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Assessing the efficacy of washing methods in reducing multi-pesticide residues in Brown, milled long, and milled basmati Rice

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ABSTRACT

Pesticides are vital for protecting crops from diseases but pose risks to human health and the environment, requiring careful evaluation. This study examines pesticide residues in rice and strategies for their removal. Brown, long-milled, and basmati-milled rice samples were spiked with 121 pesticides from different categories (e.g., carbamates, organophosphates, neonicotinoids, triazolobenzothiazoles) at 20 and 50 μg/mL to evaluate residue levels. Pesticides were extracted using the QuEChERS (quick, easy, cheap, effective, rugged, and safe) method and analyzed via High Performance Liquid Chromatography coupled with mass spectrometry. Residue removal was tested using washing methods with and without vinegar. Results showed that long-grain milled rice had higher pesticide residues, and adding vinegar significantly enhanced their removal. These findings contribute to improving food safety practices by providing insights into effective pesticide residue mitigation in rice.

1. Introduction

The Food and Agriculture Organization (FAO) of the United Nations defines pesticides as "*any substance or mixture of substances or biological ingredients intended for repelling, destroying or controlling any pest or regulating plant growth*" (Food and Agriculture Organization, 2021). Globally, only about 1 % of the pesticides applied each year are effectively used to target insect pests on crops. This inefficiency not only raises agricultural production costs but also adversely affects the safety and quality of agricultural products and the surrounding environment (Tudi et al., 2021). Recent studies estimate annual pesticide usage at roughly 2 million tons, distributed as follows: herbicides at 47.5 %, insecticides at 29.5 %, fungicides at 17.5 %, and other types of pesticides at 5.5 % (Bondareva & Fedorova, 2021). Pesticides are categorized using various criteria, including their chemical classes, functional groups, modes of action, and levels of toxicity.

Despite ongoing efforts to decrease usage or find alternatives, the reality is that the use of pesticides remains essential to prevent food loss (Melo et al., 2020). However, excessive pesticide uses leads to environmental repercussions, including air, soil, and water pollution, and

Abbreviations: DNC, Dinitrocarbanilide or 1,3-bis(4-nitrophenyl)urea; EFSA, European Food Safety Authority; ESI, Electrospray Ionization; FAO, Food and Agriculture Organization; HPLC-MS/MS, High-Performance Liquid Chromatography Tandem Mass Spectrometry; LOQ, Limit of Quantification; ML, Maximum Level; MRL, Maximum Residue Levels; PF, Processing Factors; PSA, Primary Secondary Amine bonded silica; QuEChERS, Quick, Easy, Cheap, Effective, Rugged, and Safe; RAC, Raw Agricultural Commodities; TPP, Triphenylphosphate.

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both acute and long-term effects on non-target organisms within agro-ecosystems. Additionally, it poses a threat of toxicity to both users and consumers of food. Furthermore, the misuse of pesticides, as highlighted by Melo et al. (2020), can contribute to the resurgence of pests.

Pesticides can have a range of toxic effects on human health and the environment, depending on their chemical structure, exposure level, and duration. Acute exposure to pesticides, particularly organophosphates and carbamates, can cause neurotoxicity, leading to symptoms such as headaches, dizziness, nausea, respiratory distress, and, in severe cases, convulsions or death (Hernández et al., 2013). Chronic exposure has been linked to endocrine disruption, reproductive toxicity, developmental disorders, and an increased risk of cancers, particularly in agricultural workers and populations exposed through contaminated food and water (Hernández et al., 2013). Some pesticides, such as neonicotinoids, also harm non-target species like pollinators, disrupting ecosystems. Due to these risks, regulatory measures are of great importance and aim to limit pesticide residues in food and promote safer alternatives.

Rice serves as the most important and primary cereal crop for a significant share of the global population. It is the main energy source in 17 countries in Asia and the Pacific, 9 in the Americas, and 8 in Africa (Shakoori et al., 2018). Worldwide, rice accounts for 20 % of the calories consumed, playing a crucial role in the diet of over 3.5 billion people (Shakoori et al., 2018).

Rice is categorized based on grain length into long (> 6.0 mm), medium (> 5.2 mm and < 6.0 mm), and short (≤ 5.2 mm) and is available in both brown and milled forms. In brown rice, the grain preserves nearly all its bran and embryo. Conversely, milled rice undergoes milling, resulting in the removal of its bran layer. Consequently, milled or white rice, unlike brown rice, exhibits lower levels of vitamins, minerals, and fiber.

Basmati milled grain distinguishes itself through a distinct aromatic profile derived from specific varieties. Basmati rice features intermediate amylose content and shares the same grain biometry as long-milled rice, as emphasized in the study by Pereira et al. (2024). However, it displays a unique chemical composition with higher protein and fiber content than other long-grain types. Remarkably, Basmati milled grain maintains exceptional grain integrity during the cooking process, a noteworthy aspect highlighted in the research (Pereira et al., 2024).

Pareja et al. (2011) made a table with the main pesticides used in rice (49) comparing the MRLs between the Codex Alimentarius, the European Union, Brazil, the USA, Korea, and Taiwan. The most utilized pesticides are, for example, azoxystrobin, carbaryl, diazinon, propiconazole, and tebuconazole. These data demonstrate that legislation differs between countries in the pesticides and the MRLs used (Pareja et al., 2011).

Buprofezin, chlorpyrifos, edifenphos, EPN, fenobucarb, iprobenfos, isoprothiolane, and hexaconazole were the pesticides most frequently detected in paddy rice. This is reasonable given that all but fenobucarb have high octanol/water coefficients, which lead them to concentrate in the husk. Triazophos, chlorpyrifos, methamidophos, pirimiphos methyl, carbendazim, iprodione, tebuconazole, quinclorac, and tricyclazole are among the pesticides that are mostly found on white rice (Pareja et al., 2011).

Washing procedures can offer benefits by lowering pesticide concentrations but may also reduce nutrient levels. This reduction becomes particularly pronounced when dealing with enriched rice. Gray et al. (2015) demonstrated that rinsing rice removes enriched iron from its surface. When milled rice is rinsed rather than left unrinsed, the iron content decreases by approximately 75 %. In enriched milled rice, where iron is present in a water-soluble coating of the endosperm, rinsing has a more substantial impact. Conversely, brown rice, with iron in the bran layer, only experiences a 10 % reduction in iron concentration after rinsing.

Furthermore, vitamin testing on selected rice samples, conducted before and after rinsing, revealed significant reductions. After rinsing, 77 % of folate, 57 % of niacin, and 54 % of thiamin were diminished. Notably, rinsing had almost no effect on vitamins in whole-grain brown rice (Gray et al., 2015).

A study by Atungulu and Pan (2014) reported that thiamine was reduced by 22–59 % in milled rice, 1–21 % in brown rice, and 7–15 % in parboiled milled rice after washing. Riboflavin showed 11–26 % reductions in milled rice, 2–8 % in brown rice, and 12–15 % in parboiled milled rice after washing (Atungulu & Pan, 2014).

Since 2014, EFSA has conducted risk evaluations and pan-European dietary exposure analyses about the real concentrations of pesticide residues in food products. Risk assessments rely on pesticide occurrence data from official monitoring programs in Member States, consumption data from EFSA's comprehensive food consumption database, and pesticide-specific information from dossiers submitted under Regulations (EC) No 396/2005 and 1107/2009. EFSA's food consumption database utilizes the FoodEx 2 system for food categorization and description, encompassing a detailed list of food items and descriptors grouped into broader food categories. Additionally, pesticide-specific data include processing factors (PF), which describe the transfer of pesticide residues from raw agricultural commodities (RAC) to processed products. There has yet to be a global or European harmonized list of processing factors.

