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Original article (Orijinal araştırma)

Effect of different processing techniques on the residue levels of some acaricides and insecticides in gherkin pickles[1]

Farklı işleme tekniklerinin kornişon turşularındaki bazı akarisit ve insektisitlerin kalıntı seviyeleri üzerindeki etkisi

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Abstract

Gherkin plants grown in the greenhouse of Bursa Uludağ University were sprayed with different acaricides and insecticides (spiromesifen, etoxazole, deltamethrin, chlorantraniliprole, acetamiprid) at the legal field application doses in 2023. Fruits that were harvested after the pre-harvest intervals of the applied test pesticides were processed for pickle making. Pickles were produced by fermentation and canning (fresh pack) techniques. Changes in pesticide residue levels were monitored at each processing step. Processing factors for each pesticide were calculated for fermentation and canning techniques. No significant reductions were observed in the concentrations of all pesticides in raw material following harvest. On the other hand, changes in the concentrations of spiromesifen, chlorantraniliprole and acetamiprid were significant throughout both canning and natural fermentation processes. However, neither process affected the concentrations of deltamethrin and etoxazole. The stability of deltamethrin residues may be related to low pH in both types of processes, but this explanation is not suitable for etoxazole due to its increased stability under high pH conditions. Processing factors of all the tested pesticides were lower than 1 for both treatments but varied depending on the processing method and chemical characteristics and degradation mechanisms of the pesticides.

Keywords: Acaricide, canning, gherkins, fermentation, food safety, insecticide, processing factor

Öz

Bu çalışmada, Bursa Uludağ Üniversitesinin serasında yetiştirilen kornişon tipi hıyar bitkilerine, 2023 yılında önerilen uygulama dozlarında farklı akarisit ve insektisitler (spiromesifen, etoxazole, deltamethrin, chlorantraniliprole, acetamiprid) uygulanmıştır. Tüm pestisitler için hasat öncesi aralık süreleri tamamlandıktan sonra hasat edilen meyveler, turşu işleme için hazırlanmıştır. Turşular, fermantasyon ve konserve teknikleri kullanılarak üretilmiştir. Her işleme aşamasında pestisit kalıntılarındaki değişiklikler izlenmiş ve her bir pestisit için fermente ve konserve yöntemleri için işleme faktörleri hesaplanmıştır. Hasat sonrasında ham maddede uygulanan tüm pestisitlerin konsantrasyonlarında önemli bir azalma bulunmamıştır. Öte yandan, spiromesifen, chlorantraniliprole ve acetamiprid konsantrasyonlarındaki değişiklikler hem konserve hem de doğal fermantasyon işlemleri boyunca önemli bulunmuştur. Ancak, her iki işlem türü de deltametrin ve etoxazole konsantrasyonlarını etkilememiştir. Deltametrindeki bu kararlılığın, her iki işlem türünde de düşük pH ile ilişkili olabileceği düşünülse de etoxazole için bu açıklama uygun bulunmamıştır. Çünkü yüksek pH koşullarında etoxazole'ün kararlılığının arttığı bilinmektedir. Her iki işlem için de tüm pestisitlerin işleme faktörleri 1'den düşük olmakla birlikte, işleme yöntemi, pestisitlerin kimyasal yapısı ve bozunma mekanizmalarına bağlı olarak değişiklikler göstermiştir.

Anahtar sözcükler: Akarisit, konserve, kornişon, fermantasyon, gıda güvenliği, insektisit, işleme faktörü

