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Comparative study on the efficiency of pesticide residue removal in foods (Perilla Leaves, Strawberries, Apples)

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Abstract: In agricultural households cultivating vegetables and fruits, the use of various pesticides to protect crops from diseases and pests or to control weeds is widely practiced enhancing quality and productivity. However, pesticides can pose a threat to consumer health by remaining on the food surface or migrating into the food interior. Households commonly peel off skins, wash with water, or use chemical methods to remove foreign substances including residual pesticides on the food surface. In this study, we measured the washing rate by comparing the pesticide concentrations before and after washing in the leafy vegetable perilla leaves and the fruits strawberries and apples, which were intentionally exposed to pesticides. We compared washing rates using tap water, a baking soda solution, and a commercially available food-specific cleaning solution. The target pesticides for analysis were azoxystrobin, bifenthrin, boscalid, difenoconazole, flubendiamide, and indoxacarb, and the residual pesticide analysis was performed using GC-MS/MS or LC-MS/MS. The removal rates of pesticides were highest with the food-specific cleaner, followed by baking soda and tap water in order.

Key words: pesticides removal efficiency, food, commercial washing agents, baking soda, tap water, LC-MS/MS, GC-MS/MS

1. Introduction

Perilla frutescens, a species of annual herb in the mint family, has been cultivated since ancient times in East Asia, including Korea, China, and India, primarily as an herbal medicine or vegetable. However, it is believed that Korea is almost the only country where perilla is consumed as food.

Apples belong to the pome fruit family and are considered an alkaline food. They are low in calories and rich in dietary fiber, potassium, phenolic acid, quercetin, and vitamin C. Apples can be consumed raw or processed into various forms such as jam, juice, cider, liquor, vinegar, pie, tart, jelly, mousse, sherbet, among others. In Europe, apples are often used in the form of fried apple slices or apple sauce with sausage and meat dishes, and are also utilized in the preparation of curry and stew.

Strawberries are the fruit of a vine-like plant in the rose family, showing varying degrees of redness depending on the type. Their physical appearance can be classified into long and pointed shapes, heart shapes,

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and round shapes. Not overly sweet, strawberries have a refreshing taste and a caloric content of 40 kcal (or 167 kJ) per 100 g. They are abundant in minerals, and vitamins C, B, and niacin. As a fruit that is prone to bruising or softening, they are stored in the refrigerator, but the storage period is quite short.

Pesticides, comprised of various mixtures and additives, are used to control plant diseases, pests, and weeds, regulate plant growth, and enhance the quality and productivity of agricultural produce.[1,2] However, the presence of pesticide residues in food can lead not only to environmental hazards such as the generation of resistant pathogens and environmental imbalance but also poses risks to the health of producers and consumers.[3,4] Consuming food containing pesticide residues may result in effects such as neurotoxicity, carcinogenicity, reproductive anomalies, and cellular abnormalities.[5,6]

The increasing demand for fruits and vegetables among consumers has contributed to a rise in the use of pesticides on farms, resulting in a greater residual presence of these substances in soil, groundwater, and agricultural produce. Food regulatory authorities and international organizations around the world, including the Ministry of Food and Drug Safety (MFDS), have established Maximum Residual Limits (MRL) for foods.[7] These limits represent the highest permissible concentration of pesticide residues in agricultural products.

The primary reason for establishing MRLs for pesticides in food is to safeguard the health of consumers. MRLs indicate the maximum amount of residue that is allowed to remain on specific crops after the use of pesticides, regulating the levels to ensure they are within safe limits. MRLs are determined through various studies and toxicity assessments, providing quantitative standards to assure consumers that the consumption of such foods will not pose health risks. When pesticide residues are below the established safe levels, consumers can safely consume the respective crops. This system helps minimize health concerns related to pesticide use and contributes to maintaining the safety of agricultural produce, thereby enhancing consumer trust in the food supply chain.