EFSA, therefore, launched the project "Database of processing techniques and processing factors compatible with the EFSA food classification and description system FoodEx 2" (Scholz, Herrmann, et al., 2018; Scholz, van Donkersgoed, et al., 2018). The project is divided into 3 specific objectives: Objective 1: Set a list of processing methods based on a fair number of regulatory investigations supported by up-to-date data from the food processing sector and published literature; Objective 2: Establish a connection between the EFSA FoodEx 2 food categorization and description system and all raw and relevant processed items considered in the compendium; Objective 3: Collecting and reevaluating these processing studies, the results of which are recorded in EFSA's Reasoned Opinions (in accordance with Regulation (EC) No 396/2005, Article 12) as well as in the organization's Conclusions and Scientific Reports (under the framework of Regulation (EC) No 1107/2009). The compendium's representative processing approaches will be used to validate the research findings, and a database containing the processing factors that arise from the studies' selected data will be created.

However, EFSA launched an information note on Article 20 of Regulation (EC) No 396/2005 regarding processing factors, processed and composite food, and feed. The objective of this document is to ensure that Member States (including Official Control Laboratories) will be able to implement Article 20 provisions of Regulation (EC) 396/2005 in a harmonized manner, which will eventually allow for the mutual acceptance of processing factors established by different Member States (European Commission, 2022).

This study aims to assess the impact of washing with water alone and with water and apple cider vinegar in brown, milled long, and basmati rice to reduce pesticide residues. To achieve this goal, we employed a previously validated method to simultaneously determine 121 pesticide residues by HPLC-MS/MS in rice (Carreiró et al., 2024). This research, utilizing precise analytical methods for screening multi-residues of pesticides, holds significant importance. To date, no comprehensive examination has compared various washing methods across diverse rice types for their efficacy in removing a wide array of pesticides.

2. Materials and methods

2.1. Chemicals and reagents

Chemicals including acetonitrile, methanol, (both HPLC gradient grade), toluene, ethyl acetate, n-hexane, acetone, and formic acid were obtained from Merck (Darmstadt, Germany). Water purification was performed using the Milli-Q Plus system from Millipore (Molsheim, France) at 25 °C, (resistivity of 18.2 MΩ·cm).

Pesticide standards and internal standards were supplied by Sigma-Aldrich (Madrid, Spain), specifically dinitrocarbanilide (DNC) or 1,3-bis(4-nitrophenyl) urea (DNC) and triphenylphosphate (TPP). These standards were dissolved at approximately 1 μg/mL in various solvents, including acetonitrile, methanol, ethyl acetate, toluene, acetone, and chloroform. As solubility varies among standards, selecting appropriate solvents is essential.

The mixed pesticide stock solution is made from individual standard solutions at a 5 ng/μL concentration in acetonitrile. The working solutions are made from this mixture solution. Sodium chloride and magnesium sulfate were purchased for QuEChERS from Fluka (Seelze, Germany). Sodium citrate dibasic sesquihydrate was acquired from Sigma-Aldrich in Madrid, Spain. AppliChem (Darmstadt, Germany) provided tri-sodium citrate 2-hydrate.

For clean-up, primary, secondary amine bonded silica (PSA) was purchased from Supelco (Supelclean™, Bellefonte, PA, USA), while anhydrous magnesium sulfate was purchased from AppliChem (Darmstadt, Germany).

For the contamination and washing of rice, mineral water was used. For the washing with vinegar, apple cider vinegar was used at a concentration of 5 % (*v*/v).

2.2. Samples and sampling procedure

Rice samples of various types were collected from different supermarkets in Portugal between April and June 2023 for pesticide residue analysis. The samples included long-grain rice, Basmati rice, and brown rice, all originating from Portugal. Each laboratory sample (1 kg) was homogenized using a Retsch rotor mill SK 300 equipped with a 1.00 mm trapezoidal-hole sieve. The resulting flours were thoroughly mixed to ensure complete homogenization. Approximately 50 g of each sample was stored in separate collection tubes and preserved at −20 °C until further analysis.

2.3. Methodology

2.3.1. Extraction

Pesticides were extracted from rice samples using a QuEChERS procedure, the extraction method most frequently used for pesticides residues determination (Sadighara et al., 2024), according to a protocol validated by Carreiró et al. (2024). Initially, 10 g of the sample was weighed into a 50 mL tube, followed by the addition of 20 mL of cold water, and left to stand for 1 h. Then, 10 mL of acetonitrile (ACN) was added, and the mixture was vortexed. For liquid-liquid partitioning, 6.5 g of an extraction salt mixture (composed of 4 g magnesium sulfate, 1 g sodium chloride, 1 g sodium citrate, and 0.5 g disodium hydrogen citrate sesquihydrate) was added. The mixture was vortexed for 1 min and centrifuged at 4000 rpm for 5 min.

Subsequently, 6 mL of the extract was subjected to dispersive solid-phase extraction (d-SPE) by combining it with a mixture of primary-secondary amine-bonded silica (PSA) and anhydrous magnesium sulfate (1.05 g). To this, 1 mL of the extract was added to 220 mL of ACN in an Eppendorf tube, mixed, and centrifuged at 4500 rpm for 2 min. A volume of 500 μL of the extract was then combined with 25 μL of an internal standard solution in a Mini-Uniprep™ vial. The final extract was analyzed using electrospray ionization (ESI)-based triple-quadrupole high-performance liquid chromatography-tandem mass spectrometry (HPLC–MS/MS) (Figure S1).

2.3.2. Sample preparation

This step was adapted from the methodology outlined by Shakoori et al. (2018). Prior to the washing process, two solutions were prepared for contaminating the three rice varieties (long-grain, brown, and basmati): one with a pesticide concentration of 20 μg/L and another with 50 μg/L, in order to evaluate whether the effectiveness of washing or processing in reducing pesticide residues is affected by the initial contamination level. For the 20 μg/L solution, 1.6 mL of a mixed pesticide solution (5000 μg/L) was diluted in 400 mL of water, while for the 50 μg/L solution, 4 mL of the mixed pesticide solution was diluted in 400 mL of water.

Approximately 200 g of each rice variety was submerged in separate beakers containing the respective solutions. After contamination, the rice samples were air-dried at room temperature for 24 h by spreading them on trays and leaving them exposed to sunlight until fully dried. For each experimental condition (washing and washing with apple cider vinegar), 20 g sub-samples of rice were used.

2.3.2.1. Washing. A portion of each rice (20 g) was washed with mineral water and soaked in 100 mL of water for 20 min. After soaking, the samples were crushed and subsequently analyzed. (Figure S2).

2.3.3. 2-washing with apple cider vinegar

A portion of the rice samples (20 g) was washed with mineral water and soaked in 95 mL of this water and 5 mL of vinegar for 20 min. The samples were crushed and then analyzed.

2.4. Processing factors and percentage of reduction

The reduction of pesticide residues during processing was assessed by calculating the processing factor (PF) using the following equation:

$$PFs = \frac{C_a}{C_{b.}}$$

Where,

Ca is the pesticide concentration in processed samples (mg/kg)

C_b is the pesticide concentration in non-processed samples (mg/kg)

If PF < 1, this indicates a reduction in pesticide concentration. If PF > 1, this indicates an increase in pesticide residue concentration.

