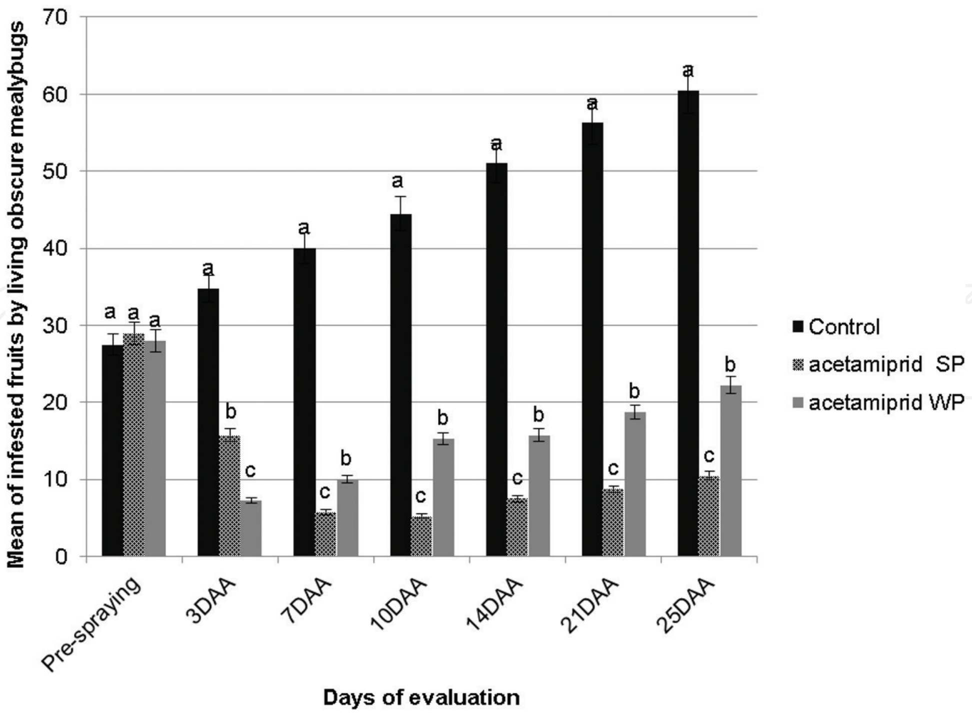

Figure 7. Mean of infested fruit by obscure mealybugs according to the treatment of acetamiprid formulations. Values followed by different letters indicate significant differences with $p < 0.05$ (ANOVA, Tukey's test).

three different apple growth stages [59]. Even when both SP and SL form solutions, these formulations differ on its coformulants and the concentration of active ingredient contained proportionally therein. Thus, even if in this work an equal amount of active ingredient per hectoliter per hectare has been dosed, the proportion and type of surfactants, carriers, or others will not be equivalent.

In general terms, results from the literature are not conclusive with respect to the effect of different formulations in residue deposits and behavior of pesticides, perhaps because of the difficulty of isolating other factors that also affect the degradation of residues such as species and varieties; use of adjuvants; types and concentration of coformulants; fruit growth;

Mean of living obscure mealybugs on fruits according to acetamiprid formulation by evaluation moment (DAA)

Treatment	Prespraying	3DAA	7DAA	10DAA	14DAA	21DAA	25DAA
Control	33.50a	42.75a	48.00a	55.00a	57.00a	61.50a	62.25a
Soluble powder	29.00a	15.75b	7.00b	5.50c	7.75c	9.00c	10.75c
Wettable powder	28.00a	7.25c	11.25b	15.25b	17.00b	18.75b	22.25b
F	**2.60**	**79.16**	**282.59**	**282.08**	**168.09**	**234.43**	**238.61**
***p* value**	**0.13**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**

Means followed by different letters indicate significant differences with $p < 0.05$ (ANOVA, Tukey's test).

Table 4. Mean of living obscure mealybugs on fruits according to the treatment of acetamiprid formulations.