Therefore, consumers must be aware of the importance of thoroughly washing the surface of fruits and vegetables before consumption, even if the pesticides that have penetrated beneath the surface are disregarded. This washing removes any harmful residues that may have adhered or been absorbed onto the surface.[8]

Several techniques are utilized to eliminate residual pesticides in food, the selection of which often depends on the nature of the food and its consumption pattern. These approaches include rinsing, peeling, blanching, pulverizing, and chemical treatments, all with the aim to make the food safe for consumption.[9,10] The most prevalent technique applicable for domestic usage involves scrubbing the surface of the food with tap water, or using commercially available food-specific cleaning agents that incorporate chemicals and are dissolved in water. Another alternative encompasses heat treatments such as blanching and sterilization to eradicate pesticide residues. Although this method is deemed safe from a health perspective, it could potentially have adverse effects on the color, texture, aroma, and flavor profile of the food.

Washing food with tap water is a common and economical method used in almost every household to wash fruits and vegetables. It helps remove contaminants, including dissolved pesticides, from various types of fruits and vegetables.[11] The efficiency of pesticide removal in this method varies depending on the concentration of pesticides and the type of washing operation, and water alone may not be an effective cleaner. Foods coated with wax, for example, have high surface tension and cannot be effectively wetted, making it difficult to penetrate and remove pesticides effectively.[12]

Tap water has limited effectiveness in removing pesticide residues because many pesticides are lipophilic. Therefore, food-specific cleaning solutions are also used to decompose pesticides in vegetables and fruits. A solution with a small amount of surfactant added to water significantly reduces the surface tension of water, allowing it to spread over the surface, penetrate dust, and remove dust from the surface.[13,14]

The washing power of cleaners varies depending on their type, and the washing effect can also vary depending on the type of pesticide and the characteristics of the food. Therefore, this study aimed to provide basic data for the development of food-specific cleaners for consumers' health by comparing the cleaning abilities of tap water itself, four commercially available surfactant-based cleaners, and baking soda. Also, in this study, considering the representativeness of foods commonly consumed by Koreans, leafy vegetables such as perilla leaves and fruits such as strawberries and apples were chosen to measure the washing rate. In this paper, six pesticides selected for the study are those corresponding to the initial precision inspection pesticide testing items conducted upon the importation of food. Additionally, four detergents were chosen, limited to products produced by a specific company and currently available in the market.

In this study, food samples (perilla leaves for leafy vegetables, and strawberries and apples for fruits) were intentionally exposed to pesticides. The removal rate of residual pesticides was measured by comparing the concentrations of pesticides before and after washing. Although there are various methods for measuring residual pesticides in food,[15-18] a reliable method was chosen according to the official method of the Ministry of Food and Drug Safety (MFDS), which includes sample preparation methods and measurement using GC-MS/MS and LC-MS/MS.[19,20]

2. Experimental

2.1. Materials

2.1.1. Samples

The target samples used in this study, which took into account the representativeness of food, were leafy vegetables like perilla leaves and fruits like strawberries and apples, all purchased from an eco-friendly specialty store located in Seongnam City, Gyeonggi Province, South Korea for use as test samples. The purchased samples, according to the criteria and standards of the MFDS's Multiresidue Methods for Pesticides by Method II, were analyzed using only the edible portion of the produce.

The blank samples used for constructing the calibration curve were confirmed through pre-experimental testing to be free of the target pesticides. The pesticides applied to the target samples included six types: boscalid, azoxystrobin, flubendiamide, difenoconazole, indoxacarb, and bifenthrin. These pesticides were commercially available products purchased from the market (Seongnam City, Korea)

2.1.2. Standards

The standards used in the chromatography/mass spectrometry, namely boscalid, azoxystrobin, flubendiamide, difenoconazole, indoxacarb, and bifenthrin, were purchased from Accustandard (New Haven, CT, USA). The acetonitrile, acetone, dichloromethane, and hexane used for sample preparation and instrumental analysis were products of Burdick & Jackson (Honeywell, USA), while the sodium chloride and diethylene glycol were products of Samchun Chemicals (PyeongTaek, Korea).

2.1.3. Apparatus

The homogenizer was model NFM-3611S from NUC Electronics (DaeGu, Korea), the rotary evaporator was N-1110 SW from EYELA (Tokyo, Japan), the propylsilyl cartridges and aminopropyl cartridges were products of Biotage (EU), and the membrane filters were purchased from Membrane Solutions (NanTong, China).