The percentage reduction (% Re) was calculated using the equation:

$$\%Re = (1 - PFs) \times 100$$

2.5. Statistical analysis

Statistical analysis was conducted to assess the impact of washing processes on pesticide concentrations in the three rice varieties. Differences among treatments were analyzed using one-way ANOVA, followed by Tukey's post-hoc test for pairwise comparisons. A significance level of $p < 0.05$ was considered statistically significant. All calculations were conducted using the FactoMineR package (Lê et al., 2008) within the R statistical software environment (R Foundation for Statistical Computing, Vienna, Austria).

Results are reported as mean values accompanied by their respective standard deviations (SD), calculated from three independent replicates ($n = 3$). This robust approach enabled the identification of statistically significant variations in pesticide concentrations attributable to the different washing treatments, providing a comprehensive assessment of their impact.

3. Results

While pesticides often accumulate on the outer layers of grains, residues can still be present in husk-free rice due to systemic pesticide absorption during cultivation, post-harvest treatments, or cross-contamination. Given that rice is a staple food consumed daily by a large population, even low levels of pesticide residues can contribute to chronic dietary exposure, increasing the risk of adverse health effects over time. Therefore, understanding the extent of contamination and evaluating the effectiveness of washing and processing in reducing pesticide residues in rice with removed husks is crucial for ensuring food safety and protecting public health.

To calculate the pesticide reduction throughout the washing processes, it is important to ascertain the pesticide concentration in

Table 1
Mean concentrations (±SD, $n = 3$), mean values of processing factors (PF), and reductions (%) of the pesticides in unprocessed long-grain rice samples after washing (50 μg/kg). Different letters within the same row indicate statistically significant differences ($p < 0.05$).

Pesticides	Unprocessed Samples	Washing			Washing with Vinegar		
	Concentration ± SD	Concentration ± SD	PF	Reduction (%)	Concentration ± SD	PF	Reduction (%)
Acetamiprid	19.2 ± 1. 37^{a}	12.5 ± 1.32^{b}	0.65	34.7	< LOQ	–	>50.0
Azoxystrobin	32.9 ± 3.18^{a}	13.2 ± 2.00^{b}	0.40	59.8	11.3 ± 1.36^{b}	0.34	65.6
Bixafen	32.7 ± 0.38^{a}	24.3 ± 1.21^{b}	0.74	25.8	19.8 ± 0.16^{c}	0.60	39.4
Boscalid	28.0 ± 1.90^{a}	15.0 ± 0.72^{b}	0.54	46.4	11.7 ± 1.80^{b}	0.42	58.2
Bupirimate	35.2 ± 3.45^{a}	16.1 ± 1.63^{b}	0.46	54.2	11.6 ± 0.72^{b}	0.33	67.1
Buprofezin	34.4 ± 1.74^{a}	19.5 ± 0.98^{b}	0.57	43.4	15.2 ± 1.72^{c}	0.44	55.6
Cadusafos	34.5 ± 4.45^{a}	11.8 ± 0.65^{b}	0.34	65.8	9.56 ± 1.77^{b}	0.28	72.3
Carbaryl	25.4 ± 0.52^{a}	19.3 ± 0.95^{b}	0.76	24.0	13.2 ± 1.67^{c}	0.52	48.3
Carbendazim	24.2 ± 0. 37^{a}	18.3 ± 1.67^{b}	0.76	24.4	12.1 ± 1.20^{c}	0.50	50.0
Carbofuran	14.6 ± 1.15^{a}	9.85 ± 0.80^{b}	0.68	32.4	<LOQ	–	>31.0
Carboxin	<LOQ	<LOQ	–	–	<LOQ	–	–
Chlorantraniliprole	22.8 ± 0. 09^{a}	14.1 ± 0.02^{b}	0.62	38.2	9.53 ± 0.21^{c}	0.42	56.0
Chlorfenvinphos	36.1 ± 0.88^{a}	22.0 ± 1.61^{b}	0.61	34.0	18.6 ± 1.34^{c}	0.51	48.5
Chlorpyrifos-methyl	4.0 ± 0.16^{a}	15.9 ± 0.46^{b}	0.66	33.8	14.8 ± 1.88^{b}	0.62	38.4
Coumaphos	<LOQ	<LOQ	–	–	<LOQ	–	–
Cyprodinil	30.0 ± 1.39^{a}	14.9 ± 0.61^{b}	0.50	50.4	11.5 ± 0.91^{c}	0.38	61.7
Diazinon	37.3 ± 0.23^{a}	31.7 ± 1.27^{b}	0.85	15.1	27.3 ± 0.00^{c}	0.73	26.8
Difenoconazole	32.7 ± 3.68^{a}	12.8 ± 0.80^{b}	0.39	61.0	10.3 ± 1.66^{b}	0.32	68.4
Diflubenzuron	37.6 ± 2.88^{a}	19.2 ± 0.65^{b}	0.51	48.9	17.8 ± 1.59^{b}	0.47	52.6
Dimethoate	13.3 ± 0.89^{a}	10.7 ± 1.02^{b}	0.80	20.0	6.63 ± 0.64^{c}	0.50	50.3
Dimethomorph	26.7 ± 1.80^{a}	14.8 ± 1.18^{b}	0.55	44.5	13.4 ± 0.64^{b}	0.50	49.7
Diniconazole	40.6 ± 2.5^{a}	26.5 ± 1.00^{b}	0.65	34.6	22.1 ± 0.04^{c}	0.54	45.5
DMST	24.9 ± 0.38^{a}	13.9 ± 0.12^{b}	0.56	44.2	11.6 ± 0.54^{c}	0.47	53.4
EPN	21.5 ± 5.47	<LOQ	–	>53.6	<LOQ	–	>53.6
Epoxiconazole	41.2 ± 3.3^{a} 0	21.3 ± 1.02^{b}	0.52	48.3	16.9 ± 0.43^{b}	0.41	59.0
Ethoprophos	27.3 ± 2.22^{a}	13.4 ± 1.13^{b}	0.49	50.9	9.67 ± 1.14^{b}	0.35	64.6
Etrimfos	<LOQ	<LOQ	–	–	<LOQ	–	–
Fenamidone	36.3 ± 3.64^{a}	12.4 ± 0.85^{b}	0.34	65.9	9.83 ± 1.28^{b}	0.27	72.9
Fenamiphos sulfone	14.8 ± 0.42^{a}	11.31 ± 1.14^{b}	0.76	23.5	7.02 ± 0.17^{c}	0.47	52.6
Fenamiphos sulfoxide	16.8 ± 1.69^{a}	<LOQ	–	>40.4	<LOQ	–	>40.4
Fenarimol	39.6 ± 2.00^{a}	23.3 ± 1.07^{b}	0.59	41.4	20.0 ± 0.14^{b}	0.51	49.4
Fenoxycarb	35.7 ± 4.11^{a}	12.9 ± 1.75^{b}	0.36	63.8	10.4 ± 1.43^{b}	0.29	71.0
Fenpropidin	37.2 ± 2.94^{a}	18.5 ± 1.36^{b}	0.49	50.7	<LOQ	–	>73.1
Fenpropimorph	39.9 ± 1.93^{a}	19.1 ± 0.63^{b}	0.48	52.0	14.0 ± 0.35^{c}	0.35	64.9
Fenthion oxon sulfone	23.3 ± 2.55^{a}	9.88 ± 0.35^{b}	0.42	57.1	<LOQ	–	>57.1
Fenthion oxon sulfoxide	11.3 ± 1.15	<LOQ	–	>11.3	<LOQ	–	>11.3
Fenthion oxon	23.8 ± 1.07	<LOQ	–	>58	<LOQ	–	>58
Fenthion sulfoxide	23.2 ± 1.29^{a}	11.53 ± 1.24^{b}	0.45	54.8	<LOQ	–	>57
Fluquinconazole	31.6 ± 0.02^{a}	19.5 ± 1.83^{b}	0.61	38.8	18.0 ± 1.17^{b}	0.57	43.1
Flutriafol	30.9 ± 2.55^{a}	13.2 ± 0.57^{b}	0.43	57.3	11.5 ± 1.11^{b}	0.37	62.8
Fonofos	<LOQ	<LOQ	–	–	<LOQ	–	–
Fosthiazate	16.9 ± 1.57^{a}	13.8 ± 0.45^{b}	0.81	18.7	<LOQ	–	>40.9
Hexythiazox	13.2 ± 3.31	<LOQ	–	>24.4	<LOQ	–	>24.4
Indoxacarb	25.3 ± 1.61^{a}	23.4 ± 3.34^{ab}	0.92	7.70	18.8 ± 0.72^{b}	0.74	25.9
Iprodione	26.9 ± 1.38^{a}	21.8 ± 1.63^{b}	0.81	18.7	17.2 ± 1.47^{c}	0.64	36.0
Iprovalicarb	34.7 ± 3.69^{a}	15.5 ± 0.88^{b}	0.44	55.4	13.8 ± 2.75^{b}	0.40	60.3
Isoprocarb	22.6 ± 1.02^{a}	15.7 ± 2.33^{b}	0.69	30.6	10.79 ± 0.83^{c}	0.48	52.3
Isoprothiolane	<LOQ	<LOQ	–	–	<LOQ	–	–
Isoproturon	22.8 ± 1.86^{a}	10.9 ± 0.52^{b}	0.48	52.0	9.67 ± 0.76^{b}	0.42	56.2
Linuron	28.8 ± 1.77^{a}	21.1 ± 1.70^{b}	0.73	26.7	17.4 ± 0.91^{c}	0.60	39.5
Mepanipyrim	38.4 ± 2.23^{a}	24.4 ± 1.43^{b}	0.63	36.6	19.7 ± 1.3^{c}	0.51	48.8
Metaflumizone	<LOQ	<LOQ	–	–	<LOQ	–	–
Metalaxyl	13.9 ± 1.60^{a}	9.66 ± 0.36^{b}	0.70	30.4	4.87 ± 0.50^{c}	0.35	64.9
Metalaxyl-M	14.8 ± 1.66^{a}	9.20 ± 0.26^{b}	0.62	37.9	<LOQ	–	>32.5
Metazachlor	21.3 ± 0.56^{a}	15.9 ± 1.48^{b}	0.75	25.3	11.3 ± 0.65^{c}	0.53	47.0
Metconazole	37.8 ± 1.17^{a}	24.70 ± 1.64^{b}	0.65	34.7	21.5 ± 1.36^{b}	0.57	43.2
Methiocarb	30.7 ± 1.66^{a}	13.0 ± 1.76^{b}	0.55	44.7	15.2 ± 1.78^{b}	0.50	50.4
Metrobromuron	28.1 ± 2.80^{a}	16.0 ± 0.01^{b}	0.57	42.9	11.9 ± 0.67^{c}	0.42	57.7
Metribuzin	20.3 ± 0.71^{a}	10.4 ± 0.49^{b}	0.51	49.0	<LOQ	–	>50.8
Oxadixyl	12.8 ± 0.84^{a}	9.25 ± 2.10^{b}	0.72	21.8	<LOQ	–	>21.8
Paclobutrazole	38.6 ± 2.54^{a}	17.4 ± 0.89^{b}	0.45	54.9	13.9 ± 0.96^{b}	0.36	64.0
Parathion	23.0 ± 1.44^{a}	18.0 ± 1.10^{b}	0.78	21.8	15.3 ± 0.38^{c}	0.66	33.6
Parathion-methyl	16.3 ± 1.49^{a}	11.3 ± 0.42^{b}	0.69	30.5	9.54 ± 1.84^{b}	0.59	41.5
Penconazole	40.6 ± 0.95^{a}	23.8 ± 1.51^{b}	0.59	41.4	21.0 ± 2.10^{b}	0.52	48.4
Pencycuron	29.1 ± 2.80^{a}	17.1 ± 0.86^{b}	0.59	41.1	15.1 ± 0.45^{b}	0.52	48.1
Phenthoate	34.8 ± 4.02^{a}	21.6 ± 2.45^{b}	0.62	37.9	18.9 ± 3.15^{b}	0.54	45.6
Phosphamidon	<LOQ	<LOQ	–	–	<LOQ	–	–
Pirimiphos-ethyl	<LOQ	<LOQ	–	–	<LOQ	–	–
Pirimiphos-methyl	32.9 ± 3.94^{a}	8.86 ± 0.90^{b}	0.27	73.0	6.48 ± 0.98^{b}	0.20	80.3
Prochloraz	22.0 ± 4.50^{a}	11.4 ± 0.82^{b}	0.52	48.1	12.9 ± 1.31^{b}	0.59	41.2
Profenofos	27.4 ± 1.83^{a}	13.6 ± 1.15^{b}	0.49	50.5	11.8 ± 1.40^{b}	0.43	56.8

