

Evaluation of Residual Patterns of Cyantraniliprole, Ethaboxam, Fludioxonil, and Metalaxyl in Jujube (*Ziziphus jujuba* Mill.)

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Abstract: This study was performed to evaluate the residual patterns of cyantraniliprole, ethaboxam, fludioxonil, and metalaxyl in jujube (*Ziziphus jujuba* Mill.) in field trials. Jujubes were collected at different pre-harvest days and subjected to modified QuEChERS sample preparation methods after dried or not. Jujube samples were extracted with organic solvents for pesticide residue analysis using liquid chromatography-tandem mass spectrometry (LC/MS/MS). Residual concentrations in fresh jujube ranged from 0.02 to 0.12 mg/kg for cyantraniliprole, including metabolites, ranged from 0.22 to 1.01 mg/kg for ethaboxam, ranged from 0.05 to 0.53 mg/kg for fludioxonil, and ranged from 0.16 to 2.26 mg/kg for metalaxyl. The biological half-lives for cyantraniliprole, ethaboxam, fludioxonil, and metalaxyl were 8.6, 10.7, 7.1, and 6.3 days, respectively. Based on residue data, the Pre Harvests Intervals (PHIs) were suggested as follows: cyantraniliprole, 2 times applications 7 days before harvest (DBH); ethaboxam, 3 times applications 14 DBH; fludioxonil, 2 times applications 21 DBH; metalaxyl, 3 times applications 7 DBH. The risk assessment based on the percentage of acceptable daily intake indicated that all pesticides were found to be at safe levels, each below 0.05%. These findings provide foundational data for the registration of the tested pesticides in jujube, contributing to pesticide safety and the establishment of effective pest management strategies in jujube cultivation.

<https://doi.org/10.5338/KJEA.2025.44.52>

Agric. Environ. Sci. 2025, 44, 555-570

Received: December 2, 2025

Revised: December 8, 2025

Accepted: December 13, 2025

Published: December 19, 2025

Online ISSN: 2233-4173

Print ISSN: 1225-3537



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Keywords: Cyantraniliprole, Ethaboxam, Fludioxonil, Jujube, Metalaxyl

Introduction

The improper use of pesticides can result in residue accumulation in agricultural commodities, thereby posing potential risks to consumer health. This issue is directly linked to the safety of agricultural products and has thus been recognized as a critical concern. In South Korea, the establishment of Maximum Residue Limits (MRLs) and the Positive List System (PLS) has been implemented, applying a strict default limit (0.01 mg/kg) to commodities lacking established MRLs and thereby restricting the use of non-registered pesticides. However, these strict regulations pose difficulties for minor crops with limited cultivation areas. Private companies often avoid registering pesticides due to low economic feasibility. Consequently, farmers face challenges such as the inability to select appropriate pesticides for pest

and disease control, an increased risk of control failure, and a higher likelihood of producing non-compliant products [1]. To address these problems and expand farmers' access to safe pesticides, the Rural Development Administration (RDA) has been implementing an official registration program. Based on data obtained from crop residue trials and efficacy/phytotoxicity tests, the RDA registers pesticides that are necessary for specific crops.

Jujube fruit is widely consumed in traditional foods and valued as a medicinal ingredient due to its rich content of various bioactive compounds [2]. In recent years, jujube has emerged as a high-value crop, with its cultivation area steadily increasing. According to the RDA Pesticide Safety Information System (as of September 2025), 189 pesticides are currently registered for use on jujube, enabling control of major pests and diseases. Nevertheless, this number remains limited compared with major crops such as apple (599) and pepper (305). Moreover, the repeated use of pesticides with the same mode of action may accelerate the development of resistant pathogens. Additionally, formulation choice may vary depending on cultivation conditions such as open-field versus protected environments. Therefore, expanding the range of available pesticides is crucial for suppressing resistance development and enabling farmers to select products suitable for their cultivation environment, thereby contributing to stable jujube production.

The pesticides investigated in this study were cyantraniliprole, ethaboxam, fludioxonil, and metalaxyl. Cyantraniliprole, a diamide insecticide, targets ryanodine receptors in insect muscle cells, inducing abnormal calcium release and causing muscle contraction and paralysis [3]. Mainly used to control downy mildew and *Phytophthora*-related diseases, ethaboxam has been reported in the U.S. EPA human health risk assessment to inhibit β -tubulin assembly and cell division in pathogenic oomycetes, thereby suppressing mycelial growth, sporulation, and zoospore germination. Widely used against gray mold, Sclerotinia rot, anthracnose, and other fungal diseases, fludioxonil is a phenylpyrrole fungicide. It disrupts fungal osmoregulation by interfering with mitogen-activated protein (MAP) kinase and histidine kinase signaling pathways, ultimately leading to cell death [4]. Primarily used to control diseases caused by Oomycetes, metalaxyl is an acylanilide fungicide that inhibits fungal RNA polymerase I, thereby blocking nucleic acid synthesis and suppressing pathogen growth [5].

This study aimed to evaluate the residue behavior of cyantraniliprole, ethaboxam, fludioxonil, and metalaxyl in fresh and dried jujube, to provide basic evidence for establishing safe-use standards and MRLs, and to assess the associated human health risks. A specific objective was to compare the residue characteristics of cyantraniliprole, as particular attention was required to compare residue characteristics between the formulation already registered for jujube (5% dispersible concentrate, DC) and the 10.26% oil dispersion (OD) formulation used in this study. Moreover, the findings of this study may serve as foundational data for their official registration because fludioxonil, ethaboxam, and metalaxyl are not currently registered for use on jujube. Ultimately, this study is expected to contribute to ensuring jujube production and supporting the development of effective pest management strategies.

Results and Discussion

Method validation

Method validation was performed based on the criteria presented in the Ministry of Food and Drug Safety (MFDS) Practical Guide to the Pesticide Residue Analytical Methods of the Korean Food Code [6], RDA Notice No. 2023–25 (Appendix 14: Standards and Methods for Crop Residue Trials), and the European Commission guideline SANTE/11312/2021 [7]. The validation parameters included the proportion of interfering substances in untreated samples, linearity of calibration curves (R^2), back-calculated concentrations, recovery, relative standard deviation (RSD), and ion ratio consistency.