2.2. Sample preparation and solutions

2.2.1. Method of pesticide exposure for the sample

The concentrations of the pesticide solutions were prepared based on the standard usage guidelines or the instructions provided on the product packaging. The reason for diluting the soaking concentration rather than using the pesticide standard application rate is to account for factors such as rain-induced wash-off, photodegradation under sunlight, or removal during the harvesting process, which may lead to the reduction of pesticide residues. Perilla leaves and strawberries were immersed in a solution diluted ten-fold, while apples were immersed in a solution diluted two-fold. After preparing the diluted pesticide solutions, *Table* 1. Concentrations of the standard guideline and exposure concentrations for experiments

Pesticides	Standard Guideline	Perilla leaves, Strawberries (mg/L)	Apples (mg/L)
Boscalid	13.3 g / 20 L	66.5	332.5
Azoxystrobin	10 mL /20 L	50	250
Difenoconazole	10 g / 20 L	50	250
Indoxacarb	3.3 g / 20 L	16.5	82.5
Bifenthrin	5 g / 20 L	25	125
Flubendiamide	5 mL / 20 L	25	125

the target samples were immersed for one min to ensure exposure to the pesticides. They were then removed from the solution and allowed to naturally dry for 18 hours in a hood, thus preparing them as samples for the unwashed test.

The concentrations and dilution ratios used according to the standard usage guidelines for the pesticides are described in *Table* 1.

2.2.2. Preparation of cleaning solution and cleaning method

1) Commercial washing agent and baking soda washing

The preparation method of the washing solution is as follows. Baking soda was prepared by adding 10 g per 1 L of water for all target samples. In the case of four types of commercial washing agents, for Perilla leaves, 2.5 mL per 1 L of water was added; for strawberries, 5 mL per 1 L of water was added; and for apples, 10 mL per 1 L of water was added.

The samples prepared in 2.2.1 were immersed in the prepared baking soda solution and commercial washing agent solution for 3 min, then cleaned with running tap water for 1 min. After 18 hours of natural drying inside a hood, they were used as samples for the washing test.

2) Washing with running water (Tap Water)

The samples also underwent the following washing procedure with running water, then naturally dried for 18 hours inside a hood, and used as samples for the washing test.

For apples, they were rubbed horizontally with both hands for 10 times for 10 sec, and vertically with both hands for 10 sec, 10 times. The top part around the stem was rubbed from the center outward for 10 sec, 10 times, and the bottom part from the center outward for 10 sec, 10 times. After that, they were again rubbed horizontally and vertically each for 10 sec, 10 times. Each apple was rinsed for a min.[21]

For strawberries, approximately 200 g (6-7 pieces) were placed on a sieve basket and turned under running water. The part covered with the sepal was raised upwards and rinsed for 1 min, after which the sepal was removed.

For Perilla leaves, the front side was rinsed under running water for 5 sec while spreading the folded parts with hands, and the backside was also rinsed under running water for 5 sec while spreading the folded parts with hands. Each leaf was rinsed for 10 sec, and six leaves were rinsed for 1 min in total.

3) Repetitive testing

To enhance the precision and accuracy of the experiment, repetitive analyses were performed on the samples. The number of repetitions was as follows: commercial cleaning agents were tested twice, baking soda was tested three times, tap water was tested three times, and the samples that were not washed and used as a control group were tested three times.

2.2.3. Sample preparation

For the analysis of pesticide residues, the pesticide testing method specified in the “Food Code (Ministry of Food and Drug Safety Notification No. 2023-29, revised on April 31, 2023) was used: ▶ Chapter 8. General Testing Methods ▶ 7. Analysis of Residual Pesticides in Food ▶ 7.1 General Food ▶ 7.1.2 Multiresidue Multicomponent Analysis Method ▶ 7.1.2.2 Multiresidue Multicomponent Analysis Method-Method 2”.[19]

The sample preparation for the instrumental analysis was conducted in the following order: sample preparation → grinding → weighing and extraction → purification → final test solution preparation (*Fig.* 1).

Following the cleaning method described in “2.2.2 Preparation of Cleaning Solution and Cleaning Method”, the edible parts of the samples were collected for use. In the case of apples, the pedicel, core, and calyx were removed, and the skin was considered as the edible portion. For strawberries, the edible portion was collected after removing the calyx, and for Perilla leaves, the edible portion was after removing the tip. Approximately 500 g of the sample was placed into a large grinder (cutter mixer) for grinding.