(*continued on next page*)

Table 1 (*continued*)

Pesticides	Unprocessed Samples	Washing			Washing with Vinegar		
	Concentration ± SD	Concentration ± SD	PF	Reduction (%)	Concentration ± SD	PF	Reduction (%)
Propiconazole	41.7 ± 4.10[a]	14.5 ± 1.21[b]	0.35	65.4	12.1 ± 1.51[b]	0.29	71.1
Propyzamide	33.3 ± 0.02[a]	20.3 ± 2.50[b]	0.61	39.1	16.7 ± 2.10[b]	0.50	49.9
Prothioconazole-desthio	39.8 ± 2.33[a]	15.3 ± 0.50[b]	0.38	61.5	12.6 ± 1.54[b]	0.32	68.4
Pyrazophos	34.0 ± 1.30[a]	23.4 ± 0.93[b]	0.69	31.3	19.9 ± 1.85[b]	0.58	41.6
Pyrimethanil	36.2 ± 1.73[a]	23.6 ± 1.08[b]	0.65	34.8	16.2 ± 1.08[c]	0.45	55.2
Quinoxyfen	12.9 ± 0.62[a]	9.28 ± 0.30[b]	0.71	28.3	8.21 ± 0.17[c]	0.63	36.5
Rotenone	18.6 ± 1.10	<LOQ	–	> 46.2	<LOQ	–	> 46.2
SpinosadA	29.0 ± 0.81[a]	13.6 ± 1.49[b]	0.47	53.1	8.72 ± 0.52[c]	0.30	69.9
SpinosadD	27.2 ± 0.64[a]	14.8 ± 0.75[b]	0.54	45.6	10.1 ± 1.18[c]	0.37	62.9
Spiroxamine	37.8 ± 3.24[a]	17.7 ± 0.93[b]	0.47	53.1	8.82 ± 0.53[c]	0.23	76.6
Tebuconazole	<LOQ	<LOQ	–	–	<LOQ	–	–
Tebufenpyrad	31.6 ± 2.46[a]	19.9 ± 1.31[b]	0.63	37.0	16.9 ± 1.77[b]	0.53	46.5
Terbuthylazine	35.3 ± 0.29[a]	23.9 ± 2.11[b]	0.68	32.1	20.7 ± 1.91[b]	0.59	41.4
Tetraconazole	39.5 ± 3.04[a]	15.7 ± 1.33[b]	0.40	60.1	13.9 ± 2.20[b]	0.35	64.9
Thiabendazole	26.2 ± 4.61[a]	12.8 ± 1.76[b]	0.49	51.3	10.5 ± 1.76[b]	0.40	60.1
Thiacloprid	28.1 ± 2.20[a]	14.6 ± 1.31[b]	0.52	48.2	12.4 ± 1.01[b]	0.44	56.1
Tricyclazole	26.6 ± 1.56[a]	13.9 ± 0.71[b]	0.52	47.6	11.2 ± 0.28[c]	0.42	57.9
Triflumuron	32.0 ± 3.84[a]	11.7 ± 1.07[b]	0.37	63.3	9.15 ± 0.82[b]	0.29	71.4
Zoxamide	27.5 ± 0.01[a]	23.0 ± 1.32[b]	0.84	16.2	19.8 ± 0.44[c]	0.72	28.0
Fludioxonil	24.2 ± 2.00[a]	24.1 ± 1.16[b]	1.00	0.21	24.9 ± 0.05[b]	1.03	+ 3.00