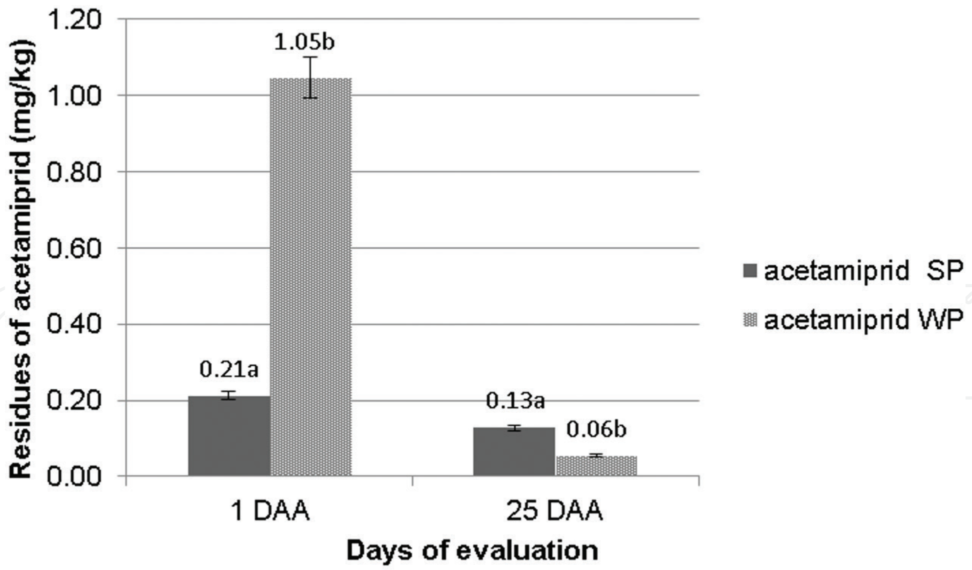

Figure 8. Initial and final residues of acetamiprid quantified for each formulation. Values followed by different letters indicate significant differences with $p < 0.05$ (ANOVA).

climatic conditions; spraying method; measuring technique; and pesticide physicochemical properties between others [60–62].

3.5. Efficacy of l-cyhalothrin formulations

Although both formulations showed insecticidal activity against *C. pomonella*, significant differences between both formulations were observed since the first evaluation (**Figure 9**). Zeon

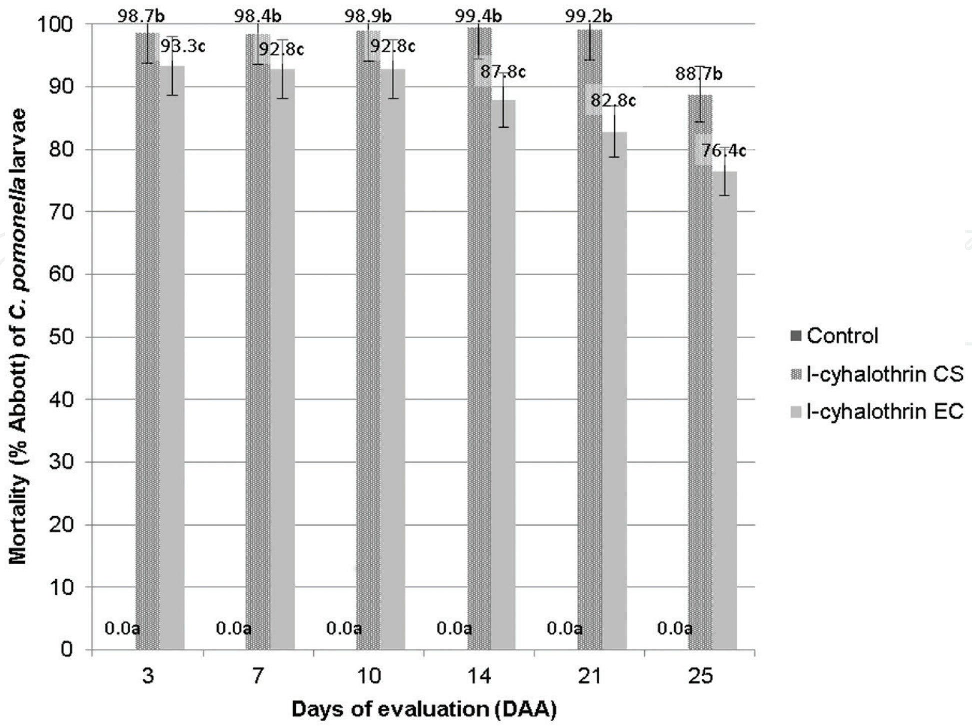

Figure 9. Mortality (% Abbott) of *C. pomonella* larvae according to the treatment of l-cyhalothrin formulations. Values followed by different letters indicate significant differences with $p < 0.05$ (ANOVA, Tukey's test).

(CS) formulation showed better efficacy, with the longer stable control period. Key difference between Zeon technology and EC formulation is that the first one encapsulates the active ingredient in small capsules with thin walls; instead, the second one comprises the active ingredient, a solvent, and emulsifiers. This enables for Zeon formulation quick "knockdown" of insects coupled with long-term persistence [63, 64], properties that were observed in this study. Even when they observed differences between efficacy parameters of both formulations, some authors propose that other parameters as application rate should be considered [65], which, in the present study, is a constant factor for the comparison of both formulations allowing us to conclude without other variables. One work conducted to evaluate efficacy against *Cydia molesta* founded that in the laboratory and in the field, the toxicity to *C. molesta* larvae of microencapsulated (CS) l-cyhalothrin was similar to that of the emulsifiable concentrate (EC) formulation. However, the same work proposed that different toxicity responses were obtained when evaluating its effect on the predator *Typhlodromus pyri* Scheuten, where CS formulation results significantly more toxic than EC formulation in pyrethroid-susceptible predator population [66].

