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Dynamics of Karate Zeon and Calypso Detoxification in Carrot Roots and their Impact on Crop Quality

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ABSTRACT

The dynamics of detoxification of the pesticides Karate Zeon (lambda-cyhalothrin) and Calypso (thiacloprid) in carrot roots, as well as their impact on the main quality indicators of the crop, were studied. The experiments were conducted in the Mantash community of Shirak province, where carrot crops were sprayed with Karate Zeon (at a rate of 0.2 L/ha) and Calypso (0.1–0.15 L/ha). Following the treatments, the dynamics of pesticide detoxification in the root crops were monitored, and at harvest, the main quality indicators of both treated and untreated carrots were assessed. The results showed that Calypso detoxifies more rapidly than Karate Zeon. Fifteen days after application, the concentration of Calypso in carrot roots had decreased to the maximum residue level (MRL) of 0.05 mg/kg. In contrast, residues of Karate Zeon at this point still exceeded the permissible limit by more than tenfold (MRL = 0.01 mg/kg). However, by the end of the "waiting period" - 20 days after application - both pesticides had fully dissipated, and no residues were detected in the carrot roots. Under the conditions of the Shirak region, the use of these pesticides in carrot cultivation does not negatively affect the main quality indicators of the crop. On the contrary, a statistically significant accumulation of β-carotene was observed in the treated roots.

Introduction

Carrots *(Daucus carota L.)* are among the most important root vegetables cultivated worldwide. They are rich in essential nutrients, including vitamins, carotenoids, minerals (such as potassium, magnesium, iron, phosphorus, and calcium), soluble carbohydrates, and dietary fiber. Of particular note is their high content of β-carotene, a precursor of vitamin A, which plays a vital role in human health. β-carotene and vitamin A possess strong antioxidant properties, helping to protect cellular membranes - particularly in the brain - against oxidative damage by neutralizing reactive radicals derived from polyunsaturated fatty acids and hydrogen. Carrots are also an important source of nicotinic acid (vitamin PP), a key coenzyme involved in redox reactions, metabolic regulation, and the restoration of damaged tissues (Victoria-Campos, et al., 2022; Miazek, et al., 2022; Kim, et al., 2023; Tufail, et al., 2024; Tian, et al., 2024).

Like all root vegetables, carrots are susceptible to damage from various pests, which can significantly impact both the yield and quality of the crop.

Calypso and Karate Zeon insecticides are among the preparations used to control the main carrot pests, the carrot fly and the leafhopper.

Carrots, as root vegetables, accumulate agrochemical residues differently from foliar crops, making it essential to investigate how systemic and non-systemic insecticides behave within their tissues over time. Moreover, beyond their pesticidal role, such chemicals may interact with plant metabolic pathways, influencing the synthesis of important bioactive compounds such as antioxidants and sugars.

This study aims to evaluate the detoxification dynamics and physiological effects of Calypso and Karate Zeon in carrot roots following foliar application. Special attention is given to their impact on key quality indicators, including ascorbic acid, β-carotene, and soluble sugars. By comparing these two insecticides, we aim to clarify the trade-offs between efficacy, residue safety, and potential nutritional implications in carrot cultivation.

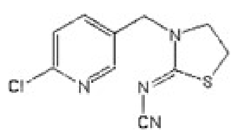
Materials and methods

The field trials were carried out in the Mantash community of the Shirak region. Carrot crops were treated with Calypso (0.15 L ha^{-1}) and Karate Zeon (0.20 L ha^{-1}) to control carrot flies *(Psila rosae)* and leafhoppers *(Empoasca spp.)*.

Calypso (active ingredient: thiacloprid)

Calypso is a systemic insecticide designed to control a wide range of pests in vegetables, field crops, orchards, and herbs. Calypso acts as both a contact and stomach poison, exhibiting systemic activity. It is effective at relatively low application rates and is known for its excellent compatibility with plants.

Structural formula:

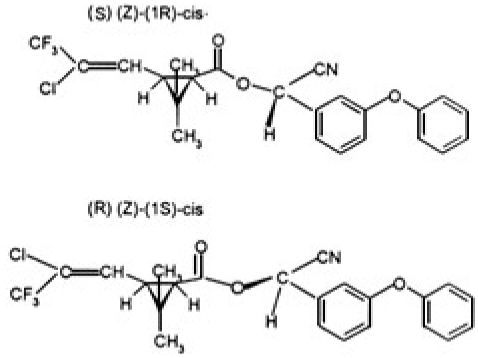


N-[3-(6-chloropyridin-3-ylmethyl)-thiazolidin-2-ylidene]-cyanimide(IUPAC).