Interfering substances in untreated samples did not exceed 30% of the limit of quantitation (LOQ) for target pesticides, indicating adequate selectivity. The values of coefficient determination (R^2) for calibration curves in all samples were higher than 0.98, indicating good linearity (Table 1). The back-calculated concentrations were within 80–120% of their theoretical values, confirming

Table 1. Calibration equations and coefficient values of determination (R^2) for the target pesticides in fresh and dried jujube

Pesticide	Commodity	Linear equation	R^2
Cyantraniliprole	Fresh jujube	$y = 2453491.8071x - 2347.2763$	0.9886
	Dried jujube	$y = 1028875.3341x + 576.4288$	0.9897
IN-J9Z38	Fresh jujube	$y = 1562956.1302x - 1996.9582$	0.9996
	Dried jujube	$y = 1131952.2661x - 1612.7002$	0.9904
Ethaboxam	Fresh jujube	$y = 4049678.3556x + 7914.8286$	0.9901
	Dried jujube	$y = 3106814.9622x - 429.4050$	0.9964
Fludioxonil	Fresh jujube	$y = 590478.5009x - 178.2676$	0.9983
	Dried jujube	$y = 410090.9936x - 346.0378$	0.9816
Metalaxyl	Fresh jujube	$y = 30204362.8414x + 48781.1990$	0.9991
	Dried jujube	$y = 33683963.5967x + 48895.2990$	0.9982

Table 2. Recoveries and RSD of the target pesticides in fresh and dried jujube

Pesticide	Commodity	Fortification level (mg/kg)	Recovery (%)	
			Mean $\pm$ SD ^{a)}	RSD ^{b)} (%)
Cyantraniliprole	Fresh jujube	0.01	109.6 $\pm$ 5.5	5.0
		0.1	85.7 $\pm$ 3.4	4.0
		1.0	83.9 $\pm$ 2.4	2.9
	Dried jujube	0.01	90.9 $\pm$ 18.9	20.8
		0.1	85.9 $\pm$ 4.3	5.0
		1.0	85.5 $\pm$ 8.9	10.4
IN-J9Z38	Fresh jujube	0.01	107.5 $\pm$ 8.7	8.1
		0.1	92.1 $\pm$ 6.9	7.5
		1.0	92.7 $\pm$ 3.9	4.2
	Dried jujube	0.01	93.8 $\pm$ 8.1	8.6
		0.1	86.3 $\pm$ 2.9	3.4
		1.0	84.9 $\pm$ 1.6	1.9
Ethaboxam	Fresh jujube	0.01	82.1 $\pm$ 4.8	5.9
		0.1	78.3 $\pm$ 3.6	4.6
		1.0	79.5 $\pm$ 8.7	10.9
	Dried jujube	0.01	85.1 $\pm$ 2.0	2.4
		0.1	79.3 $\pm$ 1.7	2.1
		10.0	79.2 $\pm$ 1.2	1.5
Fludioxonil	Fresh jujube	0.01	96.2 $\pm$ 5.1	5.3
		0.1	88.9 $\pm$ 2.3	2.6
		1.0	88.7 $\pm$ 2.7	3.0
	Dried jujube	0.01	88.3 $\pm$ 6.5	7.4
		0.1	84.0 $\pm$ 2.2	2.6
		10.0	79.3 $\pm$ 6.4	8.1
Metalaxyl	Fresh jujube	0.01	79.8 $\pm$ 6.5	8.1
		0.1	94.5 $\pm$ 1.4	1.5
		1.0	93.1 $\pm$ 3.1	3.3
	Dried jujube	0.01	87.5 $\pm$ 5.5	6.3
		0.1	92.0 $\pm$ 1.3	1.4
		10.0	91.0 $\pm$ 3.7	4.1

^{a)} Standard deviation.^{b)} Relative standard deviation.

the suitability of the calibration models. The mean recovery values for cyantraniliprole ranged from 83.9 to 109.6% in fresh jujube and from 85.5 to 90.9% in dried jujube. The mean recovery values for its metabolite IN-J9Z38 ranged from 92.1 to 107.5% in fresh jujube and from 84.9 to 93.8% in dried jujube. The mean recovery values for ethaboxam ranged from 78.3 to 82.1% in fresh jujube and from 79.2 to 85.1% in dried jujube. The mean recovery values for fludioxonil ranged from 88.7 to 96.2% in fresh jujube and from 79.3 to 88.3% in dried jujube. The mean recovery values for metalaxyl ranged from 79.8 to 94.5% in fresh jujube and from 87.5 to 92.0% in dried jujube. All pesticides met the RDA guidelines for pesticide residue analysis acceptance criteria for recovery and RSD at each fortification level (Table 2). The relative ion ratios between standard and sample solutions were within $\pm 30\%$. Overall, these results validated the established analytical method for determining cyantraniliprole, ethaboxam, fludioxonil, and metalaxyl residues in both fresh and dried jujube.

Storage stability

Storage stability was evaluated by analyzing samples stored at -20°C for 24–32 days. The recovery ranges for cyantraniliprole were from 84.3–89.0% in fresh jujube and 79.6–83.7% in dried jujube, and for its metabolite IN-J9Z38 were from 88.7–94.2% in fresh jujube and 82.3–87.2% in dried jujube. The recovery ranges for ethaboxam were from 75.5–101.4% in fresh jujube and 76.4–79.8% in dried jujube. The recovery ranges for fludioxonil were from 88.0–89.6% in fresh jujube and 80.8–87.7% in dried jujube. The recovery ranges for metalaxyl were from 89.5–92.4% in dried jujube (Supplementary Table 1).