Legend: DMST- *N*,*N*-dimethyl-N′-p-tolysulphamide; EPN- O-ethyl O-4-nitrophenyl phosphonothiate.

unprocessed rice samples. Replicates ($n = 2$) of each rice sample (unprocessed and washed) are shown in Tables 1 and S1 for long-grain rice, Tables 2 and S2 for brown rice and Tables 3 and S3 for basmati rice. Certain pesticides were below the limit of quantification (LOQ), making it impossible to quantify their reduction. In these cases, the pesticide's corresponding LOQ was used to estimate the minimum percentage reduction.

3.1. Long-grain rice: Effect of washing process in pesticide residues

3.1.1. Unprocessed samples

At a level of contamination of 20 μg/kg, out of the 121 pesticide residues in the mixture used to contaminate the samples, 97 pesticides were quantifiable. Of these, 40 exceeded their LOQ, including azoxystrobin (a strobilurin), buprofezin (a pyrimidine), and diniconazole (a triazole), among others. The average concentration of the analyzed pesticides ranged from 5.4 to 16.7 μg/kg.

At a level of contamination of 50 μg/kg, 97 pesticides could be quantified from the same initial mixture of 121 residues but certain pesticides were below the LOQ in the unprocessed samples. These include carboxin (a carboxanilide), coumaphos (an organophosphate), etrimfos (an organophosphate), fonofos (an organophosphate), isoprothiolane (a dithiolane), metaflumizone (a semicarbazone), phosphamidon (an organophosphate), pirimiphos-ethyl (an organophosphate), and tebuconazole (a triazole). The mean concentration of the studied pesticides was between 11.3 and 41.7 μg/kg (Tables 1 and S1).

3.1.2. Effects of washing and washing with apple cider vinegar

At a level of contamination of 20 μg/kg, a reduction percentage could only be calculated for 21 out of the 97 pesticides. The washing process resulted in percentage reductions ranging from 0.5 % to 30.4 %. The highest reduction, 30.4 %, was observed for fenpropimorph (a morpholine), followed by 27.2 % for spiroxamine (a spiroketalamide).

At the level of contamination of 50 μg/kg, a reduction percentage could be determined for 86 of the 97 pesticides. The reductions varied from 0.21 % to 73 %, with certain pesticides like diazinon (an organophosphate), indoxacarb (an oxadiacin), zoxamide (a benzamide), and fludioxanil (a phenylpyrrole) showing negligible removal after washing. The greatest reduction, 73 %, was observed for pirimiphos-methyl (an organophosphate), followed by 65.9 % for fenamidone (an imidazole), 65.8 % for cadusafos (an organophosphate), and 65.4 % for propiconazole (an azole). After washing, several pesticides were below the LOQ, including EPN (an organophosphate), fenamiphos sulfoxide (an organophosphate), fenthion oxon (an organophosphate), and fenthion oxon sulfoxide (an organophosphate).

Over 40 % of the pesticides showed a reduction of 40 % to 60 %, while more than 10 % experienced a reduction of over 60 % following washing with mineral water. (Figure S3).

At the 20 μg/kg contamination level, the percentage reduction after washing with vinegar (5 %, *v*/v) varies from 13 to 39 % for pesticides above their LOQ. Most pesticides are below their LOQ, except bixafen (pirazol), chlorfenvinphos (organophosphate), diazinon (organophosphate), diniconazole (triazol), epoxiconazole (triazol), fenarimol (pyridine), flutriafol (triazol), penconazole (triazol), pyrazophos (phosphorothiolate), tebufenpyrad (pyrazol) and zoxamide (benzamide).

At the 50 μg/kg contamination level, the percentage reduction after washing with vinegar (5 %, *v*/v) varies from 26.8 to 80.3 % for pesticides above their LOQ. Vinegar washing does not affect fludioxonil, while most pesticides are significantly reduced by vinegar washing. The highest reduction occurs for the pesticide pirimiphos-methyl. As found when washing the samples with mineral water, concentrations of pesticides below the LOQ were also found after washing with vinegar. In addition to those mentioned above, more pesticides were below the LOQ, such as acetamiprid (neonicotinoid), carbofuran (carbamate), fenpropidin (unclassified), fosthiazate (organophosphate), or metribuzin (1,2,4-triazinone), among others.

Fig. 1 shows that there is a higher percentage of pesticides, with a 60 % reduction of pesticide contamination when washing with vinegar (5 %, v/v) compared to washing with just mineral water.

Fig. 2 shows the difference in pesticide concentration for the different samples (washed (1) and washed with vinegar (2)) for bixafen as representative pesticide residue in long-grain rice.

3.2. Brown rice: Effect of washing process on pesticide residues

3.2.1. Unprocessed samples

At the level of contamination of 20 μg/kg, from the 121 pesticides present in the mixture used to contaminate the sample, a total of 88 pesticides could be quantified. From these, only 38 pesticides showed values higher than LOQ, such as boscalid (carboxamide), cadusafos (organophosphate), diazinon (organophosphate), fenamidone (imidazol), flutriafol (triazol), metconazole (triazol) and tetraconazole

Table 2
Mean concentrations (±SD, n = 3), mean values of processing factors (PF), and reductions (%) of the pesticides in unprocessed brown rice samples after washing (50 μg/kg). Different letters within the same row indicate statistically significant differences ($p < 0.05$).