3.6. Residues of l-cyhalothrin formulations

Apparently, the different release rates of the active ingredient are not significantly different at their start (1 DAA) and at 25 days from the application (**Figure 10**), possibly because the microencapsulated formulations do not necessarily vary the deposition of the active ingredient residue, but their biological availability and, as it was observed, its effectiveness.

3.7. Efficacy of imidacloprid formulations

Control of *P. viburni* showed by soluble liquid (SL) and suspension concentrate formulations was similar to wettable powder (WP) formulation until 10 DAA, reflected in both the average

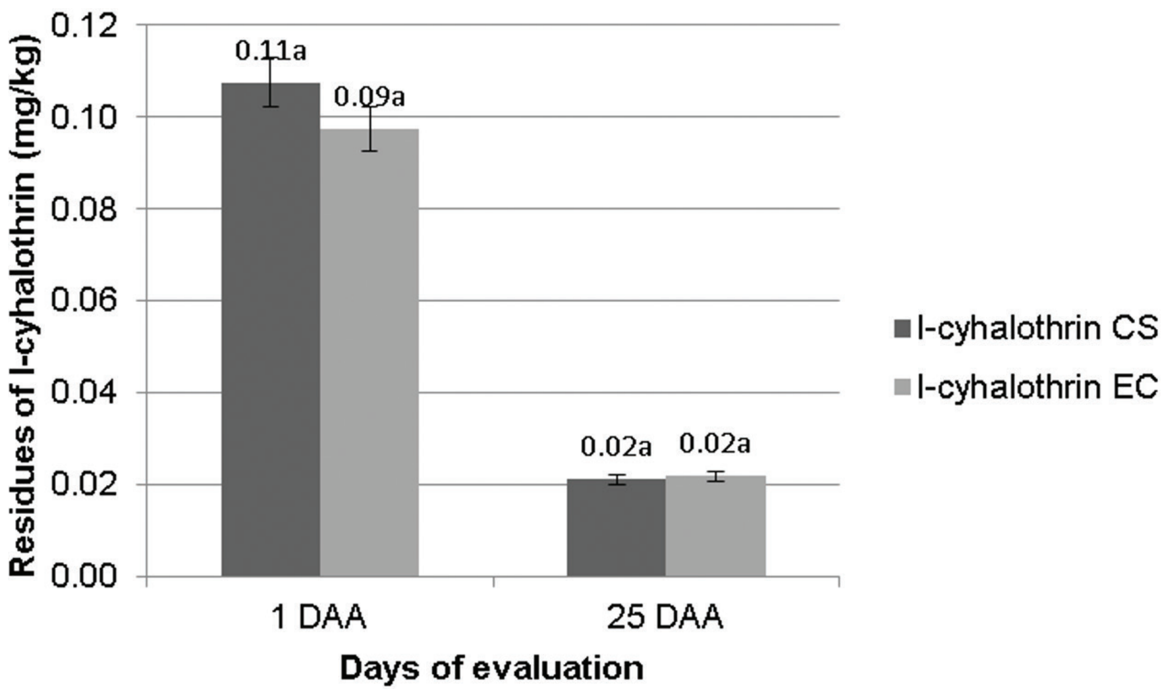

Figure 10. Initial and final residues of l-cyhalothrin quantified for each formulation. Values followed by different letters indicate significant differences with $p < 0.05$ (ANOVA).

number of fruits infested by the pest (**Figure 11**) and the mean of living mealybugs on fruits (**Table 5**); then, longer efficient period of control was obtained using SL formulation.

Imidacloprid is highly effective against mealybugs [67] and others hemipteran pest [68, 69]. It is available in different formulations (WP, SL, SC, OD, WG) registered generally according to their use intention (foliar sprays, seed treatments, and via soil application) [70]; but for the same target of control and way of use, more than one formulation can be available. The choice of one formulation or another may vary the metabolism and persistence behavior of imidacloprid [71, 72]. In our work, even though the three formulations differ in the characteristics of their coformulants, WP and SC formulations have in common that both form suspensions on water; instead, SL forms a solution. This difference could generate different responses in the mobility and translocation of the active ingredient, and therefore its availability to control the pest.

3.8. Residues of imidacloprid formulations

Both initial and final deposits of imidacloprid were higher in SL, compared with WP and SC (**Figure 12**). Even though this work presents only two points or moments of evaluation within a possible residue decline curve, we can infer that the degradation of imidacloprid residue was affected by the formulation, resulting more persistently the residue of imidacloprid generated by the formulation SL than that of the other formulations WP and SC.

On the other hand, the formulations WP and SC had similar behaviors with each other, which is coincident with what was observed in the construction of metalaxyl decline curves in grapes for WP and SC formulations of this pesticide [73].