Table 3. Residues of the target pesticides in fresh jujube at different days after the last application

Pesticide	Day after last application	Residues (mg/kg)	
		Maximum residue	Mean $\pm$ SD*
Cyantraniliprole	0	0.12	0.12 ± 0.00^a
	7	0.08	0.08 ± 0.01^b
	14	0.08	0.06 ± 0.02^b
	21	0.02	0.02 ± 0.00^c
IN-J9Z38	0	< LOQ	-
	7	< LOQ	-
	14	< LOQ	-
	21	< LOQ	-
Total cyantraniliprole	0	0.12	0.12 ± 0.00^a
	7	0.08	0.08 ± 0.01^b
	14	0.08	0.06 ± 0.02^b
	21	0.02	0.02 ± 0.00^c
Ethaboxam	0	1.01	0.91 ± 0.11^a
	7	0.95	0.87 ± 0.09^a
	14	0.52	0.45 ± 0.07^b
	21	0.29	0.25 ± 0.04^c
Fludioxonil	0	0.53	0.48 ± 0.06^a
	7	0.18	0.17 ± 0.01^b
	14	0.17	0.17 ± 0.01^b
	21	0.05	0.05 ± 0.00^c
Metalaxyl	0	2.26	2.12 ± 0.21^a
	7	0.94	0.80 ± 0.12^b
	14	0.63	0.60 ± 0.02^b
	21	0.20	0.18 ± 0.02^c

* Standard deviation,

^{a-c} different letters within a column indicate significant differences at $p < 0.05$ according to Duncan's multiple range test (DMRT).

All four pesticides met acceptance levels guided by the RDA for a fortification level of 0.1 mg/kg, which requires recoveries between 70–120% and RSD values of 20% or less. These results indicate that no significant degradation or loss of the pesticides occurred during frozen storage, indicating that the target compound was chemically stable during the tested periods.

Dissipation of pesticide residues in fresh jujube

Based on the residue definitions, the maximum residues of cyantraniliprole in fresh jujube were 0.12 mg/kg at 0 days and 0.02 mg/kg at 21 days after the final application (Table 3). The maximum residues of ethaboxam were 1.01 mg/kg at 0 days and 0.29 mg/kg at 21 days. Fludioxonil showed maximum residues of 0.53 mg/kg at 0 days and 0.05 mg/kg at 21 days, while metalaxyl showed residues of 2.26 mg/kg and 0.20 mg/kg at the same time points (Table 3). The dissipation rates calculated from mean residues over 21 days were 83.3% for cyantraniliprole, 72.5% for ethaboxam, 89.6% for fludioxonil, and 91.5% for metalaxyl. All four pesticides showed decreasing trends over time. Cyantraniliprole, fludioxonil, and metalaxyl showed significant reductions between 0 and 7 days, and between 14 and 21 days, whereas ethaboxam showed insignificant reduction between 0 and 7 days but decreased significantly thereafter until 21 days.

Since the jujube fruit had already reached maturity at the time of the first application, growth dilution was considered negligible. Instead, environmental factors during the trial period (mid-August to mid-September), including high temperature, rainfall, and solar radiation, likely contributed to dissipation through photodegradation, volatilization, and wash-off. Additional factors such as plant metabolism, microbial degradation on the fruit surface, and hydrolysis under moisture and temperature conditions may also have contributed.

Although initial residues (0-day residues) generally correlated with active ingredient concentrations in the spray mixtures, they were not strictly proportional. Given that the same spraying conditions were applied across fields, these differences were likely due to physicochemical properties (e.g., water solubility, log P, vapor pressure) and formulation characteristics. A previous study also found that despite the spray concentration of boscalid being 1.8 times higher than that of pyraclostrobin, the initial residues of pyraclostrobin were 1.2–1.8 times higher across different fields [8].

Table 4 summarizes the regression equations, the values of coefficient determination, and biological half-lives obtained from the dissipation curves shown in Fig. 1. All R^2 values were approximately 0.9, indicating good fitting to first-order kinetics. The calculated biological half-lives were 8.6 days for cyantraniliprole, 10.7 days for ethaboxam, 7.1 days for fludioxonil, and 6.3 days for metalaxyl. Ethaboxam showed the longest half-life, indicating the highest persistence, while metalaxyl dissipated most rapidly. Previous studies reported half-lives of 11.0–13.2 days for boscalid and 6.1–12.7 days for pyraclostrobin in jujube [8], which were generally consistent with our results. Differences among compounds likely reflect their physicochemical properties, formulations, and environmental conditions during the trials.

Evaluation of pre harvest intervals in fresh jujube

According to the MFDS MRL list, the MRLs for fresh jujube are 1 mg/kg for cyantraniliprole and 0.3 mg/kg for fludioxonil, while no MRLs are established for ethaboxam or metalaxyl. In South Korea, MRLs are determined based on either mean maximum residue levels across test plots or three times the highest observed residue, depending on the number of field trials [9]. The

Table 4. Regression equations (first-order kinetics), coefficient values of determination (R^2), and biological half-lives of the target pesticides in fresh jujube

Pesticide	Commodity	Regression equation	R^2	Half-life (days)
Cyantraniliprole	Fresh jujube	$y = 0.1362e^{-0.081x}$	0.9076	8.6
Ethaboxam	Fresh jujube	$y = 1.0786e^{-0.065x}$	0.9137	10.7
Fludioxonil	Fresh jujube	$y = 0.4491e^{-0.097x}$	0.8970	7.1
Metalaxyl	Fresh jujube	$y = 2.0722e^{-0.11x}$	0.9542	6.3

0-day maximum residue of cyantraniliprole (0.12 mg/kg) was far below the MRL, indicating adequate safety. However, twice applications up to 7 days before harvest appear acceptable for cyantraniliprole because pre harvest intervals (PHIs) are generally not established as 0 days. In the case of fludioxonil, it was assessed that limiting application to two times 21 days before harvest would be appropriate. Meanwhile, residues of ethaboxam and metalaxyl at 21 days exceeded the PLS limit (0.01 mg/kg), indicating an urgent need to establish MRLs to support their official registration and safe-use recommendations. Using the OECD MRL calculator, the proposed MRLs were estimated at 2.0 mg/kg for ethaboxam and 4.0 mg/kg for metalaxyl. Based on these values, three times applications up to 14 days before harvest for ethaboxam and up to 7 days before harvest for metalaxyl were considered as PHIs (Table 5).

Residue characteristics and MRL assessment in dried jujube

The maximum residues of cyantraniliprole in dried jujube were 0.42 mg/kg at 0 days and 0.11 mg/kg at 21 days. IN-J9Z38, which was below the LOQ in fresh jujube, was detected at 0.01–0.03 mg/kg in dried jujube due to concentration during dehydration. The maximum residues were 4.11 mg/kg at 0 days and 0.79 mg/kg at 21 days for ethaboxam, 1.99 mg/kg at 0 days and 0.19 mg/kg at 21 days for fludioxonil, and 7.18 mg/kg and 0.67 mg/kg for metalaxyl at 0 and 21 days, respectively (Table 6). All pesticides exhibited increased residues after drying due to moisture loss.