The ground sample of 50 g was accurately weighed and placed in a mixing extraction grinding bottle, and 100 mL of acetonitrile was added. The mixture was homogenized with a mixing extraction grinder for 2-3 min, then vacuum filtered through a Buchner funnel lined with filter paper. The filtrate was transferred to a 500 mL separatory funnel containing 10-15 g of sodium chloride, capped, and shaken vigorously. It was then left to stand until the layers were completely separated. The acetonitrile layer was passed through anhydrous sodium sulfate for dehydration and the volume was made up to 100 mL with additional acetonitrile.

Under reduced pressure, the acetonitrile layer (20 mL) was evaporated in a water bath at a temperature below 40 °C to volatilize the solvent. For pesticides measured by gas chromatography, 0.2 mL of acetone containing 2 % diethylene glycol was added before evaporating under reduced pressure. For pesticides subjected to gas chromatographic analysis, the residues were dissolved in 4 mL of hexane containing 20 % acetone, and for pesticides subjected to liquid chromatographic analysis, the residues were dissolved in 4 mL of dichloromethane containing 1 % methanol.

2.2.4. Purification and final test solution preparation

1) Pesticides measured by gas chromatography

A Florisil cartridge was conditioned by discarding 5 mL of hexane at a flow rate of 2-3 drops per second, followed by washing with 5 mL of hexane containing 20 % acetone at the same rate. The extract, dissolved in 4 mL of hexane containing 20 % acetone, was loaded onto the top of the cartridge, and eluted at a flow rate of 1-2 drops per second into a test tube. While the cartridge was still wet with solvent, it was eluted again with 5 mL of hexane containing 20 % acetone, and the eluent was collected in the same test tube. The eluent was then evaporated under a gentle stream of nitrogen at a temperature below 40 °C, and the residues were dissolved in hexane containing 20 % acetone, brought up to a fixed volume, and then filtered through a 0.45 μm PTFE membrane filter to create the test solution.

2) Pesticides measured by liquid chromatography

An aminopropyl cartridge was conditioned by discarding 5 mL of dichloromethane at a flow rate of 2-3 drops per second. The extract, dissolved in 4 mL of dichloromethane containing 1 % methanol, was loaded onto the top of the cartridge, and eluted at a flow rate of 1-2 drops per second into a test tube. While the cartridge was still wet with solvent, it was eluted again with 7 mL of dichloromethane containing 1 % methanol, and the eluent was collected in the same test tube. The eluent was then evaporated under a gentle stream of nitrogen, the residues were dissolved in acetonitrile, brought up to a fixed volume, and then filtered through a 0.2 μm PTFE membrane filter to create the test solution.

2.3. Chromatographic analysis

Bifenthrin, difenoconazole, and indoxacarb were analyzed by GC-MS/MS method, while azoxystrobin, boscalid, and flubendiamide were analyzed using the LC-MS/MS method. The product ions with higher intensity were used as quantitative ions and are

Table 2. Parameters of the MRM method for determination by GC-MS/MS

Pesticides	Precursor ion (m/z)	Product ion (m/z)	Collision Energy (eV)
Bifenthrin	181	166 167	15 15
Difenoconazole (2 isomer)	323	265 202	14 28
Indoxacarb	218	203	10

Table 3. Conditions for HPLC mobile phase in gradient elution

Time (min)	Mobile phase A (%)	Mobile phase B (%)
0.0	85	15
1.0	85	15
1.5	40	60
10.0	10	90
12.0	10	90
12.1	2	98
16.0	2	98
16.1	85	15
20.0	85	15

shown in *Table* 2 and *Table* 3.

2.3.1. Gas chromatography-tandem mass spectrometry (GC-MS/MS) Analysis

Bifenthrin, difenoconazole, and indoxacarb were analyzed using GC-MS/MS. The Shimadzu GCMS-TQ8040 tandem mass spectrometer (Shimadzu, Kyoto, Japan) was used for the analysis, with a Shimadzu SH-Rxi-5Sil MS capillary column (30 m × 0.25 mm, 0.25 µm) being employed. The carrier gas used was helium (1.5 mL/min). The initial column temperature was set at 90 °C and held for 3 min, then ramped up at a rate of 20 °C/min to 120 °C, and then increased at a rate of 8 °C/min to 300 °C, where it was held for an additional 3 min. The temperature of the injection port was 280 °C and the sample was injected in the splitless mode at 1 µL.