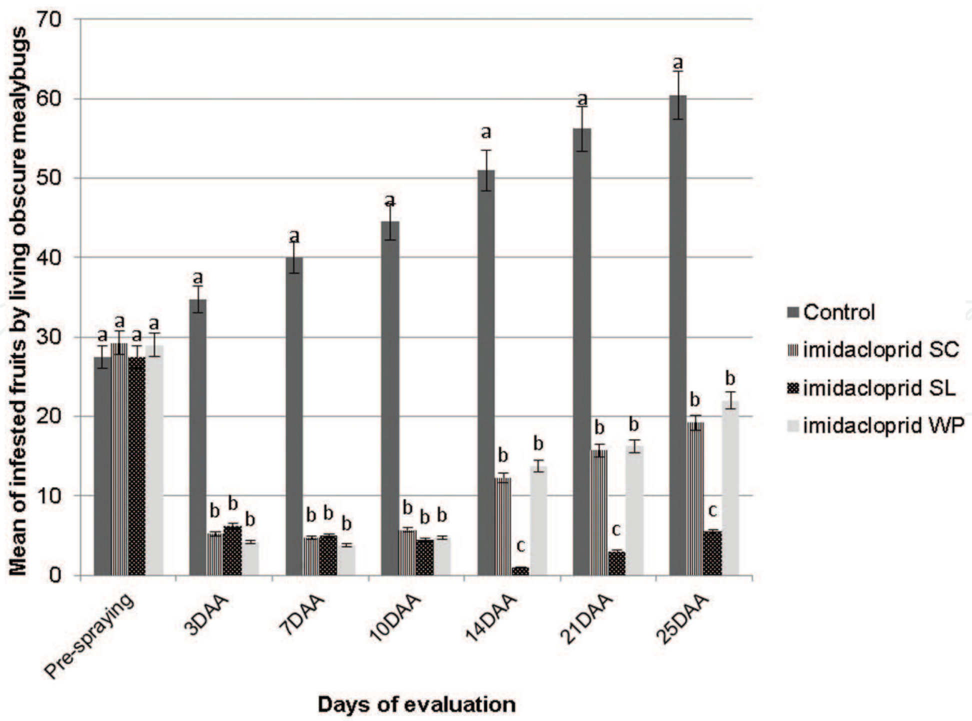

Figure 11. Mean of infested fruit by obscure mealybugs according to the treatment of imidacloprid formulations. Values followed by different letters indicate significant differences with $p < 0.05$ (ANOVA, Tukey's test).

Mean of living obscure mealybugs on fruits according to imidacloprid formulation by evaluation moment (DAA)							
Treatment	**Prespraying**	**3DAA**	**7DAA**	**10DAA**	**14DAA**	**21DAA**	**25DAA**
Control	33.50a	42.75a	48.00a	55.00a	57.00a	61.50a	62.25a
Suspension concentrate	36.50a	5.25b	4.75b	6.25b	12.75b	16.00b	19.75b
Soluble liquid	36.00a	6.25b	5.00b	5.00b	1.75c	3.50c	6.75c
Wettable powder	35.75a	4.25b	3.75b	4.75b	14.5b	17.00b	24.50b
F	**0.51**	**10.12**	**29.31**	**33.09**	**20.82**	**23.49**	**17.13**
***p* Value**	**0.68**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**

Means followed by different letters indicate significant differences with $p < 0.05$ (ANOVA, Tukey's test).

Table 5. Mean of living obscure mealybugs on fruits according to the treatment of imidacloprid formulations.

In all the cases studied on this research (except both formulations of l-cyhalothrin), concentration of active ingredient contained in 1 l or kg of each commercial product varied with their respective comparison. Thus, even though all treatments were performed to look for the same dose of active ingredient per hectare, there was always a variation in the content of adjuvants, surfactants, inerts, or other contents according to the formulation. In the case of l-cyhalothrin, the variations passed through the type of coformulants in addition to the differentiating characteristics of the rate of release of the active ingredient, but not in the concentration of active ingredient. For Food and Agriculture Organization (FAO), two pesticides may not be classified as equivalent even when they have the same concentration of active ingredient, as their similarity depends on the type of formulations. Nor does it apply nominally similar products from other manufacturers or at all those where the active ingredient is produced