In South Korea, separate MRLs are established for food in which pesticides may become concentrated during processing, such as dried agricultural commodities [10]. The MRLs for dried jujube are 1.5 mg/kg for cyantraniliprole and 2.0 mg/kg for fludioxonil, while no MRLs exist for ethaboxam or metalaxyl. The maximum residue level of total cyantraniliprole in dried jujube at 0 days was 0.42 mg/kg, which is about 0.28 times the MRL, indicating a sufficient safety margin. The maximum residue level of fludioxonil at 7 days was 0.69 mg/kg, which is about 0.35 times the MRL. Thus, for fludioxonil, safety in dried jujube was ensured even when the pre-harvest interval was shorter than the 21-day interval recommended for fresh jujube. However, since safe-use standards are fundamentally set based on fresh commodities, it was judged that consumer safety for dried jujubes would also be ensured if the proposed safety standards for fresh jujubes are followed for cyantraniliprole and fludioxonil.

The proposed MRLs for dried jujube calculated using the OECD MRL calculator were 7.0 mg/kg for ethaboxam and 15.0 mg/kg for metalaxyl. The maximum residue of ethaboxam at 14 days was 1.70 mg/kg, corresponding to about 0.24 times the proposed MRL, whereas the maximum residue of metalaxyl at 7 days was 3.70 mg/kg, which was about 0.25 times the proposed MRL. Both pesticides, therefore, met the safety margin at their respective pre-harvest intervals. These results were consistent with those derived from fresh jujube. The proposed MRLs for dried jujube are listed in Table 7.

Processing factors

The mean drying yield of jujube was approximately 30%, consistent with the moisture contents reported in the National Standard Food Composition Table (70.2 g/100 g) and in the Bokjo cultivar used in this study (72.9 g/100 g) [11], confirming appropriate drying.

The processing factors calculated from mean residues before and after drying were 3.25–5.00 for cyantraniliprole, 2.91–4.21

Table 5. Proposed pre-harvest interval (PHI) and number of applications for fresh jujube

Pesticide	Commodity	MRL* (mg/kg)	PHI (days)	Number of application
Cyantraniliprole	Fresh jujube	1.0 (established)	7	2
Ethaboxam	Fresh jujube	2.0 (proposed)	14	3
Fludioxonil	Fresh jujube	0.3 (established)	21	2
Metalaxyl	Fresh jujube	4.0 (proposed)	7	3

* Maximum residue limit, "Established" indicates MRLs officially established by MFDS, "Proposed" indicates values calculated using the OECD MRL Calculator (Version 2, 2020).

Table 6. Residues of the target pesticides in dried jujube at different days after the last application

Pesticide	Day after last application	Residues (mg/kg)	
		Maximum residue	Mean $\pm$ SD*
Cyantraniliprole	0	0.40	0.37 $\pm$ 0.03
	7	0.34	0.32 $\pm$ 0.02
	14	0.29	0.25 $\pm$ 0.03
	21	0.09	0.09 $\pm$ 0.01
IN-J9Z38	0	0.02	0.02 $\pm$ 0.00
	7	0.03	0.03 $\pm$ 0.00
	14	0.03	0.02 $\pm$ 0.01
	21	0.02	0.02 $\pm$ 0.01
Total cyantraniliprole	0	0.42	0.39 $\pm$ 0.03
	7	0.37	0.35 $\pm$ 0.02
	14	0.32	0.28 $\pm$ 0.04
	21	0.11	0.10 $\pm$ 0.01
Ethaboxam	0	4.11	3.83 $\pm$ 0.44
	7	2.68	2.53 $\pm$ 0.25
	14	1.70	1.60 $\pm$ 0.16
	21	0.79	0.75 $\pm$ 0.03
Fludioxonil	0	1.99	1.96 $\pm$ 0.03
	7	0.69	0.65 $\pm$ 0.05
	14	0.56	0.50 $\pm$ 0.06
	21	0.19	0.16 $\pm$ 0.03
Metalaxyl	0	7.18	7.01 $\pm$ 0.16
	7	3.70	3.21 $\pm$ 0.46
	14	3.20	2.73 $\pm$ 0.41
	21	0.67	0.60 $\pm$ 0.07

* Standard deviation.

Table 7. Established and proposed MRLs for the target pesticides in dried jujube

Pesticide	Commodity	MRL* (mg/kg)
Cyantraniliprole	Dried jujube	1.5 (established)
Ethaboxam	Dried jujube	7.0 (proposed)
Fludioxonil	Dried jujube	2.0 (established)
Metalaxyl	Dried jujube	15.0 (proposed)

* Maximum residue limit, "Established" indicates MRLs officially established by MFDS, "Proposed" indicates values calculated using the OECD MRL Calculator (Version 2, 2020).

for ethaboxam, 2.94–4.08 for fludioxonil, and 3.31–4.55 for metalaxyl (Table 8). These were comparable to the theoretical factor (100 / mean drying yield, about 3.33%) and similar to previously reported factors for methoxyfenozide and thiacloprid in jujube (1.89–4.20) [12]. There were no significant differences in processing factors among pesticides ($p < 0.05$), indicating that no compound exhibited disproportionately high or low concentration after drying.

The differences between theoretical and actual residues in dried jujube ranged from -0.01 to $+0.08$ mg/kg for cyantraniliprole, -0.37 to $+0.80$ mg/kg for ethaboxam, -0.07 to $+0.36$ mg/kg for fludioxonil, and -0.06 to $+0.73$ mg/kg for metalaxyl (Table 8). These deviations showed no consistent pattern of increase or decrease, suggesting that neither degradation nor volatilization oc-

Table 8. Comparison of observed and theoretical residues in dried jujube and their processing factors

Pesticide	Day after last application	Average residues (mg/kg)			Processing factors ^{b)}
		Fresh jujube	Dried jujube	Theoretical value in dried jujube ^{a)}	
Cyantraniliprole	0	0.12	0.39	0.40	3.25
	7	0.08	0.35	0.27	4.38
	14	0.06	0.28	0.20	4.67
	21	0.02	0.10	0.07	5.00
Ethaboxam	0	0.91	3.83	3.03	4.21
	7	0.87	2.53	2.90	2.91
	14	0.45	1.60	1.50	3.56
	21	0.25	0.75	0.83	3.00
Fludioxonil	0	0.48	1.96	1.60	4.08
	7	0.17	0.65	0.57	3.82
	14	0.17	0.50	0.57	2.94
	21	0.05	0.16	0.17	3.20
Metalaxyl	0	2.12	7.01	7.07	3.31
	7	0.80	3.21	2.67	4.01
	14	0.60	2.73	2.00	4.55
	21	0.18	0.60	0.60	3.33

^{a)} Theoretical residues in dried jujube calculated as average residues (mg/kg) in fresh jujube ÷ (drying yield / 100).