The ionization method for the mass spectrometer was electron ionization (EI) at 70 eV, the ion source temperature was set at 230 °C, and the Multiple Reaction Monitoring (MRM) mode was used for tandem mass analysis. The conditions used for MRM were as follows (*Table* 2).

2.3.2. Liquid chromatography-tandem mass spectrometry (LC-MS/MS) Analysis

Azoxystrobin, boscalid, and flubendiamide were analyzed using LC-MS/MS. The Shimadzu LCMS-8050 model (Shimadzu, Kyoto, Japan) was used for the analysis, and the column employed was a Shiseido Capcell Core C18 (2.1 mm × 150 mm, 2.7 µm). The volume of the sample injection was 10 µL. The flow

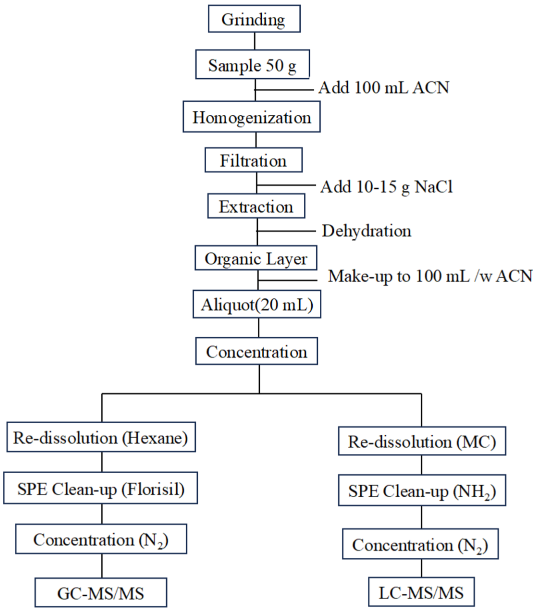

Fig. 1. Schematic diagram of sample preparation for GC-MS/MS and LC-MS/MS analysis.

rate of mobile phase was 0.3 mL/min, and the gradient method was used with mobile phase A (aqueous solution containing 0.1 % formic acid and 5 mM ammonium formate) and mobile phase B (methanol containing 0.1 % formic acid and 5 mM ammonium formate). The conditions of gradient elution were as follows (*Table* 3).

The ionization method of the mass spectrometer was ESI (Electrospray Ionization), with an interface voltage of 4.0 kV and an interface temperature of 150 °C. The Collision Induced Dissociation (CID) gas was argon, set at 270 kPa. For tandem mass analysis, the MRM mode was used. The conditions used for MRM were as follows (*Table* 4).

Table 4. Parameters of the MRM method for determination by LC-MS/MS

Pesticides	Precursor ion (m/z)	Product ion (m/z)	Collision Energy (eV)
Azoxystrobin	404.1	372.20 344.20	-15 -25
Boscalid	343.0	307.20 140.10	-20 -21
Flubendiamide	680.9	254.05 274.00	+27 +17

3. Results and Discussion

The comparative test for the washing ability of four commercial food cleaning agents, baking soda, and tap water (hereafter referred to as 'water washing') on leafy vegetables such as perilla leaves and fruits like strawberries and apples were evaluated by measuring the pesticide removal rate after washing. The pesticide removal rate (washing rate) was calculated by applying the pesticide residue levels measured in the control group, which was intentionally treated with pesticides, and the pesticide residue levels measured after washing with detergents, to the following formula:

$$Removal\ Rate\ \% = \left(1 - \frac{Residual\ Concentration\ of\ Treated\ Sample}{Residual\ Concentration\ of\ Control\ Sample}\right) \times 100$$

The physical properties and Maximum Residual Limit (MRL) for the six pesticides compared in this study are presented in *Table* 5.

Octanol/water partition coefficient, often represented as $K_{o/w}$ or log $K_{o/w}$, is a measure of the distribution of a chemical compound between octanol (an organic solvent) and water. It is used to assess the compound's lipophilicity or hydrophilicity, which can provide insights into its solubility and potential for bioaccumulation.

In the context of pesticides or other chemicals, a higher octanol/water partition coefficient suggests greater lipophilicity, indicating a preference for organic phases like lipid tissues over aqueous environments. Conversely, a lower coefficient suggests a higher affinity for water. This information is valuable in understanding how a substance may behave in biological systems, its potential for environmental persistence, and its ability to accumulate in living organisms.