Karate Zeon (active ingredient: lambda-cyhalothrin)

A pyrethroid insecticide intended for the protection of potato, grain, technical, vegetable, fruit, and many other crops from a complex of leaf-gnawing and sucking pests, including mites. It is a fast-acting, broad-spectrum contact insecticide. It works by disrupting the function of sodium channels in insect nerve cells, leading to paralysis and death.

Structural formula:



(S,R)--cyano-3-phenoxybenzoic (1R,1S)-cis-3-(2-chloro-3,3,3-terfluoropropenyl)-2,2-termethyl-cyclopropanecarboxylate (1:1)

The chemical group and physical properties of these compounds are presented in Table 1.

Table 1. Chemical Group and Physical Properties of Thiacloprid and Lambda-Cyhalothrin*

Property	Thiacloprid (Calypso)	Lambda-cyhalothrin (Karate Zeon)
Chemical group	Neonicotinoid	Pyrethroid
Water solubility	High (~184 mg/L)	Very low (~0.005 mg/L)
Lipophilicity	(Log Kow) ~1.26 (moderate)	~6.9 (very high)
Volatility	Low (≈ 3.3×10^{-7} Pa)	Low (≈ 2×10^{-5} Pa)

The values come from EFSA, FAO, and PubChem pesticide profiles

*Composed by the authors.

To determine the residues of the insecticides mentioned, carrot root samples were collected at 1.5, 10, 15, and 20 days after spraying.

The main qualitative indicators of carrots were assessed at the peak of ripening. In carrot roots, titratable acidity was measured by titration, sugar content by Bertrand's method, ascorbic acid by Murry's method, and β-carotene by the colorimetric method (Yermakov, et al., 1987).

Residual amounts of Karate Zeon and Calypso in the root crops were determined using TLC on Silufol plates (Guideline, 1992).

Statistical Analysis: All experiments were performed in quadruplicate, and the results are presented as Mean ± SD (Standard Deviation). Statistical comparisons were conducted using one-way ANOVA with a significance level of $p \leq 0.05$. Significant differences between treatments for various traits were assessed using the least significant difference (LSD) method Tukey HSD analysis.

Results and discussions

Studies on the detoxification dynamics of Karate Zeon and Calypso showed that within the first five days after application, their dissipation rates in carrot roots are nearly identical (Table 2).

During the first five days after application, residue levels of both pesticides decreased by 38.3–38.9 % compared to the first day. This rate of decline is typical for many pesticides, as plants recognize these compounds as foreign substances and activate defense mechanisms - such as enhanced metabolism, increased enzyme activity, and physiological responses - to neutralize them. Over time, this response diminishes as the residues no longer pose a significant threat to plant function (Zhang, et al., 2024).

Although both insecticides exhibited some similarity in early-phase detoxification kinetics - particularly within the first 24 hours - their long-term residue dynamics diverged markedly. Fifteen days after application, Calypso residues in carrot roots had decreased to the maximum permissible level (MRL = 0.05 mg/kg, ГН 1.2.3539-18), while residues of Karate Zeon remained over ten times higher than its MRL (0.01 mg/kg). Nevertheless, by day 20 - the standard pre-harvest interval - residues of both compounds were undetectable, indicating eventual detoxification through distinct pathways.

The observed detoxification dynamics of Calypso in carrots align with previous reports highlighting the rapid dissipation of thiacloprid in various crops. In Serbia, field trials revealed a 72 % decline in pepper fruit residues within two days post-application (Lazić, 2015), and studies on cowpeas indicated a short half-life of 1.1–1.5 days (Li, 2022), underscoring the compound's fast degradation rate.

These differences in detoxification patterns and physiological behavior reflect the distinct chemical nature, systemic properties, and modes of action of the two insecticides. The rapid decline of thiacloprid, particularly characteristic of systemic insecticides like Calypso, is closely tied to plant detoxification physiology. Enzymatic activity is most pronounced in the leaves, where systemic compounds are initially translocated. As thiacloprid reaches root tissues, the reduced metabolic activity slows its breakdown. In contrast, non-systemic insecticides such as Karate Zeon may bind to soil particles and be taken up passively by the roots, leading to prolonged persistence in root tissues. Over time, their concentrations decline through slower metabolic degradation, dilution from root growth, or environmental dissipation.

At the biochemical level, the degradation of lambda-cyhalothrin - the active ingredient in Karate Zeon - occurs through photolysis, hydrolysis, microbial metabolism, and plant enzymatic detoxification. The compound undergoes typical degradation routes involving soil and plant cytochrome P450 monooxygenases, while microbial species such as Pseudomonas, Serratia, and Bacillus spp. further catalyze its breakdown. These processes also transform its major metabolite, 3-phenoxybenzoic acid (3-PBA), contributing to overall detoxification. (He, et al., 2008; Djouaka, et al., 2018).