^{b)} Means followed by the same letter are not significantly different at $p < 0.05$ according to Duncan's multiple range test (DMRT).

curred during drying.

Previous studies reported processing factors (weight-based residue ratios before/after drying) of 0.87–0.98 for methoxyfenozide and thiacloprid in jujube [12], indicating that some pesticides may undergo thermal decomposition or volatilization during drying. Other studies have noted that the extent of pesticide reduction after drying depends on physicochemical properties, such as thermal stability and volatility [13]. Additionally, compounds with low vapor pressure and high log Kow values tend to exhibit minimal loss during dehydration [14].

As shown in Supplementary Table 2, the decomposition temperatures of all pesticides tested in this study were higher than the drying temperature (55°C), making thermal degradation unlikely. Additionally, the vapor pressures of cyantraniliprole, ethaboxam, and fludioxonil are below 10^{-5} Pa, indicating negligible volatility. Metalaxyl has a relatively higher vapor pressure of 0.75 mPa, but it would still be unlikely to volatilize under the drying conditions used in this study.

Overall, actual residues in dried jujube closely matched or exceeded theoretical values, and considering the physicochemical properties, none of the pesticides appeared to undergo degradation or volatilization during drying. Thus, residue increases in dried jujube were attributable primarily to concentration effects from moisture loss.

Risk assessment

According to the toxicological reference values in the RDA Pesticide Safety Information System, the ADIs of cyantraniliprole, ethaboxam, fludioxonil, and metalaxyl are 0.057, 0.055, 0.400, and 0.080 mg/kg bw/day, respectively. The measured maximum residues in fresh jujube were 0.12, 1.01, 0.53, and 2.26 mg/kg, and in dried jujube were 0.42, 4.11, 1.99, and 7.18 mg/kg, respectively. Based on these values, the %ADI in fresh jujube was calculated as 0.001% for cyantraniliprole, 0.009% for ethaboxam, 0.001% for fludioxonil, and 0.014% for metalaxyl, whereas the %ADI values in dried jujube were 0.004%, 0.037%, 0.002%, and 0.045%, respectively (Table 9).

For both fresh and dried jujube, %ADI values were below 0.05%, attributable to the very low daily consumption of jujube

Table 9. Risk assessment of the target pesticides in fresh and dried jujube

Pesticide	Commodity	ADI ^{a)} (mg/kg bw/day)	EDI ^{b)} (mg/kg bw/day)	%ADI ^{c)}
Cyantraniliprole	Fresh jujube	0.057	6.00×10^{-7}	0.001
	Dried jujube		2.10×10^{-6}	0.004
Ethaboxam	Fresh jujube	0.055	5.05×10^{-6}	0.009
	Dried jujube		2.06×10^{-5}	0.037
Fludioxonil	Fresh jujube	0.400	2.65×10^{-6}	0.001
	Dried jujube		9.95×10^{-6}	0.002
Metalaxyl	Fresh jujube	0.080	1.13×10^{-5}	0.014
	Dried jujube		3.59×10^{-5}	0.045

^{a)} Acceptable daily intake.

^{b)} Estimated daily intake.

^{c)} %ADI: (EDI/ADI) $\times$ 100. Values were rounded at the fourth decimal place and presented to three decimal places.

(0.0003 kg/day), and which resulted in estimated daily intakes (EDIs) below 10^{-5} . Although the maximum residue of fludioxonil (0.53 mg/kg) exceeded the MRL (0.3 mg/kg), its %ADI remained extremely low because its ADI is relatively high at 0.4 mg/kg bw/day. However, as daily intake estimates are based on average consumption, individual variation may exist, underscoring the need for establishing safe-use standards and MRLs. Generally, %ADI values below 10% are considered to pose no significant health concern [15]. All pesticides examined in this study fell well within this threshold. Therefore, the dietary risks associated with the consumption of jujube treated with the four pesticides were evaluated to be within a safe range.

Materials and Methods

Test pesticides

The pesticides used in this study were cyantraniliprole 10.26% oil dispersion (OD), ethaboxam 15% suspension concentrate (SC), fludioxonil 20% suspension concentrate, and metalaxyl 25% wettable powder (WP). The commercial products were Cycob (FarmHannong Co., Ltd.), Tellus (InBio Co., Ltd.), Sapphire (Syngenta Korea), and InBio Metacyl (InBio Co., Ltd.), all purchased from local pesticide distributors. The chemical structures and physicochemical properties of these pesticides are presented in Supplementary Table 2.

Field trials

Field trials were conducted in an open-field orchard located in Singwang-myeon, Hampyeong-gun, Jeollanam-do, from 19 August to 19 September 2024. Nine-year-old jujube trees (cv. Bokjo), which are commonly cultivated in South Korea, were used. Four treatment groups with three replicates each were established, and one tree was assigned per replicate. An untreated control was included. The planting distance was 4 m $\times$ 2.5 m. For cyantraniliprole, the treatment schedules were set at 30–21 days before harvest, 21–14 days, 14–7 days, and 7–0 days. For ethaboxam, fludioxonil, and metalaxyl, the schedules were 30–21 days, 30–21–14 days, 21–14–7 days, and 14–7–0 days (Supplementary Fig. 1). Dilution ratios were 1:4,000 for cyantraniliprole 10.26% OD, 1:1,000 for ethaboxam 15% SC, 1:2,000 for fludioxonil 20% SC, and 1:1,000 for metalaxyl 25% WP. The diluted solutions were applied using a rechargeable sprayer (PES-H18G, PASECO, Ansan, Korea) until run-off, with an application volume of 253 L per 10 a.