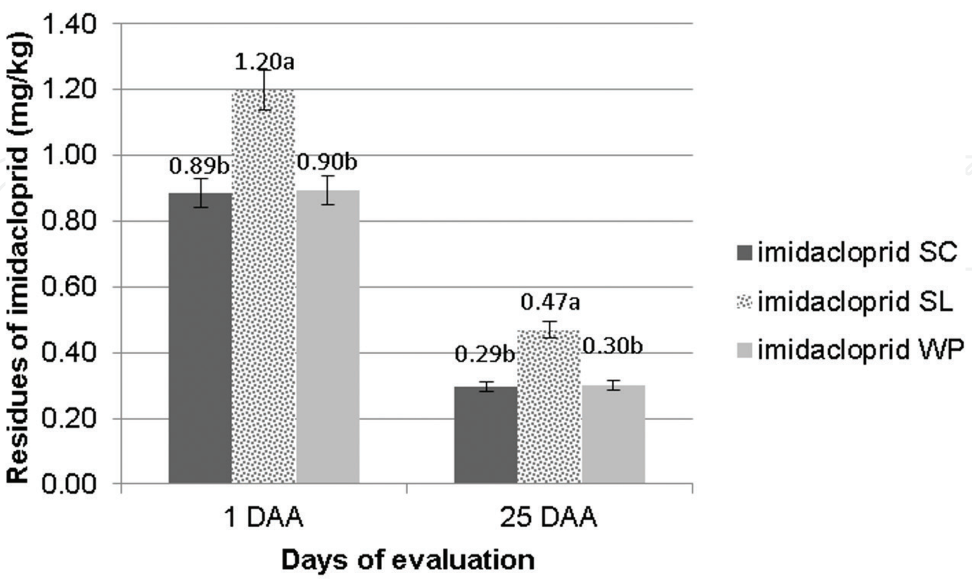

Figure 12. Initial and final residues of imidacloprid quantified for each formulation. Values followed by different letters indicate significant differences with $p < 0.05$ (ANOVA).

by other synthesis methods [74]; inferring that, it is expected that there are certain variations in its practical behavior, whether in its pattern of residues, biological behavior, or efficacy. Accordingly, in the pesticide registry and its establishment of maximum residue limits, it is suggested that information is submitted for the formulation to be registered, and, if a new formulation is to be introduced, it is suggested to carry out collaborative trials (even between different manufacturers) that previously demonstrate that the variations made in the new formulation will not change the pattern of residues [41]. The information generated in these studies is not public.

While the chemical industry posits that some formulations do not imply significant variations between them [74], there is a lot of confidential information that is not known to the end user, which prevents easily discriminating when variations are expected or when not. For the same reason, and because the effectiveness or protection periods may be severely affected by variations between formulations, further comparative inquiries are required to discriminate between product profiles for pest control.

4. Conclusions

Pesticide formulations would have a significant impact on the biological effect for the studied pesticides. Efficacy, knockdown effect and period of effectiveness protection can be affected by formulation of an insecticide. All these parameters are determinant in the design of an application program of insecticides, but in most cases are unknown by the user, the farmer, generating consequently that a greater number of applications are realized. This increases the impact on the environment and likely the costs associated with pest management.

On the other hand, when insecticide residue can be affected by formulation (both in the initial deposit and in its persistence), other parameters inherent to the active ingredient and the capacity of detection and quantification of the measurement technique may be mediating the real importance that the formulation may have on the behavior of the residue. In this chapter, the formulation was determinant in the residual pattern of acetamiprid, imidacloprid, and diazinon, but not for l-cyhalothrin. Future complementary works may focus on considering other interaction between variables such as relevance of the type and concentration of coformulants; fruit growth stage; climatic conditions and spraying method; and fruit or vegetable species, since all of them dynamically seem to affect in some degree the behavior of the insecticide residue generated. This in turn suggests that in some cases the estimation of preharvest intervals calculated for certain active ingredients may be affected by the formulation used in the baseline studies, generating the risk of an underestimation of that interval.

Therefore, when formulations of the same active ingredient are widely available, it is desirable to have independent declination curves of insecticide residue for at least those which differ drastically in type of coformulants or adjuvants and its concentration of active ingredient, considering that there is a risk of significant variations in the behavior of the residue.

Author details

Karina Buzzetti

Address all correspondence to: karinabuzzetti@agridev.cl

Consultant Agri Development Ltd., Santiago, Chile

References

[1] Hall ER. Spray deposits: Opportunities for improved efficiency of utilization v/a quality. Quantity and Formulation. Phytoparasitica. 1997;**25**:39S-52S

[2] Stephenson GR, Ferris IG, Holland PT, Nordberg M. Glossary of terms relating to pesticides. (IUPAC recommendations 2006). Pure and Applied Chemistry. 2006;**78**:2075-2154

[3] Aktar MW, Sengupta D, Chowdhury A. Impact of pesticides use in agriculture: Their benefits and hazards. Interdisciplinary Toxicology. 2009;**2**:1-12

[4] Coelho S. European pesticide rules promote resistance, researchers warn. Science. 2009;**323**:450

[5] Lorman A. Chapter 3: Encouraging improved pesticide formulation: Data protection for inert ingredients. In: Foy CL, Pritchard DW, editors. Pesticide Formulation and Adjuvant Technology. CRC Press; 1996. pp. 25-32

[6] FAO. International Code of Conduct on the Distribution and Use of Pesticides. Rome: Food and Agricultural Organisation; 2005. 36 p

[7] van Valkenburg W, editor. Pesticide formulations. New York: Marcel Dekker; 1973. 481 p