Pesticides	Unprocessed Samples	Washing			Washing with Vinegar		
	Concentration ± SD	Concentration ± SD	PF	Reduction (%)	Concentration ± SD	PF	Reduction (%)
Acetamiprid	14.5 ± 0.13^{a}	14.4 ± 0.93^{a}	0.99	0.33	10.9 ± 2.01^{b}	0.76	24.4
Azoxystrobin	23.8 ± 1.21^{a}	17.9 ± 0.85^{b}	0.75	25.0	10.1 ± 2.61^{c}	0.42	57.7
Bixafen	13.0 ± 0.78^{a}	12.7 ± 0.88^{a}	0.97	2.72	<LOQ	–	> 23.3
Boscalid	20.9 ± 1.13^{a}	14.8 ± 1.11^{b}	0.71	29.3	11.3 ± 2.88^{b}	0.54	46.1
Bupirimate	17.6 ± 0.54^{a}	10.5 ± 1.38^{b}	0.59	40.7	<LOQ	–	> 43.3
Buprofezin	12.1 ± 1.10^{a}	11.5 ± 0.13^{a}	0.95	4.80	<LOQ	–	> 17.1
Cadusafos	16.5 ± 2.72^{a}	11.7 ± 1.18^{b}	0.71	29.3	<LOQ	–	> 69.7
Carbaryl	23.2 ± 2.63	<LOQ	–	> 56.8	<LOQ	–	> 56.8
Carbofuran	14.0 ± 0.84^{a}	13.8 ± 1.31^{ab}	0.99	1.09	10.6 ± 1.63^{b}	0.76	24.3
Carboxin	<LOQ	<LOQ	–	–	<LOQ	–	–
Chlorantraniliprole	13.0 ± 1.51^{a}	11.8 ± 0.73^{a}	0.91	9.08	11.7 ± 1.05^{b}	0.90	10.4
Chlorfenvinphos	16.1 ± 1.23^{a}	13.5 ± 0.30^{a}	0.84	15.8	13.1 ± 2.30^{a}	0.82	18.3
Chlorpyrifos-methyl	<LOQ	<LOQ	–	–	<LOQ	–	–
Diazinon	14.3 ± 0.70^{a}	13.5 ± 0.44	0.94	5.44	<LOQ	–	> 30.0
Difenoconazole	16.0 ± 1.03^{a}	10.4 ± 1.46^{b}	0.65	35.0	<LOQ	–	37.3
Diflubenzuron	18.4 ± 1.87^{a}	15.4 ± 0.26^{ab}	0.84	16.3	13.4 ± 2.32^{b}	0.73	27.2
Dimethomorph	10.4 ± 0.74	<LOQ	–	> 4.21	<LOQ	–	> 4.21
EPN	17.2 ± 0.90	<LOQ	–	> 41.9	<LOQ	–	> 41.9
Epoxiconazole	27.8 ± 0.96^{a}	17.1 ± 1.20^{b}	0.62	38.4	13.9 ± 0.75^{c}	0.50	50.1
Ethoprophos	23.1 ± 0.96^{a}	17.4 ± 1.02^{b}	0.75	25	11.7 ± 2.62^{c}	0.51	49.5
Etimfos	<LOQ	<LOQ	–	–	<LOQ	–	–
Fenamidone	26.2 ± 1.18^{a}	13.8 ± 1.81^{b}	0.53	47.3	<LOQ	–	> 61.9
Fenamiphos sulfone	13.2 ± 0.97^{a}	13.6 ± 1.00^{a}	1.03	+ 3.00	11.8 ± 2.12^{a}	0.89	10.8
Fenamiphos sulfoxide	24.3 ± 3.34^{a}	18.6 ± 0.73^{b}	0.77	23.3	19.0 ± 1.13^{b}	0.78	21.8
Fenarimol	22.9 ± 0.43^{a}	15.9 ± 0.56^{b}	0.69	30.5	15.0 ± 1.76^{b}	0.66	34.3
Fenoxycarb	25.7 ± 0.99^{a}	13.9 ± 2.70^{b}	0.54	45.9	<LOQ	–	> 61.1
Fenpropidin	23.0 ± 1.18^{a}	12.0 ± 1.05^{b}	0.52	47.8	14.5 ± 2.44^{b}	0.63	37.0
Fenpropimorph	22.1 ± 1.13^{a}	12.0 ± 0.69^{b}	0.54	45.7	15.8 ± 1.37^{c}	0.71	28.7
Fenpyroximate	<LOQ	<LOQ	–	–	<LOQ	–	–
Fenthion oxon sulfone	11.4 ± 0.29^{a}	<LOQ	–	> 12.3	<LOQ	–	> 12.3
Fenthion oxon sulfoxide	16.2 ± 0.40	12.4 ± 0.59^{b}	0.76	23.7	<LOQ	–	> 38.4
Fenthion oxon	12.8 ± 0.61	<LOQ	–	> 21.9	<LOQ	–	> 21.9
Fenthion sulfoxide	29.2 ± 1.11^{a}	27.8 ± 0.81^{a}	0.95	4.80	<LOQ	–	> 65.8
Fluopyram	21.2 ± 1.99^{a}	15.7 ± 2.39^{a}	0.74	26.2	8.76 ± 2.53^{b}	0.41	58.8
Fluquinconazole	16.8 ± 1.13^{a}	14.8 ± 0.25^{ab}	0.88	11.6	13.4 ± 1.82^{b}	0.80	19.8
Flutriafol	24.0 ± 0.31^{a}	21.5 ± 0.68^{a}	0.90	10.3	15.3 ± 3.26^{b}	0.64	36.2
Fonofos	<LOQ	<LOQ	–	–	<LOQ	–	–
Fosthiazate	18.2 ± 0.76^{a}	17.3 ± 1.05^{ab}	0.95	5.00	14.8 ± 1.61^{b}	0.81	18.9
Indoxacarb	12.3 ± 0.87	<LOQ	–	> 18.7	<LOQ	–	> 18.7
Iprodione	13.0 ± 1.92	<LOQ	–	> 23.2	<LOQ	–	> 23.2
Iprovalicarb	<LOQ	<LOQ	–	–	<LOQ	–	–
Isoprocarb	17.0 ± 1.08^{a}	17.1 ± 0.04^{a}	1.02	+ 1.90	16.8 ± 1.19^{a}	0.98	1.42
Isoprothiolane	<LOQ	<LOQ	–	–	<LOQ	–	–
Isoproturon	14.9 ± 0.83	<LOQ	–	> 32.8	<LOQ	–	> 32.8
Linuron	18.8 ± 0.41^{a}	17.7 ± 0.04^{a}	0.94	5.87	17.1 ± 1.19^{a}	0.91	8.88
Lufenuron	20.8 ± 3.63^{a}	11.6 ± 1.11^{b}	0.56	44.0	9.87 ± 2.31^{b}	0.48	52.4
Mepanipyrim	12.1 ± 0.76^{a}	11.1 ± 0.30^{a}	0.92	8.02	<LOQ	–	> 17.1
Metaflumizone	<LOQ	<LOQ	–	–	<LOQ	–	–
Metalaxyl	14.7 ± 0.64^{a}	13.1 ± 0.94^{ab}	0.89	10.5	11.1 ± 1.72^{b}	0.76	24.5
Metalaxyl-M	15.3 ± 0.81^{a}	12.5 ± 0.52^{b}	0.82	18.1	11.3 ± 1.54^{b}	0.74	25.9
Metazachlor	22.0 ± 2.66^{a}	21.2 ± 0.91^{a}	0.97	3.50	20.5 ± 3.28^{a}	0.93	6.97
Metconazole	17.2 ± 0.73^{a}	14.5 ± 0.44^{a}	0.85	15.5	16.8 ± 1.72^{a}	0.98	2.34
Methiocarb	19.8 ± 1.93^{a}	20.71 ± 0.71^{a}	0.95	4.52	18.1 ± 0.82^{a}	0.87	12.8
Metribuzin	16.5 ± 0.41^{a}	16.1 ± 1.60^{a}	0.97	2.83	11.7 ± 1.89^{b}	0.71	29.0
Oxadixyl	10.3 ± 0.56	<LOQ	–	> 3.00	<LOQ	–	> 3.00
Paclobutrazole	27.6 ± 1.00^{a}	19.4 ± 1.00^{b}	0.71	29.5	14.1 ± 2.68^{c}	0.51	48.8
Paraoxon-ethyl	<LOQ	<LOQ	–	–	<LOQ	–	–
Parathion	19.0 ± 0.93	<LOQ	–	> 47.4	<LOQ	–	> 47.4
Parathion-methyl	20.1 ± 1.20^{a}	16.6 ± 0.36^{a}	0.82	17.6	11.7 ± 3.10^{b}	0.58	41.9
Penconazole	17.8 ± 0.43^{a}	15.0 ± 0.52^{a}	0.84	16.1	16.1 ± 2.16^{a}	0.90	9.96
Pendimethalin	<LOQ	<LOQ	–	–	<LOQ	–	–
Phenthoate	14.4 ± 0.50^{a}	11.5 ± 1.11^{b}	0.80	20.1	<LOQ	–	30.7
Phosphamidon	<LOQ	<LOQ	–	–	<LOQ	–	–
Phoxim	16.8 ± 0.15^{a}	9.35 ± 1.61^{b}	0.56	44.3	<LOQ	–	> 70.2
Pirimiphos-ehtyl	<LOQ	<LOQ	–	–	<LOQ	–	–
Pirimiphos-methyl	14.5 ± 0.39^{a}	6.76 ± 1.50^{b}	0.46	53.4	<LOQ	–	> 65.6
Prochloraz	11.8 ± 0.59	<LOQ	–	> 15.4	<LOQ	–	> 15.4
Profenofos	13.2 ± 0.60^{a}	10.1 ± 1.35^{b}	0.77	23.5	<LOQ	–	> 24.5
Propiconazole	20.4 ± 0.96^{a}	12.4 ± 1.79^{b}	0.61	39.1	<LOQ	–	> 51.0
Propyzamide	18.1 ± 0.92^{a}	15.7 ± 0.54^{ab}	0.87	13.3	14.6 ± 1.95^{b}	0.81	19.5
Prothioconazole desthio	26.5 ± 0.84^{a}	16.9 ± 1.76^{b}	0.64	36.1	11.9 ± 3.13^{b}	0.45	54.9