Meteorological conditions during the trial period were obtained from the Yeonggwang weather station near the experimental field and are shown in Supplementary Fig. 2. Rainfall did not affect the pesticide applications before or after treatment. Samples were collected approximately two hours after the final application on 19 September 2024. For each replicate, more than 2 kg

of uniformly developed jujube fruits were harvested, with an average fruit weight of approximately 15 g. Of these, 1 kg was used for fresh jujube analysis. The calyxes were removed, and the fruits were homogenized with dry ice. The remaining 1 kg was dried at 55°C for 48 hours using a multifunctional dryer (HKT-300, Narotech, Naju, Korea), homogenized, and used for dried jujube analysis. All homogenized samples were stored at -20°C until analysis.

Chemicals and instruments

Standard solutions of cyantraniliprole (1003.2 µg/mL in acetonitrile), ethaboxam (1002.1 µg/mL in methanol), fludioxonil (1005.2 µg/mL in acetone), and metalaxyl (1003.6 µg/mL in acetone) were purchased from Kemidas Co., Ltd. (Gunpo, Korea). The standard of IN-J9Z38, the metabolite of cyantraniliprole (200.2 µg/mL in acetonitrile), was obtained from AB Solution (Hwaseong, Korea).

Acetonitrile, dichloromethane, sodium chloride (GR grade), and celite 545 (CP grade) were purchased from Duksan Pure Chemicals (Ansan, Korea), and anhydrous sodium sulfate (GR grade) was obtained from Samchun Chemical (Pyeongtaek, Korea). Distilled water was prepared using EXL[®]5 U Analysis (VIVAGEN, Seongnam, Korea). HPLC-grade acetonitrile, methanol, and acetone (Burdick & Jackson, Muskegon, USA) were used for standard preparation, and HPLC-grade acetonitrile, water, and ACS-grade formic acid (Sigma-Aldrich, St. Louis, USA) were used for instrumental analysis.

The instruments used for extraction and liquid-liquid partitioning included an orbital shaker (HB-203L, Hanbaek Scientific, Bucheon, Korea), a vacuum pump (DOA-P704-AC, GAST Manufacturing, Benton Harbor, USA), and a funnel shaker (C-SKR, Changshin Scientific, Seoul, Korea). Concentration under reduced pressure was performed using a rotary evaporator (RE100-pro, DLAB Scientific, Beijing, China), a vacuum pump (Vacstar Control, IKA, Staufen, Germany), and a cooling circulator (CF312L, YAMATO Scientific, Tokyo, Japan). Nitrogen evaporation was performed using a nitrogen evaporator (MGS-3100, EYELA, Tokyo, Japan) with high-purity nitrogen gas (≥99.9%, Daechang Gas, Jangseong, Korea).

Preparation of standard solutions

Cyantraniliprole and IN-J9Z38 standards were dissolved in acetonitrile to prepare 100 mg/L stock solutions. The two stock solutions were mixed and diluted to 5 mg/L, then further diluted with acetonitrile to obtain working solutions of 0.005, 0.01, 0.02, 0.05, 0.1, 0.15, and 0.2 mg/L.

Ethaboxam was dissolved in methanol to prepare a 100 mg/L stock solution and diluted with acetonitrile to prepare working solutions in the range of 0.005–0.2 mg/L. Fludioxonil and metalaxyl stock solutions (100 mg/L) were prepared in acetone and diluted with acetonitrile to prepare the same concentration range.

Matrix-matched standards were prepared by evaporating 1 mL of extract from an untreated sample to dryness under nitrogen and reconstituting it with 1 mL of working solution. One microliter of the solution was injected into the LC-MS/MS system, and calibration curves were constructed based on the corresponding peak areas. The calibration range consisted of six concentrations (0.01–0.2 mg/L), and the lowest concentration (0.005 mg/L) was used only for detection but excluded from calibration.

Pesticide residue analysis

The homogenized fresh or dried jujube (10 g) was extracted with 50 mL of acetonitrile by shaking at 180 rpm for 60 minutes. For dried jujube, 50 mL of distilled water was added prior to extraction and allowed to hydrate for 30 minutes. The extract was filtered under vacuum through a Büchner funnel packed with celite 545, and the residue was rinsed with 50 mL of acetonitrile. The filtrate was transferred to a separatory funnel containing 100 mL of distilled water and 50 mL of saturated sodium chloride solution, followed by partitioning with 100 mL of dichloromethane at 230 rpm for 10 minutes. The dichloromethane layer was dried through a funnel packed with anhydrous sodium sulfate. A second partition was performed with 50 mL of dichloromethane, and the organic layers were combined and evaporated at 40°C. The residue was reconstituted in 10 mL of acetonitrile and filtered

through a 0.2 µm PTFE syringe filter before LC–MS/MS analysis. Instrumental conditions and MRM transitions are provided in Supplementary Tables 3 and 4. Total cyantraniliprole residues were calculated using equation (1), according to the residue definition of the National Institute of Agricultural Sciences [16].

$$\text{Total cyantraniliprole residue} = \text{Cyantraniliprole residue} + (\text{IN-J9Z38 residue} \times 1.04^*) \quad (1)$$

$$*1.04 \text{ (The conversion factor)} = 473.72 \text{ (MW of cyantraniliprole)} / 455.70 \text{ (MW of IN-J9Z38)}$$

Recovery and storage stability tests

Recovery tests were conducted by fortifying 10 g of untreated fresh and dried jujube with mixed standards of cyantraniliprole and IN-J9Z38, and individual standards of ethaboxam, fludioxonil, and metalaxyl at three fortification levels: the method limit of quantitation (MLOQ, 0.01 mg/kg), at 10 times the MLOQ, and an expected residue level. Each fortification level was prepared in triplicate. The fortified samples were allowed to stand for 30 minutes and analyzed using the procedures described above. The method limit of quantitation was calculated using equation (2), according to the Practical Guide of the MFDS [6].

$$\text{MLOQ (mg/kg)} = [\text{Instrumental LOQ}^* \text{ (ng)} / \text{Injection volume (}\mu\text{L)}] \times [\text{Final extract volume (mL)} / \text{Sample weight (g)}] \quad (2)$$

$$* \text{ Instrumental LOQ (ng)} = \text{The lowest calibration level (mg/L)} \times \text{Injection volume (}\mu\text{L)}$$

Storage stability tests were performed by fortifying 10 g of untreated fresh jujube (on the day of harvest) and 10 g of untreated dried jujube (after drying) with mixed standard solutions of cyantraniliprole and IN-J9Z38, as well as individual standard solutions of ethaboxam, fludioxonil, and metalaxyl, at a level equivalent to ten times the method limit of quantitation (0.1 mg/kg). Each fortification level was prepared in triplicate. The fortified samples were allowed to stand for 30 minutes and then stored at –20°C until analysis. The samples were subsequently analyzed using the procedures described above.