[8] Carmine S. Pesticide Formulation and Delivery Systems: 33rd Volume, "Sustainability: Contributions from Formulation Technology". ASTM International; 2014. 185 p

[9] Knowles A. Recent developments of safer formulations of agrochemicals. The Environmentalist. 2008;**28**:35-44

[10] Lagaly G. Pesticide–clay interactions and formulations. Applied Clay Science. 2001;**18**: 205-209

[11] Kah M, Beulke S, Tiede K, Hofmann T. Nanopesticides: State of knowledge, environmental fate, and exposure modeling. Critical Reviews in Environmental Science and Technology. 2013;**43**:1823-1867

[12] Stenersen J. Chemical Pesticides Mode of Action and Toxicology. CRC Press; 2004. 277 p

[13] Wang CJ, Liu ZQ. Foliar uptake of pesticides—Present status and future challenge. Pesticide Biochemistry and Physiology. 2007;**87**:1-8

[14] Marrs GJ, Middleton MR. The formulation of pesticides for convenience and safety. Outlook on Agriculture. 1973;**7**:231-235

[15] Leonas KK. Effect of pesticide formulation on transmission: A comparison of three formulations. Bulletin of Environmental Contamination and Toxicology. 1991;**46**:697-704

[16] Tsuji K. Microencapsulation of pesticides and their improved handling safety. Journal of Microencapsulation. 2001;**18**:137-147

[17] Diehl KE, Stoller EW. Effect of simulated rainfall, insecticide formulation, and insecticide application method on the interaction between nicosulfuron and terbufos in corn (*Zea mays*). Weed Technology. 1995;**9**:80-85

[18] Lancaster SH, Jordan DL, Johnson PD. Influence of graminicide formulation on compatibility with other pesticides. Weed Technology. 2008;**22**:580-583

[19] Gwynne RN. Globalisation, commodity chains and fruit exporting regions in Chile. Tijdschrift voor Economische en Sociale Geografie. 1999;**90**:211-225

[20] Melo O, Engler A, Nahuehual L, Cofre G, Barrena J. Do sanitary, phytosanitary, and quality-related standards affect international trade? Evidence from Chilean fruit exports. World Development. 2014;**54**:350-359

[21] Buzzetti K, Chorbadjian RA, Nauen R. Resistance Management for San Jose Scale (Hemiptera: Diaspididae). Journal of Economic Entomology. 2015;**108**:2743-2752

[22] Ecobichon DJ. Pesticide use in developing countries. Toxicology. 2001;**160**:27-33

[23] Elbert A, Haas M, Springer B, Thielert W, Nauen R. Applied aspects of neonicotinoid uses in crop protection. Pest Management Science. 2008;**64**:1099-1105

[24] Narkiewicz-Jodko J, Rogowska M. The effectiveness of new formulations of diazinon: Basudin 600 EW and Diazol 50 EW in the control of large white butterfly (*Pieris brassicae* L.). Vegetable crops. Research Bulletin. 2000;**52**:69-73

[25] Solomon KR, Williams WM, Mackay D, Purdy J, Giddings JM, Giesy JP. Properties and uses of chlorpyrifos in the United States. In: Giesy JP, Solomon KR, editors. Ecological Risk Assessment for Chlorpyrifos in Terrestrial and Aquatic Systems in the United States. Springer International Publishing; 2014. pp. 13-34

[26] He LM, Troiano J, Wang A, Goh K. Environmental chemistry, ecotoxicity, and fate of lambda-cyhalothrin. Reviews of Environmental Contamination and Toxicology. 2008;**195**:71-91

[27] Kodandaram MH, Rai AB, Haldar J. Novel insecticides for management of insect pest in vegetable crops: A review. Journal of Vegetation Science. 2010;**37**:109-123

[28] Knight AL. Cross-resistance between azinphos-methyl and acetamiprid in populations of codling moth, *Cydia pomonella* (L.)(Lepidoptera: Tortricidae), from Washington State. Pest Management Science. 2010;**66**:865-874

[29] Brunner JF, Beers EH, Dunley JE, Doerr M, Granger K. Role of Neonicotinyl insecticides in Washington Apple Integrated Pest Management. Part I. Control of Lepidopteran Pests. Journal of Insect Science. 2005;**5**:14

[30] Carnegie AJM. Woolly aphid of apple, *Eriosoma lanigerum* (Hsm.), and its control in southern Rhodesia. Bulletin of Entomological Research. 1963;**53**:609-619

[31] Agnello AM, Spangler SM, Reissig WH, Lawson DS, Weires RW. Seasonal development and management strategies for Cornstock Mealybug (Homoptera: Pseudococcidae) in New York Pear Orchards. Journal of Economic Entomology. 1992;**85**:212-225