3.1. Evaluation based on types of pesticides

The washing efficiencies according to the types of pesticides are presented in *Table* 6.

For boscalid, the cleaning rates of commercially available cleaners for the three types of food, perilla leaves, apples, and strawberries, ranged from 96.8 % to 97.8 %, with an average cleaning rate of 97.5 %. The order of cleaning rates for all the comparison targets was commercial cleaners > baking soda > water cleaning (*Table* 6).

In the case of azoxystrobin, the cleaning rates of commercially available cleaners for the three types of food ranged from 98.9 % to 99.2 %, with an average cleaning rate of 99.0 %. The order of cleaning rates for all the comparison targets was commercial cleaners > baking soda > water cleaning. Azoxystrobin, which exhibits relatively high water-solubility or low octanol/water partition coefficient compared to other pesticides, showed high washing efficiency even in tap water, although there may be some variation depending on the type of food.

For difenoconazole, four types of detergents exhibited washing efficiencies ranging from 90.2 % to 96.4 %, with an average of 93.7 %. One detergent showed a cleaning efficacy similar to baking soda, and the washing effect by tap water was somewhat lower compared to other pesticides (76. 5%).

In the case of indoxacarb, commercially available cleaners for the three types of food showed cleaning

Table 5. Physical properties and MRL for the six pesticides[19,22]

Pesticides	Use	MRL (mg/kg)			Half Life (day)	O/W Partition Coefficient (log $K_{o/w}$) (25 °C)	Water Solubility (mg/L) (20 °C)
		Perilla leaves	Apples	Strawberries			
Boscalid	Fungicide	30	1.0	5.0	261-345	2.96	4.6
Azoxystrobin	Fungicide	20	2.0	1.0	112-150	2.50	6
Difenoconazole	Fungicide	7.0	0.8	0.5	324-860	4.4	5
Indoxacarb	Insecticide	20	3.0	1.0	147-233	4.65	0.2
Bifenthrin	Insecticide	10	0.5	0.5	276-416	6.0	10^{-3}<
Flubendiamide	Insecticide	15	0.8	1.0	250-301	4.2	0.299

Table 6. Pesticide removal rate of food according to pesticides (Unit: %, n = 3)

Pesticide	Food	Detergent-1	Detergent-2	Detergent-3	Detergent-4	*Average	Baking soda	water
Boscalid	Perilla leaves	99.9	99.9	99.9	99.9	99.9	99.7	99.1
	Apple	94.6	98.2	96.0	97.6	96.6	89.4	82.4
	Strawberries	95.8	95.4	96.2	96.0	95.8	91.2	79.8
	Average	96.8	97.8	97.4	97.8	97.5	93.4	87.1
Azoxystrobin	Perilla leaves	99.8	99.7	99.6	99.5	99.6	99.7	99.2
	Apple	98.7	98.7	99.6	98.7	98.9	98.3	89.3
	Strawberries	99.0	98.5	98.2	98.4	98.6	97.4	94.6
	Average	99.2	99.0	99.1	98.9	99.0	98.5	94.4
Difenoconazole	Perilla leaves	99.6	99.8	99.7	99.8	99.7	96.8	77.8
	Apple	79.3	89.3	90.7	87.1	86.6	87.7	66.6
	Strawberries	91.7	100.0	92.0	94.8	94.6	86.6	85.2
	Average	90.2	96.4	94.1	93.93	93.7	90.4	76.5
Indoxacarb	Perilla leaves	98.8	99.5	98.8	98.7	99.0	95.4	83.9
	Apple	96.4	98.4	98.2	99.1	98.0	94.8	83.2
	Strawberries	87.3	77.5	87.3	90.2	85.5	76.5	53.9
	Average	94.1	91.8	94.8	96.0	94.2	88.9	73.7
Bifenthrin	Perilla leaves	99.7	99.4	99.6	99.9	99.6	98.1	97.3
	Apple	96.8	97.8	98.7	98.7	98.0	94.4	89.8
	Strawberries	100.00	99.0	100.0	98.1	99.3	76.70	69.90
	Average	98.9	98.7	99.4	98.9	99.0	89.8	85.7
Flubendiamide	Perilla leaves	99.7	99.6	99.8	99.7	99.7	97.5	97.4
	Apple	98.0	98.0	99.0	96.0	97.8	97.0	80.20
	Strawberries	98.0	100.0	98.0	98.0	98.5	93.2	92.5
	Average	98.6	99.2	98.9	97.9	98.7	95.9	90.0