Biological half-lives

Biological half-lives were calculated using first-order kinetics. The dissipation constant (k) was obtained from equation (3), and the half-life ($t_{1/2}$) was calculated as $0.693/k$.

$$C_t = C_0 \times e^{-kt} \quad (3)$$

$$t_{1/2} = \ln 2 / k = 0.693/k$$

C_t , residue at time t ; C_0 , initial residue; t , days after treatment; k , dissipation constant (day^{-1}); $t_{1/2}$, biological half-life (days).

MRL estimation

For pesticides without established maximum residue limits, proposed MRLs were estimated using the OECD MRL calculator (version 2, OECD, 2020) based on the 12 residue data points.

Drying yield

Drying yield was calculated according to equation (4).

$$\text{Drying yield (\%)} = \text{Weight after drying (g)} / \text{Weight before drying (g)} \times 100 \quad (4)$$

Processing factor

Processing factors were calculated using equation (5), based on the ratio of residues in dried jujube to those in fresh jujube, following the MFDS principles for establishing food standards [17].

$$\text{Processing factor} = \text{Residue after processing (mg/kg)} / \text{Residue before processing (mg/kg)} \quad (5)$$

Risk assessment

The percentage of acceptable daily intake (%ADI) was calculated according to equation (6) [18]. The %ADI was obtained by dividing the estimated daily intake (EDI) by the acceptable daily intake (ADI) and multiplying the result by 100. The EDI (mg/kg bw/day) was calculated by multiplying the maximum residue (mg/kg) by the daily consumption of jujube (0.0003 kg per day, based on the 2023 statistics of the Korea Health Industry Development Institute) and dividing by the average Korean body weight (60 kg). The ADI, defined as the maximum daily intake that can be consumed over a lifetime without adverse health effects, was obtained from the toxicity exposure information provided in the RDA Pesticide Safety Information System.

$$\text{ADI (\%)} = \text{EDI* (mg/kg bw/day)} / \text{ADI (mg/kg bw/day)} \times 100 \quad (6)$$

$$\text{*EDI (mg/kg bw/day)}$$

$$= \text{Maximum residue (mg/kg)} \times \text{Daily consumption of jujube (kg/day)} / \text{Average Korean body weight (60kg)}$$

Statistical analysis

Temporal changes in pesticide residues were analyzed using SPSS Statistics version 29 (IBM Corporation, Armonk, USA). One-way analysis of variance (ANOVA) followed by Duncan's multiple range test (DMRT) was performed to determine significant differences at $p < 0.05$.

Data Availability: All data are available in the main text or in the Supplementary Information.

Author Contributions: Ki HO and Shin J conducted the experiments, performed investigation and data curation, and wrote the manuscript; Kim CH financed the research; Kim SH edited the manuscript; Kim IS provided overall supervision and critical feedback on the manuscript.

Notes: The authors declare no conflict of interest

Acknowledgments: This work was supported by Rural Development Administration (RDA), Republic of Korea (Project No. RS-2024-00350204).

Additional Information:

Supplementary information The online version contains supplementary material available at <https://doi.org/10.5338/KJEA.2025.44.52>

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Peer review information Agricultural and Environmental Sciences thanks the anonymous reviewers for their contribution to the peer review of this work.

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Supplemental Table 1. Storage stability of the target pesticides in fresh and dried jujube at –20°C (fortification level: 0.1 mg/kg)

Pesticide	Commodity	Storage period (days)	Recovery (%)	
			Mean $\pm$ SD ^{a)}	RSD ^{b)} (%)
Cyantraniliprole	Fresh jujube	32	86.9 $\pm$ 2.4	2.8
	Dried jujube	31	81.3 $\pm$ 2.2	2.7
IN-J9Z38	Fresh jujube	32	91.4 $\pm$ 2.8	3.1
	Dried jujube	31	85.4 $\pm$ 2.7	3.2
Ethaboxam	Fresh jujube	27	88.8 $\pm$ 13.0	14.6
	Dried jujube	26	77.8 $\pm$ 1.8	2.3
Fludioxonil	Fresh jujube	29	88.8 $\pm$ 0.8	0.9
	Dried jujube	30	84.9 $\pm$ 3.6	4.2
Metalaxyl	Fresh jujube	25	91.6 $\pm$ 2.3	2.5
	Dried jujube	24	90.7 $\pm$ 1.5	1.7

^{a)} Standard deviation,

^{b)} Relative standard deviation.

Supplemental Table 2. Chemical structure and physicochemical properties of the target pesticides

Pesticide	Cyantraniliprole (CT)	IN-J9Z38 (metabolite of CT)		
Chemical structure				
Molecular weight	473.72 g/mol	455.70 g/mol		
Degradation point	350°C	-		
Log K _{ow} (pH 7)	2.02 (20°C)	-		
Vapor pressure (mPa)	5.13 $\times$ 10 ⁻¹² (20°C)	-		
Pesticides	Ethaboxam	Fludioxonil	Metalaxyl	
Chemical structure				
Molecular weight	320.43 g/mol	248.19 g/mol	279.33 g/mol	
Degradation point	Melting point (185°C, decomposes)	306°C	Melting point: 72°C, Boiling point: 394.3°C	
Log K _{ow} (pH 7)	2.89 (20°C)	4.12 (20°C)	1.75 (25°C)	
Vapor pressure (mPa)	8.10 $\times$ 10 ⁻² (20°C)	3.90 $\times$ 10 ⁻⁴ (20°C)	7.50 $\times$ 10 ⁻¹ (20°C)	