(*continued on next page*)

Table 2 (*continued*)

Pesticides	Unprocessed Samples	Washing			Washing with Vinegar		
	Concentration ± SD	Concentration ± SD	PF	Reduction (%)	Concentration ± SD	PF	Reduction (%)
Pyrazophos	13.7 ± 1.47[a]	12.1 ± 0.32[a]	0.88	11.7	12.8 ± 0.43[a]	0.93	6.38
Pyrimethanil	14.8 ± 0.79[a]	11.5 ± 0.48[b]	0.78	21.8	11.9 ± 1.97[ab]	0.80	19.6
Quinoxyfen	6.55 ± 0.12	<LOQ	–	> 23.7	<LOQ	–	> 23.7
Rotenone	12.7 ± 0.90	<LOQ	–	> 21.5	<LOQ	–	> 21.5
SpinosadA	15.7 ± 0.30[a]	11.3 ± 0.76[b]	0.72	28.2	13.6 ± 2.44[ab]	0.87	13.4
SpinosadD	16.3 ± 2.47[a]	12.9 ± 2.08[a]	0.79	21.0	<LOQ	–	> 38.5
Spiroxamine	23.7 ± 1.25[a]	13.1 ± 1.24[b]	0.55	44.6	17.0 ± 3.13[b]	0.72	28.4
Tebuconazole	<LOQ	<LOQ	–	–	<LOQ	–	–
Tebufenpyrad	13.2 ± 0.64[a]	11.8 ± 0.27[a]	0.89	10.7	12.3 ± 1.26[a]	0.94	6.45
Terbuthylazine	11.5 ± 1.11[a]	10.1 ± 0.17[a]	0.88	11.6	<LOQ	–	> 12.7
Tetraconazole	23.3 ± 1.47[a]	13.8 ± 1.79[b]	0.59	40.9	10.2 ± 2.98[b]	0.44	56.3
Thiabendazole	25.7 ± 0.35[a]	23.0 ± 0.43[b]	0.89	10.6	21.5 ± 0.34[c]	0.84	16.1
Thiacloprid	20.3 ± 2.29[a]	19.3 ± 1.19[a]	0.95	5.01	15.7 ± 1.96[a]	0.77	22.6
Triadimefon	19.3 ± 0.51[a]	17.2 ± 0.11[b]	0.89	10.8	18.9 ± 1.31[ab]	0.98	2.05
Triadimenol	24.5 ± 0.91[a]	20.8 ± 0.72[a]	0.85	15.0	16.7 ± 2.53[b]	0.68	32.1
Tricyclazole	22.1 ± 1.18[a]	22.5 ± 1.80[a]	1.03	+ 3.00	17.2 ± 3.18[a]	0.78	22.1
Fludioxonil	18.6 ± 1.51[a]	14.9 ± 1.32[b]	0.80	20.1	20.3 ± 1.52[a]	1.09	+ 9.00

Legend: DMST- *N,N*-dimethyl-N′-p-tolysulphamide; EPN- O-ethyl O-4-nitrophenyl phosphonothiate.

(triazol), among others. The average concentration of the analyzed pesticides ranged from 5.1 to 15.8 μg/kg, with dimethomorph (a morpholine) having the lowest concentration and triadimenol (a triazole) the highest.

At the 50 μg/kg contamination level, 88 out of the 121 pesticides in the mixture used for contamination were quantifiable, but some pesticides in the unprocessed samples were below the LOQ. These include carboxin (a carboxanilide), etrimfos (an organophosphate), fenpyroximate, fonofos (an organophosphate), isoprothiolane (a dithiolane), metaflumizone (a semicarbazone), phosphamidon (an organophosphate), pirimiphos-ethyl (an organophosphate), and tebuconazole (a triazole).

The average concentration of the studied pesticides ranged from 6.6 to 29.2 μg/kg, with quinoxyfen (a phenoxyquinoline) having the lowest concentration and fenthion sulfoxide (an organophosphate) having the highest (Tables 2 and S2).

3.2.2. *Effect of washing and washing with apple cider vinegar*

At the 20 μg/kg contamination level, from the 97 quantifiable pesticides, percentage reduction could only be determined for 13 pesticides. The reductions after washing ranged from 1.2 % to 7.5 %, with the highest reduction (7.5 %) observed for spiroxamine (a spiroketalamide), and the lowest for thiacloprid (a neonicotinoid).

At the 50 μg/kg contamination level, percentage reduction was calculated for 62 out of the 97 pesticides. The reductions ranged from 0.3 % to 53.4 %, with some pesticides, including acetamiprid (a neonicotinoid), carbofuran (a carbamate), fenamiphos sulfone (an organophosphate), and tricyclazole (a triazolobenzothiazole), not being significantly removed by washing. The greatest reduction, 53.4 %, was for pirimiphos-methyl (an organophosphate), while the lowest reduction was for acetamiprid (a neonicotinoid). Several pesticides were below the LOQ after washing, including carbaryl (a carbamate), carboxin (a carboxanilide), EPN (an organophosphate), indoxacarb (an oxadiacin), and parathion (an organophosphate).

More than 40 % of the pesticides showed a reduction of 0–20 %, while over 10 % had reductions between 40 and 50 % after washing with mineral water (Figure S4).

At the contamination level of 20 μg/kg, after washing with vinegar (5 %, *v*/v), all of the pesticides are below their LOQ, except four pesticides, fenpropidin (not classified), flutriafol (triazol), spinosad A (spinosyn) and spiroxamine (spiroketalamide), with 50.0, 50.5, 35.6 e 48.5 %, percentage of reduction, respectively.