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Introduction

Pesticide use is generally unavoidable in agricultural practices to prevent the losses due to pests. The use of agrochemicals is considered safe for humans and other non-target organisms when applied at the approved dosages and in accordance with pre-harvest interval regulations (Banshtu et al., 2018). However, improper uses of these chemicals or harvesting before the recomended pre-harvest interval (PHI), generally result in pesticide residues in the fresh commodities (Gonzalez-Rodriguez et al., 2011). Pesticide residue levels may change depending on the pH, light exposure, temperature and moisture content of the environment, and the degradation levels may vary depending on the structure and the formulation of the active compound (Regueiro et al., 2015; Hepsag & Kizildeniz, 2021). Additionally, food processing techniques have a significant effect on the pesticide residue levels of the processed products (Maden & Yildirim Kumral, 2020). Alteration in pesticide levels affected by the processing method is measured by processing factor (PF). PF is determined by calculating the ratio of pesticide residue concentration in the processed product to that in the corresponding raw material (EC, 2005). PF is additionally used for the interpretation of the initial pesticide residue level of the processed food product and helps to assess its compliance with the legal requirements. It is also a necessary tool for the assessment of acute and chronic health risks that may occur with the exposure to the processed foods contaminated with pesticide residues (BFR, 2023). For an accurate and reliable evaluation, processing factor calculations must be performed for all active compounds and for each process type separately.

Pickling is one of the oldest and widely used food preservation method that allows long-term conservation of foods under acidic conditions (Montano et al., 2016; Behera et al., 2020). Industrially or homemade pickles are commonly categorised into two groups and named as fermented and canned (fresh pack) pickles (Stankus, 2014; Zincke et al., 2022). Despite the differences in the processing method, inhibition of pathogenic and/or spoilage microorganisms is the main target in both type of pickles. Canned pickles are not fermented, and they are immediately pasteurised by heating for the long-term conservation of the product. Fermented pickles are obtained by spontaneous or controlled fermentation by naturally occurring lactic acid bacteria (LAB). In the later processing, the pickles are firstly fermented for 2-6 weeks, and then pasteurised by heating (BFR, 2023). In both methods, low pH environment is desired and obtained with addition of vinegar in canned pickles and produced by LAB in the fermented ones. Both processing types involve a heat treatment (pasteurisation) at different steps of the production for the prolonged preservation of the products without refrigeration (BFR, 2023).

Gherkin fruits are widely used for pickle production and their pickled forms are extensively consumed worldwide in different food preparations. Many pesticides (acaricides and insecticides) are registered for cucumber/gherkin cultivation, and their residue alteration during pickle processes is not clarified with the current knowledge. Scientific data related to the impact of pickle processing on pesticide residue changes is still limited. The half-life (DT_{50}) value of a pesticide helps to estimate its degradation duration, and it is usually affected by the pH sensitivity and the chemical structure (Luyinda & Yildirim Kumral, 2023; PPDB, 2024). It has been previously demonstrated that low pH levels of different pickled commodities (olives, cabbages, tomatoes) slowed down the degradation or induced the stabilization of certain pesticides (Maden & Yildirim Kumral, 2020; Yildirim Kumral et al., 2020a; Luyinda & Yildirim Kumral, 2023). Recent studies showed that pesticide degradation might also be affected during fermentation by the activity of LAB that can metabolise pesticides (Behera et al., 2020; Yildirim Kumral et al., 2020b).

Gaps in knowledge about pesticide degradation mechanisms and limited scientific data about the transformation of pesticides during food processing sometimes hinder research efforts. Currently, only a limited number of PFs for pickles were determined and declared by the food safety authorities. The progress is so slow, and new pesticides are coming into use each passing day. However, there is still limited data on the impact of the pickling process on newly registered (for cucumber/gherkin cultivation) pesticides. This study aimed to explain the changes in the residues of extensively used pesticides (acaricides and insecticides) during the pickling of gherkins and to designate the PFs for each processing technique and the specific pesticide.

Materials and Methods

Chemicals and reagents

Pesticide standards and sample extraction-cleanup kits were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and Lab Instruments (Castellana Grotte, Italy) respectively. Other chemicals used during the experiments were of analytical grade. Names of the active chemicals, their trade names, application doses, PHIs, maximum residue limits (MRLs) and toxicological properties are given in Table 1 and Table 2.