*The average cleaning efficiency for the four detergents.

rates in the range of 91.8 % to 96.0 %, with an average cleaning rate of 94.2 %. The order of cleaning rates for all comparison targets was commercial cleaners > baking soda > water cleaning. The cleaning rate of the commercially available cleaners was significantly higher than that of water cleaning, and also showed a higher cleaning rate compared to baking soda and other pesticides. This is interpreted as due to the property of Indoxacarb being a compound with a low water solubility and high octanol/water partition coefficient.

For bifenthrin, the commercial cleaners for the three types of food showed cleaning rates in the range of 98.7 % to 99.4 %, with an average cleaning rate of 99.0 %. The order of cleaning rates for the comparison cleaners was commercial cleaners > baking soda > water cleaning. Although the physicochemical properties of bifenthrin indicate a low water solubility and a high octanol/water partition coefficient, these properties were not significantly reflected compared to the other compared pesticides. In other words, it was expected that the cleaning rate should be the lowest when cleaned only with water, but the results were not as such.

In the case of flubendiamide, the commercial cleaners for the three types of food showed cleaning rates in the range of 99.2 % to 98.9 %, with an average cleaning rate of 98.7 %. The order of cleaning rates for all comparison targets was commercial cleaners > baking soda > water cleaning. There was not a significant difference in cleaning power between commercial cleaners and baking soda.

Table 7. Pesticide removal rate of food according to washing method (Unit: %, n = 3)

Sample	Pesticides	Detergent-1	Detergent-2	Detergent-3	Detergent-4	Baking soda	Water	Average
Perilla leaves	Boscalid	99.9	99.9	99.9	99.9	99.7	99.2	99.9
	Azoxystrobin	99.8	99.6	99.6	99.5	99.7	99.2	99.6
	Difenoconazole	99.6	99.8	99.7	99.8	96.8	77.8	99.7
	Indoxacarb	98.8	99.5	98.8	98.7	95.4	83.8	98.9
	Bifenthrin	99.7	99.4	99.6	99.9	98.1	97.3	99.6
	Flubendiamide	99.7	99.6	99.8	99.7	97.5	97.4	99.7
	Average	99.6	99.6	99.6	99.6	97.9	92.8	
Apples	Boscalid	94.6	98.2	96.0	97.6	89.4	82.4	96.6
	Azoxystrobin	98.7	98.7	99.6	98.7	98.3	89.3	98.9
	Difenoconazole	79.3	89.3	90.7	87.1	87.7	66.6	86.6
	Indoxacarb	96.4	98.4	98.2	99.1	94.8	83.2	98.0
	Bifenthrin	96.8	97.8	98.7	98.7	94.4	89.8	98.1
	Flubendiamide	98.0	98.0	99.0	96.0	97.0	80.2	97.8
	Average	94.0	96.7	97.0	96.2	93.6	81.9	
Strawberries	Boscalid	95.8	95.4	96.2	96.0	91.2	79.8	95.8
	Azoxystrobin	99.0	98.5	98.2	98.4	97.4	94.6	98.6
	Difenoconazole	91.7	100.0	92.0	94.8	86.6	85.2	94.6
	Indoxacarb	87.2	77.4	87.2	90.2	76.5	53.9	85.5
	Bifenthrin	100.0	99.0	100.0	98.1	76.7	69.9	99.2
	Flubendiamide	98.0	100.0	98.0	98.0	93.2	92.5	98.8
	Average	95.3	95.1	95.3	95.9	86.9	79.3	

3.2. Evaluation based on type of food

3.2.1. Perilla leaves

The retention of pesticides on leafy vegetables like perilla can greatly differ depending on the surface condition. The rate of pesticide removal through washing varies according to morphological features such as surface area and the distribution and thickness of leaf veins.[23]

Upon examining the physical properties of six types of pesticides, it was found that compounds with a relatively high octanol/water partition coefficient (log $K_{o/w}$), i.e., hydrophobic pesticides such as difenoconazole (4.4), indoxacarb (4.6), and bifenthrin (6.0), had relatively low removal rates compared to other pesticides. For perilla leaves, water washing alone resulted in a removal rate of 77.8-97.3 % for three pesticides with a high log $K_{o/w}$, while three pesticides with a relatively low log $K_{o/w}$ (boscalid, azoxystrobin, flubendiamide) had an excellent removal rate of 97.4-99.2 %. In contrast, commercial washing agents demonstrated high removal rates of 99.0-99.9 %, regardless of the log $K_{o/w}$ value (*Table* 7).