In contrast, thiacloprid is metabolized primarily through plant-mediated enzymatic pathways involving esterases, cytochrome P450s, and glutathione S-transferases (GSTs), ensuring more rapid detoxification (Homayoonzadeh, et al., 2021).

Table 2. Dynamics of Karate Zeon and Calypso detoxification in carrot roots (mg/kg)*

Preparation	Days after treatment				
	1	5	10	15	20
Karate Zeon	0.58 ± 0.07	0.36 ± 0.06	0.23 ± 0.06	0.12 ± 0.04	0.0
Calypso	0.52 ± 0.02	0.32 ± 0.01	0.08 ± 0.06	0.02 ± 0.01	0.0

*Composed by the authors.

Table 3. Effect of Karate Zeon and Calypso on the Key Qualitative Indicators of Carrot Roots*

Variant	Titratable acidity, %	β-Carotene, mg/100g	Ascorbic acid, mg/100g	Soluble sugars, %		
				Mono-	Di-	Total
LSD**	0.03	0.08	0.03	0.19	0.32	
Control	0.17±0.008	3.02±0.06	0.30±0.04	4.2±0.26	5.2±0.32	9.4
Karate Zeon	0.15±0.007	3.63±0.11	0.43±0.03	3.9±0.17	5.8±0.37	9.7
Calipso	0.14±0.004	3.99±0.11	0.35±0.04	4.2±0.26	5.6±0.51	9.8

*Note. LSD** = Least Significant Difference at p ≤ 0.05. Values exceeding the LSD indicate statistically significant differences compared to the control.*

*Composed by the author.

Beyond residue dynamics, both insecticides influenced key biochemical and quality parameters in carrot roots. They induced modest increases in soluble sugars - mainly disaccharides (Table 3) - and more pronounced elevations in antioxidant levels. Among these, ascorbic acid and β-carotene were particularly responsive: relative to control, ascorbic acid rose by approximately 17 % under Calypso and 43 % under Karate Zeon, while β-carotene increased by 32 % and 20 %, respectively ($p = 0.001$ and $p = 0.0013$).

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These antioxidant changes form part of the plant's adaptive defense to oxidative stress, mitigating reactive oxygen species (ROS) generated during pesticide exposure. The accumulation of ascorbic acid and carotenoids indicates activation of secondary metabolite biosynthesis, a phenomenon widely reported in previous studies (Xu, et al., 2023; Wu, P., 2024; Đurić, et al., 2024).

The distinct antioxidant profiles reflect the contrasting physicochemical and physiological properties of the two insecticides. Calypso, a systemic neonicotinoid, distributes throughout plant tissues, producing a mild and transient stress that preferentially enhances β-carotene synthesis - consistent with the role of membrane-bound antioxidants in protecting against systemic perturbations. Supporting this, Dar (2015) observed that low doses of neonicotinoids increased both enzymatic and non-enzymatic antioxidants in mustard.

By contrast, Karate Zeon, a contact pyrethroid, causes more localized oxidative stress at the site of application, leading to a stronger upregulation of ascorbic acid, a rapidly acting, water-soluble ROS scavenger (Wu, 2024). The differential activation of antioxidant systems likely reflects variations in stress intensity, localization, and metabolic distribution between the two compounds.

Although both treatments slightly increased sugar content, these changes were not statistically significant and similar in magnitude. The effect may arise from temporary adjustments in carbohydrate metabolism or compensatory increases in photosynthetic activity under chemical stress conditions.

Conclusion

The comparative assessment of Karate Zeon (lambda-cyhalothrin) and Calypso (thiacloprid) reveals clear differences in their detoxification dynamics and impact on the biochemical quality of carrot roots. While both insecticides initially decline at similar rates, Calypso undergoes faster and more efficient detoxification due to its systemic nature, higher water solubility, and compatibility with plant detoxification enzymes. In contrast, Karate Zeon, being non-systemic and more persistent, detoxifies more slowly and remains in carrot roots longer.

Both insecticides cause mild physiological stress, as evidenced by increased levels of ascorbic acid and β-carotene in treated roots. These antioxidant responses suggest an adaptive defense mechanism that may also improve the nutritional quality of carrots. Calypso is more effective in promoting β-carotene in carrot root crops, while Karate Zeon has a stronger effect on ascorbic acid accumulation. A slight increase in soluble sugars is also observed, mainly due to the content of disaccharides.

These findings highlight the importance of considering both residue dynamics and physiological effects when selecting plant protection against carrot pests.

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