Table 1. Names, application doses, pre-harvest interval and maximum residue limits of pesticides

Active substance	Commercial name	Application dose	Pre-harvest interval (days)	Maximum residue limits (mg kg^{-1})
Acetamiprid (20%)	Effore	0.30 g L^{-1}	3	0.60
Etoxazole (110 g/L)	Eurogold	0.35 mL L^{-1}	3	0.01
Spiromesifen (240 g/L)	Oberon	0.50 mL L^{-1}	3	0.30
Deltamethrin (25 g/L)	Dentis	0.50 mL L^{-1}	3	0.20
Chlorantraniliprole (20%)	Coragen	0.07 g L^{-1}	1	0.30

Table 2. Toxicological features of pesticides (Pesticide Properties Database, 2023)

Chemical name	Chemical group	Mode of action	Solubility -in water at 20°C (mg l^{-1})	Boiling point (°C)	Degradation point (°C)	Octanol-water partition coefficient at pH 7, 20°C Log P	pH sensivity [DT_{50} (days) under low pH conditions]
Acetamiprid	Neonicotinoid	Nicotinic acetylcholine receptor (nAChR) competitive modulators	2950	DBB*	200	0.80	stable
Chlorantraniliprole	Diamide	Ryanodine receptor modulators	0.88	DBB	330	2.86	stable
Deltamethrin	Synthetic Pyrethroid	Sodium channel modulators	0.0002	DBB	-	4.60	stable
Etoxazole	Diphenyl oxazolin	Mite growth inhibitors affecting CHS1	0.07	DBB	293	5.52	9.60
Spiromesifen	Tetronic acid	Inhibitors of acetyl CoA carboxylase	0.13	DBB	375	4.55	107.30

*DBB: Decomposes before boiling; ** npH= No pH sensitive.

Pesticide application

Active chemicals used in the experiments were selected according to the findings of a preliminary market survey conducted during the year 2021-2022 (Hazarhun et al., 2022). The most prevalent 5 pesticides (survey study results, data not shown) detected in commercial pickled gherkin samples collected from markets were used as research material. Gherkin plants, *Cucumis sativus* L. (Cucurbitales: Cucurbitaceae) used during these experiments were grown by the research team in an experimental greenhouse at Bursa Uludağ University. The fruit samples were collected from experimental area and stored frozen (-24°C) until analysis (OECD, 2008). Pesticides were homogenously sprayed on gherkin plants at the legal application doses using an electrical atomizer (Table 1) and harvested after the specified PHI (Table 1) for all chemicals tested.

Pickling process and experimental design

Pickle processing methods were applied based on the "database of processing techniques and processing factors compatible with the EFSA food classification and description system FoodEx 2" (Scholz et al., 2018; Zincke et al., 2022) (Figure 1). In addition to pickling treatments, raw gherkin fruits were stored at chilled conditions concurrently to discriminate the effects of processing from the self-degradation of the active compounds. Details of the experiments and processing methods are summarized in Table 3. All experiments were planned and conducted in triplicate.

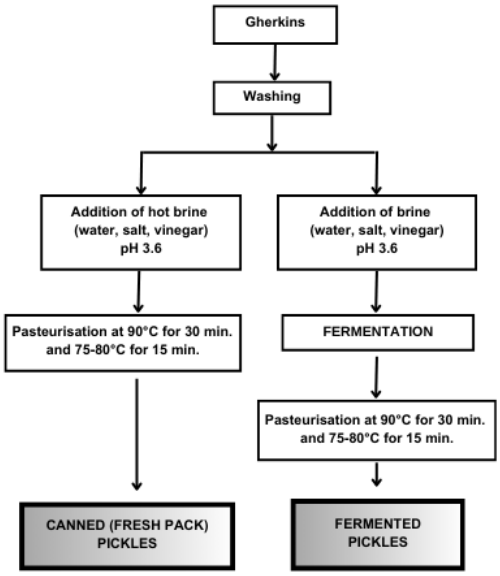

Figure 1. Experimental design and treatments.