3.2.2. Apples

In the case of apples, water washing demonstrated a removal rate of 66.6-89.8 % for three types of pesticides with a high octanol/water partition coefficient, while for three types of pesticides with a low octanol/water partition coefficient, a removal rate of 80.2-89.3 % was observed. However, four types of commercially available cleaners showed a removal rate of 86.4 %-99.0 %, regardless of the octanol/water partition coefficient of the pesticides.

3.2.3. Strawberries

In the case of strawberries, water washing showed a removal rate of 53.9 %-85.2 % for three types of pesticides with a high octanol/water partition coefficient, while a removal rate of 79.8 %-94.6 % was observed for three types of pesticides with a low octanol/water partition coefficient. Four types of commercially available cleaners demonstrated a removal rate of

84.0 %-99.7 % against all pesticides. Notably, Indoxacarb exhibited very low removal rates of 76.5 % and 53.9 % with baking soda and water washing, respectively. Bifenthrin, which has a very low water solubility, showed removal rates of 76.7 % and 69.9% with baking soda and water washing, respectively. However, in the case of commercial cleaners, a very high removal rate of 98.1 %-100.0 % was observed.

3.3. Evaluation based on type of detergents

This study assesses the cleaning efficiency of four types of detergents, labeled as Detergent-1, Detergent-2, Detergent-3, and Detergent-4, along with baking soda and tap water. The cleaning efficiency is measured as a percentage range, and the experiment involves three different fruits: perilla leaves, apples, and strawberries.

Results show that Detergent-1 and Detergent-2 exhibit cleaning efficiencies ranging from 95.3 % to 99.6 % and 95.1 % to 99.0 %, respectively. Notably, the cleaning efficiency decreases in the order of perilla leaves > apples > strawberries for both Detergent-1 and Detergent-2.

Similarly, Detergent-3 and Detergent-4 demonstrate cleaning efficiencies of 95.3-99.6 % and 95.9-99.6 %, respectively. The trends in cleaning efficiency for these two detergents align with those observed for Detergent-1 and Detergent-2 across the tested samples.

In comparison, baking soda exhibits a cleaning efficiency ranging from 86.9 % to 97.9 %, while tap water shows a relatively lower cleaning efficiency of 79.3 % to 92.8 %. This suggests that tap water, when used alone, demonstrates lower cleaning efficacy compared to specialized detergents formulated for pesticide residue removal.

4. Conclusions

In a comparison of commercially available washing agents, baking soda, and water washing on leaf vegetables like perilla leaves and fruit trees like apples and strawberries, commercial washing agents proved to be relatively effective in removing pesticides compared to baking soda or water washing methods. Commercial cleaners showed the highest average cleaning rate at 97.5 %, followed by baking soda, and water washing showed the lowest washing efficiency.

In the evaluation by pesticide type, there were differences in cleaning power depending on the characteristics of each pesticide. For example, azoxystrobin, which has high water solubility, showed a high cleaning rate even with water washing alone. In contrast, Indoxacarb, characterized by low water solubility and a high octanol/water partition coefficient, showed significantly higher cleaning rates with commercial cleaners compared to water washing.

The washing effects were evaluated for perilla leaves, apples, and strawberries respectively in the evaluation by food type. In the case of perilla leaves, commercial cleaners showed high washing rates regardless of the octanol/water partition coefficient, while water washing showed a low washing rate. For apples and strawberries, commercial cleaners effectively removed pesticides, while water washing showed limited cleaning power for some pesticides.

In conclusion, these results can be interpreted as being influenced by the properties of the pesticides and the types of the food. Commercial cleaners demonstrated a high cleaning rate compared to water washing or baking soda. Therefore, while the choice ultimately rests with consumers, the use of commercial cleaners is recommended to safely consume food.

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