[32] Mota-Sanchez D, Wise JC, Poppen RV, Gut LJ, Hollingworth RM. Resistance of codling moth, *Cydia pomonella* (L.)(Lepidoptera: Tortricidae), larvae in Michigan to insecticides with different modes of action and the impact on field residual activity. Pest Management Science. 2008;**64**:881-890

[33] González RH. Degradación de residuos de plaguicidas en huertos frutales en Chile. Serie de Ciencias Agronómicas N° 4. Facultad de Ciencias Agronómicas, Universidad de Chile, Santiago, Chile: Ograma; 2002. 163 p

[34] Cabras P, Meloni M, Gennari M, Cabitza F, Ubeddu M. Pesticide residues in lettuce. 2. Influence of formulations. Journal of Agricultural and Food Chemistry. 1989;**37**:1405-1407

[35] Angioni A, Dedola F, Garau A, Sarais G, Cabras P, Caboni P. Chlorpyrifos residues levels in fruits and vegetables after field treatment. Journal of Environmental Science and Health, Part B. 2011;**46**:544-549

[36] Korunic Z. Review diatomaceous earths, a group of natural insecticides. Journal of Stored Products Research. 1998;**34**:87-97

[37] Arthur FH. Evaluation of a new insecticide formulation (F2) as a protectant of stored wheat, maize, and rice. Journal of Stored Products Research. 2004;**40**:317-330

[38] MacLachlan D, Hamilton DA. Review of the different application rates on pesticide residue levels in supervised residue trials. Pest Management Science. 2011;**67**:609-615

[39] Kumar J, Shakil N, Khan M, Malik K, Walia S. Development of controlled release formulations of carbofuran and imidacloprid and their bioefficacy evaluation against aphid, Aphis gossypii and leafhopper, Amrasca biguttula biguttula Ishida on potato crop. Journal of Environmental Science and Health, Part B. 2011;**46**:678-682

[40] Abbott WSA. Method of computing the effectiveness of an insecticide. Journal of Economic Entomology. 1925;**18**:265-267

[41] FAO. Guidelines on Producing Pesticide Residues Data from Supervised Trials, Rome. 1990

[42] Luke MA, Doose GMA. Modification of the Luke multiresidue procedure for low moisture, non-fatty products. Bulletin of Environmental Contamination and Toxicology. 1983;**30**:110-116

[43] Luke M, Froberg JE, Masumoto HE. Extraction and clean-up of organochlorine, organophosphate, organonitrogen and hydrocarbon pesticides in produce for determination by

gas–liquid chromatography. Journal of the Association of Official Analytical Chemists. 1975;**58**:1020-1026

[44] Alder L, Greulich K, Kempe G, Vieth B. Residue analysis of 500 high priority pesticides: Better by GC–MS or LC–MS/MS? Mass Spectrometry Reviews. 2006;**25**:838-865

[45] Thakur A, Hameed S. Toxicity and persistence of some organophosphorous insecticides against San Jose scale Quadraspidiotus perniciosus Comstock. Journal of the Indian Institute of Science. 1981;**63**:121-129

[46] Gratwick M, Sillibourne JM, Tew RP. The toxicity of insecticides to larvae of the codling moth, Cydia pomonella (L.). I.—Intrinsic toxicity and persistence. Bulletin of Entomological Research. 1965;**56**:367-376

[47] O'Neil MJ, editor. The Merck Index - An Encyclopedia of Chemicals, Drugs, and Biologicals. Whitehouse Station, NJ: Merck and Co., Inc; 2006. p. 509

[48] Montemurro N, Grieco F, Lacertosa G, Visconti A. Chlorpyrifos decline curves and residue levels from different commercial formulations applied to oranges. Journal of Agricultural and Food Chemistry. 2002;**50**:5975-5980

[49] Montemurro N, Grieco F, Lacertosa G, Visconti A. Persistence of fenitrothion in oranges and clementines after treatment with emulsifiable concentrate and microencapsulate formulations. Food Additives and Contaminants. 2005;**22**:39-47

[50] Sundaram KMS. Effect of additives in the neem formulations on deposition, volatilization and persistence of azadirachtin in spruce foliage. Journal of Environmental Science & Health Part B. 1997;**32**:523-544

[51] Magalhaes LC, Walgenbach JF. Life stage toxicity and residual activity of insecticides to codling moth and oriental fruit moth (Lepidoptera: Tortricidae). Journal of Economic Entomology. 2011;**104**:1950-1959

[52] Franco JC, Suma P, Da Silva EB, Blumberg D, Mendel Z. Management strategies of mealybug pests of citrus in Mediterranean countries. Phytoparasitica. 2004;**32**:507-522

[53] Frăsin LBN, Sumedrea M. Research on the efficacy of some insecticides in San Jose scale-Quadraspidiotus perniciosus Comst. Control in Maracineni-arges fruit growing area. Annals: Food Science and Technology. 2013;**14**:405-409

[54] Couch TL, Ignoffo CM. Formulation of insect pathogens. In: Burges HD, editor. Microbial Control of Pests and Plant Diseases. New York: Academic Press; 1981. pp. 621-634