Table 3. Details of the experiments and processing methods

Treatment	Application
Chilled storage (control)	Fruits were harvested and then kept at 10±2°C during pickling treatments.
Fresh pack gherkins	Fruits were harvested, washed and transferred into glass containers. Containers were filled with brine (8% salt and 10% vinegar) and pasteurised (30 min. at 90°C, and 15 min. at 75-80°C). Stored at 22±2°C until analysis.
Fermented gherkins	Fruits were harvested, washed and transferred into glass containers. Containers were filled with brine (8% salt and 10% vinegar) and fermented for 4 weeks at 22±2°C. Pasteurised after fermentation (30 min. at 90°C, and 15 min. at 75-80°C). Stored at 22±2°C until analysis.
Fresh gherkins	Fruits were harvested and transferred into glass containers. Stored in the refrigerator (+4°C) until analysis.

Pesticide analysis

Pesticide extraction and cleaning procedures

Samples of fresh and pickled gherkins fruits were homogenised with a laboratory grinder (Retsch Knife Mill Grindomix GM300, Germany) and prepared according to Quick Easy Cheap Effective Rugged Safe (QuEChERS) method recommended for the pesticide analysis of fresh fruit and vegetables (Lehotay, 2007). Sligtly modified QuEChERS steps for extraction and cleaning are given in Figure 2 (Hazarhun et al., 2022).

Instrumental analysis

Samples prepared for the detection of pesticide concentrations were subjected to LC-MS/MS analyses. The specifications and conditions of the instrument are shown in Table 4. Information on tested pesticides is listed in Table 5.

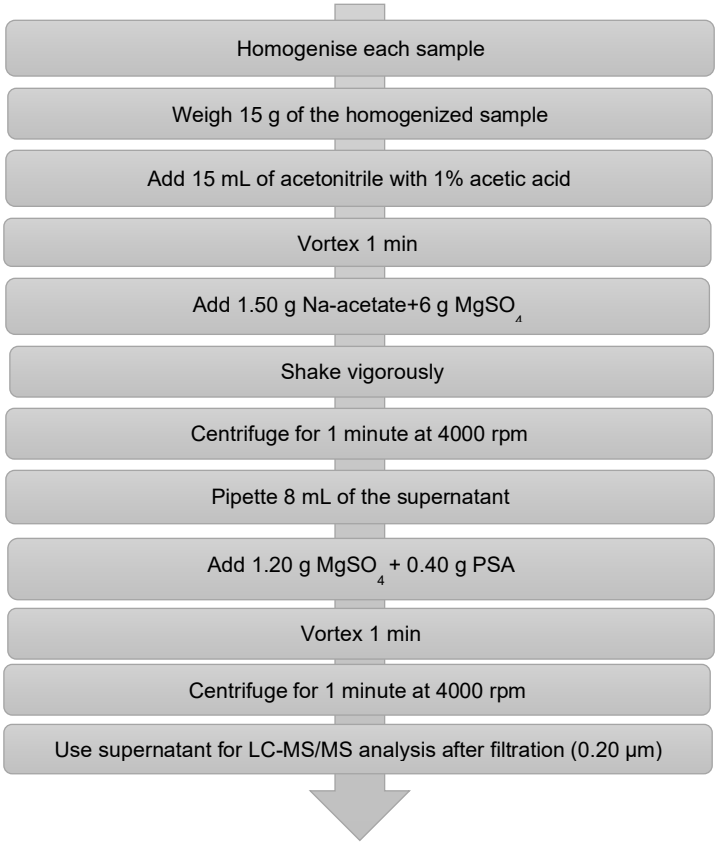

Figure 2. Analytical steps for extraction and cleaning (QuEChERS-AOAC Official Method 2007.01).