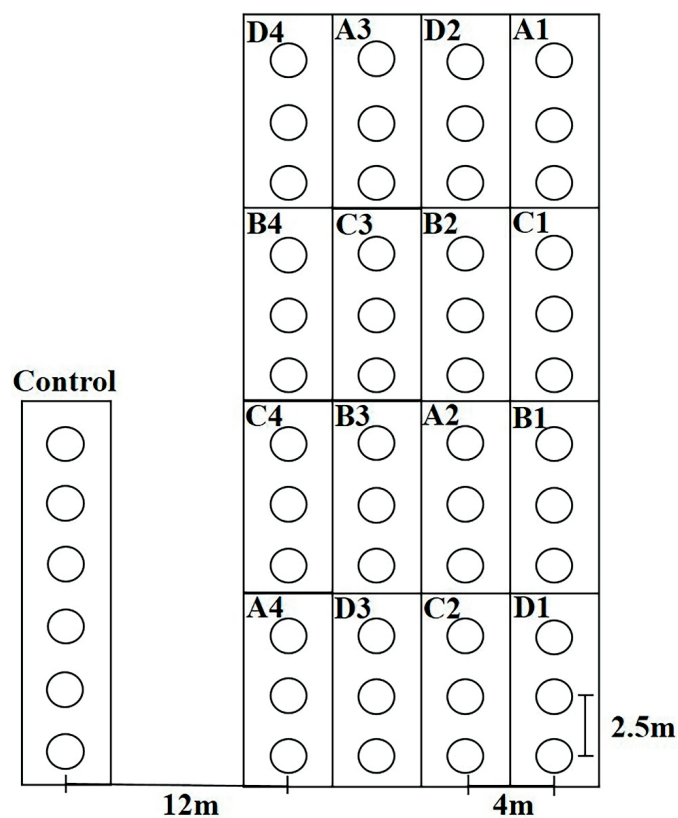
Supplemental Table 3. LC–MS/MS conditions for the analysis of the target pesticides in jujube

LC		Conditions	
Instrument		Nexera X2 coupled with LCMS-8040, Nexera X3 coupled with LCMS-8050 (Shimadzu, Kyoto, Japan)	
Column		Imtakt, Unison UK-C18HT (100 × 2.0 mm, 3.0 μm)	
Column temp.		40°C	
Flow rate		0.3 mL/min	
Injection volume		1.0 μL	
Mobile phase		A: 0.1% formic acid in water; B: 0.1% formic acid in acetonitrile	
	Pesticides	A (%)	B (%)
	Cyantraniliprole ^{a)}	20	80
	IN-J9Z38 ^{a)}	20	80
	Ethaboxam ^{b)}	30	70
	Fludioxonil ^{b)}	30	70
	Metalaxyl ^{b)}	30	70
MS		Conditions	
Nebulizing gas flow		3.0 L/min	
Drying gas flow		10.0 ^{a)} L/min, 15.0 ^{b)} L/min	
Desolvation line temp.		250°C	
Heat block temp.		400°C	

^{a)} Analyzed using LCMS-8050.^{b)} Analyzed using LCMS-8040.**Supplemental Table 4. Multiple reaction monitoring (MRM) conditions of the target pesticides**

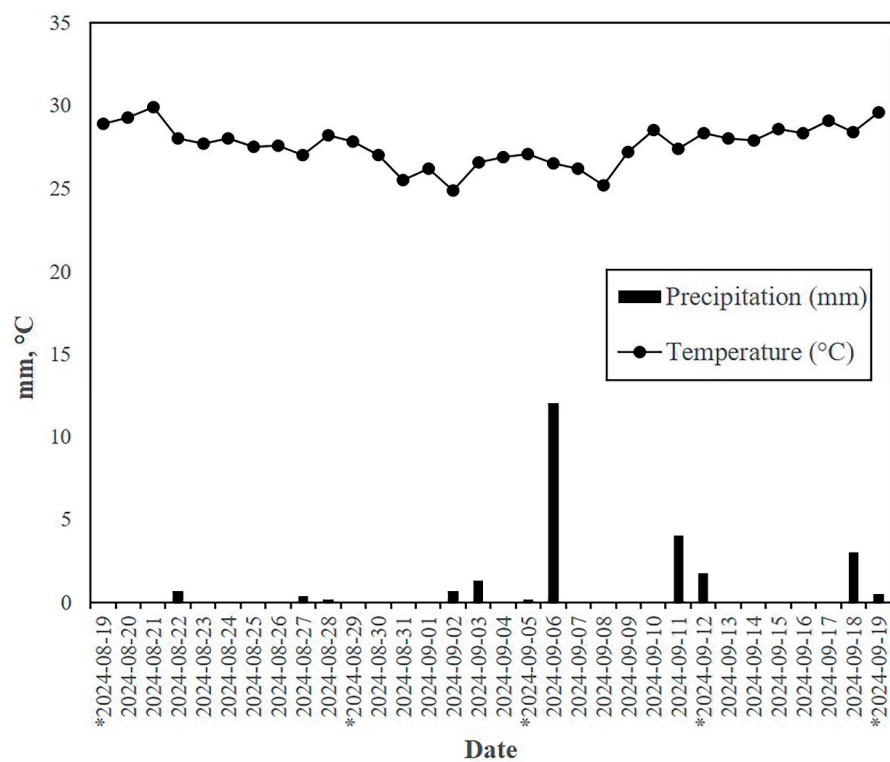
Pesticides	Ionization mode	RT ^{a)} (min)	Precursor ion (m/z)	Product ion (m/z)	CE ^{b)} (eV)
Cyantraniliprole	+	0.9	474.70	285.95	29
				443.80	18
IN-J9Z38	+	1.2	457.10	187.80	29
				112.10	42
Ethaboxam	+	1.0	321.00	183.05	23
				200.05	27
Fludioxonil	-	1.3	247.05	179.90	30
				125.95	31
Metalaxyl	+	1.2	280.05	220.05	14
				192.05	19

^{a)} RT: Retention time.^{b)} CE: Collision energy.



Supplemental Fig. 1. Field layout of treatment plots in the jujube orchard.

A–D indicate the target pesticides: A, Cyantraniliprole 10.26% OD; B, Ethaboxam 15% SC; C, Fludioxonil 20% SC; D, Metalaxyl 25% WP. Numbers 1–4 represent the application timings before harvest, with 1 indicating the earliest treatment and 4 the latest.



Supplemental Fig. 2. Changes in temperature and precipitation during the experimental period. *Pesticide application date.