[55] Becker N, Petrić D, Boase C, Lane J, Zgomba M, Dahl C, Kaiser A. Chemical control. In: Mosquitoes and their Control. Springer US; 2003. pp. 377-405

[56] Kumar J, Singh G, Palta RK, Walia S, Parsad R, Parmar BS. Field appraisal of controlled release formulations of carbofuran against the rice leaffolder, cnaphalocrocis medinalis (guenee). Indian Journal of Agricultural Science. 2006;**76**:732-735

[57] Kumar J, Shakil NA, Chandra S, Walia S, Shukla L, Parmar BS. Field appraisal of controlled release formulations of cartap hydrochloride against the rice leaf-folder, Cnaphalocrocis medinalis. Indian Journal of Agricultural Science. 2010;**80**:56-59

[58] Seaman D. Trends in the formulation of pesticides—An overview. Pest Management Science. 1990;**29**:437-449

[59] Alister C, Araya M, Becerra K, Saavedra J, Kogan M. Preharvest interval periods and their relation to fruit growth stages and pesticide formulations. Food Chemistry. 2017;**221**:548-554

[60] Balsari P, Marucco P. Sprayer adjustment and vine canopy parameters affecting spray drift: The Italian experience, In: Proceedings, International Conference on Pesticide Application for Drift Management, Washington, DC; 1989. p. 109-115

[61] Huo R, Salazar JD, Hyder K, Xu XM. Modelling non-systemic pesticide residues in fruits with initial deposit variability and weather effects. Food Additive and Contaminant. 2007;**24**:1257-1267

[62] Marin A, Oliva J, Garcia C, Navarro S, Barba A. Dissipation rates of cyprodinil and fludioxonil in lettuce and table grape in the field and under cold storage conditions. Journal of Agricultural and Food Chemistry. 2003;**51**:4708-4711

[63] Perrin RM, Wege PJ, Foster DG, Bartley MR, Browde J, Rehmke A, Scher H. Fast release capsules: A new formulation of lambda-cyhalothrin. Proceedings British Crop Protection Conference—Pests and Diseases. 1998;**1**:43-48

[64] Perić P, Dimić N, Stamenković S, Marčić D. Efficacy of lambda and gamma-cyhalothrin in *Cydia pomonella* L. and aphis pomi Deg. control. Pesticidi i fitomedicina. 2004;**19**:97-104

[65] Sims SR, Appel AG, Eva MJ. Comparative toxicity and repellency of microencapsulated and other liquid insecticide formulations to the German cockroach (Dictyoptera: Blattellidae). Journal of Economic Entomology. 2010;**103**:2118-2125

[66] Pogoda MK, Pree DJ, Marshall DB. Effects of encapsulation on the toxicity of insecticides to the oriental fruit moth (Lepidoptera: Tortricidae) and the predator Typhlodromus pyri (Acari: Phytoseiidae). The Canadian Entomologist. 2001;**133**:819-826

[67] Elbert A, Nauen A. New applications for neonicotinoid insecticides using imidacloprid as an example. In: Rami A, HorowitzIsaac I, editors. Insect Pest Management. Berlin, Heidelberg: Springer; 2004. pp. 29-44

[68] Eichner R. Imidachloprid in the Product Confidor Insecticide. ACT: National Registration Authority for Agricultural and Veterinary Chemicals; 1994. 23 p

[69] Elbert A, Nauen R, Leicht W. Imidacloprid, a novel chloronicotinyl insecticide: Biological activity and agricultural importance. In: Ishaaya I, Degheele D, editors. Insecticides with Novel Modes of Action. Springer Berlin Heidelberg. 1998. pp. 50-73

[70] Gupta S, Gajbhiye VT, Agnihotri NP. Leaching behavior of imidacloprid formulations in soil. Bulletin of Environmental Contamination and Toxicology. 2002;**68**:502-508

[71] Sarkar MA, Biswas PK, Roy S, Kole RK, Chowdhury A. Effect of pH and type of formulation on the persistence of imidacloprid in water. Bulletin of Environmental Contamination and Toxicology. 1999;**63**:604-609

[72] Sarkar MA, Roy S, Kole RK, Chowdhury A. Persistence and metabolism of imidacloprid in different soils of West Bengal. Pest Management Science. 2001;**57**:598-602

[73] Rasero FS. Características de los formulados comerciales de plaguicidas. Influencia sobre los residuos encontrados en alimentos. In: Valverde A, editor. Residuos de Plaguicidas ´96. IV Seminario Internacional sobre residuos de plaguicidas, Almería, España: PRRG, Universidad de Almería. 1998. pp. 125-140

[74] FAO. Manual sobre Elaboración y Empleo de las Especificaciones de la FAO para Productos Destinados a la Protección de las Plantas. 5ta ed. 1999. 167 p