Table 4. LC-MS/MS and GC-MS conditions

LC-MS/MS system	Agilent 1260 Infinity II HPLC and Agilent 6470 Triple Quad Liquid-Mass Spectrometry
Column	Agilent Poroshell SB-C18 Column (3x100 mm x 2.7 mm)
Ionisation mode	Electrospray ionization
Acquisition mode	Multiple-reaction monitoring (Negative and positive)
Mobile phase	A: 0.1% formic acid and 1 mM ammonium format in water B: Methanol
Gradient	0-0.5 min 70% A, 8 min 5% A, 8-12.5 min 5% A, 12.6 min. 70% A, 12.6-15 min %70 A
Flow rate	0.50 mL /min
Column temperature	45ºC
Injection volume	1 µL
Run time	15 min.
GC system	GCMS-TQ8040 NX
Column	Restek GC Column (Rtx-624, 30 m., 0.25 mmID, 1.4 µm df
Column temperature	120ºC
Flow rate	1.50 mL/min
Injection mode	(AOC-20i Plus) Splitless
Injection temperature	250.0ºC
Carrier gas	Helyum (%99.9)
Carrier gas temprature	120.0ºC
Carrier gas pressure	121.9 kPa
Total flow	19.5 mL/min
Column flow	1.50 mL/min
Column oven temprature program	0-2 min 120ºC, 2-8 min 230ºC, 8-12 min 300ºC, 12-16 min 300ºC

Table 5. Pesticide information

Chemical name	CAS number	Molecular weight	Molecular formula	Ionization	Precursor Ion	Product Ion	Collision energy (V)	Retention time (min.)
Acetamiprid	135410-20-7	222.67	$C_{10}H_{11}ClN_4$	[M+H]+	223.1	126.1, 56.2	17, 11	3.14
Chlorantraniliprole	500008-45-7	483.15	$C_{18}H_{14}BrCl_2N_5O_2$	[M+H]+	484, 482	285.9, 283.9	21, 21	6.62
Deltamethrin	52918-63-5	505.20	$C_{22}H_{19}Br_2NO_3$	[M+NH4]+	522.8	505.8, 280.6	6, 12	9.62
Etoxazole	153233-91-1	359.42	$C_{21}H_{23}F_2N_{02}$	[M+H]+	360	141, 113	15, 23	9.37
Spiromesifen	283594-90-1	370.48	$C_{23}H_{30}O_4$	[EI]	272	254, 209	6, 14	10.32

Method validation

Pesticide analysis method was validated as per the direction of Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed SANTE 11312/2021 (EURL, 2021; Hazarhun et al., 2022). Tested validation parameters for each pesticide were given in Table 6. For the validation studies pesticide-free gherkin fruits and pickles were used. The pesticide free gherkin fruits were obtained from the experimental greenhouse and a part of these fruits were processed as pickles for further validation studies. Linearity was checked with seven concentrations (2.50-250 µg kg^{-1}). Calculations of recovery rates and precision parameters were performed using the test results obtained by two analysts, at two different concentrations (10 and 50 µg kg^{-1}) and across five different time points.

Table 6. Validation parameters

Chemical name	Concentration range for calibration (µg kg^{-1})	Correlation coefficient (R^2)	LOQ (µg kg^{-1})	Spike level (µg kg^{-1})	RSDr (%)	RSDwr (%)	Mean recovery (%)
Acetamiprid	2.50-250	0.99	3.97	10 50	0.77-0.99 0.74-0.85	5.72 5.16	111.82 112.16
Chlorantraniliprole	2.50-250	0.99	3.87	10 50	5.54-13.19 2.58-4.74	13.07 10.27	99.02 106.36
Deltamethrin	2.50-250	0.99	3.00	10 50	3.75-11.68 6.86-6.88	7.93 4.72	100.49 102.05
Etoxazole	2.50-250	0.99	3.95	10 50	1.35-5.01 3.62-3.75	8.29 7.24	108.61 105.38
Spiromesifen	2.50-250	0.99	7.11	10 50	5.45-6.21 2.88-4.46	13.70 14.11	89.09 93.03

Calculation of the processing factors and residue reduction rates

Processing factors were calculated for each pesticide active compound and the processing method by dividing the residue concentration of processed product to the residue concentration of the relevant raw material (EC, 2005). Pickled samples firstly drained and separated from brine and then prepared for pesticide residue test and then used for the calculation of the PFs.

Statistical analysis

Experimental trials and analyses were performed in triplicate. The data were first evaluated for normal distribution using the Shapiro-Wilk's test. After normality test, pesticide concentration values determined at each processing stage were subjected to analysis of variance (ANOVA). To identify significant differences between groups, Tukey's multiple comparison test was subsequently applied (α=0.05). All statistical analyses were performed using JMP 7.0 software (SAS, Cary, NC).

Results and Discussion

Pesticide residue changes

Changes in pesticide concentrations during chilled storage of fresh fruits are demonstrated in Table 7. Analysis samples were taken 3 hours after pesticide application, on the harvest day and at the end of 30 days. During this period, no significant changes were observed in the levels of most pesticide residues, including acetamiprid, chlorantraniliprole, deltamethrin, and etoxazole, with the exception of spiromesifen. The significant change detected in spiromesifen levels may be attributed to the half-life of this pesticide (PPDB, 2024).

Changes in the residue levels and related reduction rates during fresh pack and fermented pickling processes are given in Tables 8 and 9. Pesticide reduction rates were calculated at the end of processing and storage for fresh pack trials and before and after fermentation for fermentation trials. Reductions in residues of spiromesifen, chlorantraniliprole and acetamiprid were significant across both canning and natural fermentation processes. When pickled trials are compared with the chilled stored raw commodities, it is observed that pickling processes significantly accelerated the degradation of acetamiprid and chlorantraniliprole (Tables 7, 8 & 9). In both pickling processes, pH levels were 3.60 at the beginning of processes due to vinegar addition (Figure 1). The effects of fermentation process on pesticide degredation have been shown in previous studies (Dordevic et al., 2013; Bajwa & Sandhu, 2014; Regueiro et al., 2015; Maden & Yildirim Kumral, 2020; Yildirim Kumral et al., 2020a; Luyinda & Yildirim Kumral, 2023). In addition, the photodegradation of pesticides were disregarded owing to the storage of the samples in the dark conditions during the experiments. In this context, the degradation of the pesticides could be one of the consequences of microbial activities (Maden & Yildirim Kumral, 2023). On the other hand, deltamethrin and etoxazole concentrations were not affected by either of the pickling processes (Table 8 and 9). This could be related with the stability of deltamethrin under acidic conditions but can not be explained with the same mechanism for etoxazole because of its high degradability under low pH conditions (PPDB, 2024; Table 2). Low water solubility (0.07 mg L^{-1}) and higher fat solubility (octanol-water partition coefficient, Log P: 5.52) of etoxazole could be the fact for non degradation of its residues (Borcakli et al., 1993; Kiai & Hafidi, 2014; Featherstone, 2016; PPDB, 2024) (Table 2). In fermentation trials, washing and brine addition steps decreased the residue levels at varying rates (17.09-49.35%) (Table 9). In the fresh pack trials, it is quite difficult to see the effects of washing because both washing, brine addition and pasteurization steps were done at the same time. However, significant degradation was observed immediately after the pasteurization step on the third day during the fresh pack trials. In this step, acetamiprid, chlorantraniliprole, and spiromesifen residues were significantly reduced by 70, 83, and 97 percent, respectively.

Table 7. Pesticide residue changes in the fresh gherkin fruits (mg kg^{-1})

Active compound	Application day** (day 0) (mg kg^{-1})	Harvest day** (day 3) (mg kg^{-1})	Storage** (day 30) (mg kg^{-1})	F_{df}; p^b
Acetamiprid	0.24±0.05 a*	0.28±0.03 a	0.24±0.02 a	$F_{2,8}$=0.47, p=0.64
Chlorantraniliprole	0.32±0.07 a	0.41±0.08 a	0.25±0.06 a	$F_{2,8}$=1.34, p=0.33
Deltamethrin	0.06±0.01 a	0.09±0.03 a	0.04±0.01 a	$F_{2,8}$=2.16, p=0.20
Etoxazole	0.08±0.02 a	0.08±0.03 a	0.03±0.01 a	$F_{2,8}$=1.97, p=0.22
Spiromesifen	0.55±0.08 ab	0.70±0.10 a	0.25±0.04 b	$F_{2,8}$=8.16, p=0.02*

* Significant at 0.05 level;

**means±standard errors followed by different letters in a row are significantly different.

Table 8. Pesticide residue changes during fresh pack trials (mg kg^{-1})

Active compound	Harvest day** (day 3) (mg kg^{-1})	Washing, brine addition and pasteurization** (day 3) (mg kg^{-1})	Reduction rate*** (%)	Storage** (day 30) (mg kg^{-1})	Reduction rate*** (%)	F_{df}; p
Acetamiprid	0.42±0.13 a	0.13±0.03 ab	69.62	0.09±0.01 b	32.28	$F_{2,8}$=5.63; p=0.04*
Chlorantraniliprole	0.45±0.15 a	0.08±0.02 b	83.15	0.07±0.01 b	10.53	$F_{2,8}$=6.46; p=0.03*
Deltamethrin	0.181±0.07 a	0.05±0.01 a	72.38	0.04±0.01 a	20.00	$F_{2,8}$=3.82; p=0.08
Etoxazole	0.11±0.03 a	0.05±0.02 a	54.21	0.06±0.02 a	-	$F_{2,8}$=1.72; p=0.26
Spiromesifen	0.70±0.10 a	0.02±0.02 b	96.69	0.01±0.00 b	69.56	$F_{2,8}$=41.74; p<0.01*

* Significant at 0.05 level;

** means±standard errors followed by different letters in a row are significantly different;

*** Reduction rates were calculated in comparison with the previous process.

Table 9. Pesticide residue changes during fermentation trials (mg kg^{-1})

Active compound	Harvest day** (day 3) (mg kg^{-1})	Washing and brine addition** (day 3) (mg kg^{-1})	Reduction rate*** (%)	After fermentation and pasteurization** (day 30) (mg kg^{-1})	Reduction rate*** (%)	F_{df}; p
Acetamiprid	0.28±0.03 a	0.22±0.05 ab	20.07	0.14±0.01 b	39.46	$F_{2,8}$=5.16; p=0.05*
Chlorantraniliprole	0.41±0.08 a	0.31±0.06 ab	25.43	0.11±0.02 b	64.59	$F_{2,8}$=7.53; p=0.02*
Deltamethrin	0.09±0.03 a	0.08±0.00 a	20.21	0.03±0.00 a	64.00	$F_{2,8}$=3.95; p=0.08
Etoxazole	0.08±0.03 a	0.04±0.00 a	49.35	0.01±0.00 a	81.18	$F_{2,8}$=4.31; p=0.07
Spiromesifen	0.70±0.10 a	0.58±0.05 a	17.09	0.01±0.00 b	98.96	$F_{2,8}$=29.82; p<0.01*

* Significant at 0.05 level;

** means±standard errors followed by different letters in a row are significantly different;

*** Reduction rates were calculated in comparison with the previous process.

Consistent with our findings, previous studies demonstrated that pasteurisation reduced pesticide residue levels to a varied extent depending on the chemical structure of each compound (Bajwa & Sandhu, 2014; Hrynko et al., 2023). No significant change in pesticide residues was detected after 30 days of storage following pasteurisation (Table 8). In fact, the storage period under dark conditions less affected pesticide residue amounts (from 0 to 32.28%) except for spiromesifen (69.56%). It is explained by the faster degradation of spiromesifen (DT_{50}= 4.1 days under laboratory conditions at 20ºC) (PPDB 2024). Thus, residual concentrations of most of the test pesticides generally remained unchanged during post-pasteurisation storage. On the other hand, higher pesticide degradation rates (39.46 to 98.96%) were detected in fermented samples compared to canned ones during 30 days of fermentation period (Table 9). Besides, spiromesifen residues decreased significantly during fermentation step compared to brine addition step. These high reductions in natural fermentation could be related to microbial activity and the pasteurisation procees. Stabilization of pH-sensitive pesticides at low pH levels reached during fermentation processes have been previously reported (Li et al., 2008; Maden & Yildirim Kumral, 2020; Yildirim Kumral et al., 2020a; Lucinda & Yildirim Kumral, 2023). Lactic acid production is a desired activity of LAB in fermented pickles for the product's microbial safety and long-term preservation (Aljahani, 2020). pH levels below 4.6 are targeted in optimum fermentation processes (Borcakli et al., 1993; Kiai & Hafidi, 2014; Featherstone, 2016). LAB's designated with generally recognised as safe (GRAS) status produce acid during fermentation which is required for the prevention of the pathogen and spoilage microorganisms by lowering the pH (Behera et al., 2020). The pH of a food also has a critical impact on the way pesticide residues change during processing, preparation and storage of the food product (Maden & Yildirim Kumral, 2020; Yildirim Kumral et al, 2020a; Luyinda & Yildirim Kumral, 2023).

Processing factors

The processing factors for all pesticides were determined as the ratio of the residue levels detected on day 30 (after pasteurisation in fermented trials and at end of storage in canned trials) to the residue levels detected on the day of harvest (Table 10). PF lower than 1 implied a reduction, whereas PF higher than 1 implied a concentration in the pesticide level of the pickles (Zhang et al., 2020). During the experiments, the PF values obtained for all of the tested pesticides and process methods were lower than 1, demonstrating that all treatments applied during the experiments caused significant degradations of the compounds (Zhang et al., 2020). But the effects of canning and fermentation processes on the concentrations of each compound showed variations depending on different degradation mechanisms (Bai et al., 2021). For instance, PFs of acetamiprid and chlorantraniliprole were lower for canning process where as PF of etoxazole was lower for fermentation process. Additionally, contradictory results about the effects of fermentation were reported by different researchers previously. Regarding the effects of fermentation on pesticide degradation, there are several research papers denoting the acceleration of the pesticide degradation (Dordevic & Durovic-Pejcev, 2015; Kong et al., 2016; Dusek et al., 2018; Xu et al., 2020), as well as others reporting the stabilisation and/or deceleration of the degradation (Maden & Yildirim Kumral, 2020; Yildirim Kumral et al., 2020a; Luyinda & Yildirim Kumral, 2023). These variations were primarily influenced by the pH of the food product as well as the chemical structure of the pesticide (Maden & Yildirim Kumral, 2020; Yildirim Kumral et al., 2020a; Luyinda & Yildirim Kumral, 2023).

Table 10. Process factors for selected pestiicdes in gherkin

	Fresh pack (canned) gherkins	Fermented gherkins
Acetamiprid	0.21	0.48
Chlorantraniliprole	0.15	0.26
Deltamethrin	0.22	0.28
Etoxazole	0.54	0.07
Spiromesifen	0.01	0.01

Conclusion

In conclusion, the results of the current study showed that different pickling methods caused diverse changes in the residue levels of the pesticides applied at the recommended doses. This provides us with at least a small amount of knowledge about the behaviour of a limited number of registered pesticides applied under acceptable conditions and concentrations. However, there is still a lack of information about the fate of many extensively used pesticides at concentrations exceeding the recommended limits. Further studies are needed to display the effects of food processing technologies on the residues of different chemicals and to generate reliable information to estimate risks that consumers may face associated with pesticide residues.

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