At the contamination level of 50 μg/kg, the percentage reduction after washing with vinegar (5 %, v/v) varies from 1.4 to 58.8 % for pesticides above their LOQ. The highest reduction occurs for the pesticide fluopyram (benzamides-pyridines).

Figure S5 shows that there is more than 20 % of the pesticides presented a reduction between 20 and 30 %, and more than 15 % of pesticides presented a reduction higher than 50 % after washing with vinegar (5 %, v/v).

3.3. *Basmati rice: Effect of washing process on the pesticide*

3.3.1. *Unprocessed samples*

At the contamination level of 20 μg/kg from the 121 pesticides present in the mixture used to contaminate the sample, a total of 88 pesticides could be quantified. From these, only 10 pesticides are greater than their LOQ, such as boscalid (carboxamide), carbaryl (carbamate), diazinon (organophosphate), fenpropidin (not classified), lufenuron (benzoylurea), pencycuron (phenylurea), prochloraz (imidazole), quinoxyfen (phenoxyquinoline), spiroxamine (spiroketalamide) and zoxamide (benzamide). The mean concentration of the studied pesticides was between 5.3 and 14.4 μg/kg, with the lowest concentration belonging to fenpropidin (not classified) and the highest concentration belonging to pencycuron (phenylurea).

At the contamination level of 50 μg/kg, from the 121 pesticides present in the mixture used to contaminate the sample, a total of 88 pesticides could be quantified. From these, 34 pesticides in the unprocessed samples were lower than the LOQ, including acetamiprid (neonicotinoid), carbendazim (benzimidazole), carbofuran (carbamate), diflubenzuron (benzoylurea), DMST (tolifluanide metabolite), oxadixyl (phenylamide), among others.

The mean concentration of the studied pesticides was in the range of 6.9–46.3 μg/kg, where the lowest concentration belongs to fenamiphos sulfone (organophosphate) and the highest concentration belongs to fenarimol (pyridine) (Tables 3 and S3).

3.3.2. *Effect of washing and washing with apple cider vinegar*

At the contamination level of 20 μg/kg, from the 97 pesticides, percentage reduction could only be calculated for two pesticides. Diazinon (an organophosphate) showed a reduction of 1.56 %, while zoxamide (a benzamide) was not significantly removed by washing.

At the 50 μg/kg contamination level, percentage reduction was determined for 40 out of the 97 pesticides. Reductions ranged from 2.9 % to 51.3 %, with fludioxonil (a phenylpyrrole) showing no significant removal by washing. The highest reduction, 51.3 %, was for spinosad A (a spinosad), and the lowest for fludioxonil (a phenylpyrrole). After washing, several pesticides were below the LOQ, including acetamiprid

Table 3
Mean concentrations (±SD, n = 3), mean values of processing factors (PF), and reductions (%) of the pesticides in unprocessed basmati rice samples after washing (50 μg/kg). Different letters within the same row indicate statistically significant differences ($p < 0.05$).

Pesticides	Unprocessed Samples	Washing			Washing with Vinegar		
	Concentration ± SD	Concentration ± SD	PF	Reduction (%)	Concentration ± SD	PF	Reduction (%)
Acetamiprid	<LOQ	<LOQ	–	–	<LOQ	–	–
Azoxystrobin	20.2 ± 1.09^{a}	12.3 ± 1.48^{b}	0.61	39.1	<LOQ	–	> 50.4
Bixafen	17.8 ± 0.13^{a}	15.1 ± 0.44^{b}	0.85	15.3	12.4 ± 0.22^{c}	0.69	30.5
Boscalid	17.9 ± 0.88^{a}	11.6 ± 1.04^{b}	0.65	35.2	9.22 ± 0.28^{c}	0.51	48.5
Bupirimate	25.1 ± 1.44^{a}	16.4 ± 1.10^{b}	0.65	35.0	15.5 ± 0.41^{c}	0.62	38.3
Buprofezin	14.7 ± 0.92^{a}	10.0 ± 0.16^{b}	0.68	31.9	11.1 ± 0.44^{b}	0.75	24.6
Cadusafos	20.5 ± 2.45	<LOQ	–	> 75.6	<LOQ	–	> 75.6
Carbaryl	30.0 ± 0.06^{a}	24.2 ± 0.18^{b}	0.81	19.4	17.7 ± 0.63^{c}	0.59	41.2
Carbendazim	<LOQ	<LOQ	–	–	<LOQ	–	–
Carbofuran	<LOQ	<LOQ	–	–	<LOQ	–	–
Carboxin	<LOQ	<LOQ	–	–	<LOQ	–	–
Chlorantraniliprole	<LOQ	<LOQ	–	–	<LOQ	–	–
Chlorfenvinphos	14.6 ± 0.98	<LOQ	–	> 31.6	<LOQ	–	> 31.6
Chlorpyrifos-methyl	<LOQ	<LOQ	–	–	<LOQ	–	–
Clofentezine	<LOQ	<LOQ	–	–	<LOQ	–	–
Coumaphos	<LOQ	<LOQ	–	–	<LOQ	–	–
Cyprodinil	14.8 ± 0.54^{a}	10.0 ± 0.37^{b}	0.68	32.0	9.99 ± 0.21^{b}	0.68	32.3
Diazinon	33.6 ± 0.56^{a}	27.8 ± 0.46^{b}	0.82	17.5	27.7 ± 0.83^{b}	0.82	17.7
Diniconazole	27.5 ± 3.39^{a}	18.0 ± 2.84^{b}	0.66	34.4	12.8 ± 0.83^{b}	0.46	53.5
Diflubenzuron	<LOQ	<LOQ	–	–	<LOQ	–	–
Dimethoate	<LOQ	<LOQ	–	–	<LOQ	–	–
Dimethomorph	21.2 ± 1.15^{a}	14.8 ± 0.70^{b}	0.70	30.1	11.4 ± 0.12^{c}	0.54	46.2
DMST	<LOQ	<LOQ	–	–	<LOQ	–	–
EPN	<LOQ	<LOQ	–	–	<LOQ	–	–
Ethoprophos	13.7 ± 1.26	<LOQ	–	> 63.5	<LOQ	–	> 63.5
Etrimfos	<LOQ	<LOQ	–	–	<LOQ	–	–
Fenamidone	35.5 ± 2.56^{a}	20.5 ± 2.30^{b}	0.58	42.3	14.0 ± 0.05^{c}	0.39	60.6
Fenamiphos sulfone	6.91 ± 0.04	<LOQ	–	> 27.6	<LOQ	–	> 27.6
Fenamiphos sulfoxide	<LOQ	<LOQ	–	–	<LOQ	–	–
Fenarimol	46.3 ± 1.14^{a}	31.4 ± 1.14^{b}	0.68	32.1	25.8 ± 0.50^{c}	0.56	44.3
Fenoxycarb	43.5 ± 3.38^{a}	33.1 ± 4.72^{b}	0.76	24.0	22.7 ± 0.96^{c}	0.52	47.9
Fenpropidin	25.1 ± 0.25^{a}	12.6 ± 0.47^{b}	0.50	50.0	15.8 ± 0.68^{c}	0.63	37.2
Fenpropimorph	27.4 ± 0.22^{a}	17.3 ± 1.17^{b}	0.63	36.7	18.2 ± 0.18^{b}	0.66	33.5
Fenpyroximate	<LOQ	<LOQ	–	–	<LOQ	–	–
Fenthion oxon sulfone	<LOQ	<LOQ	–	–	<LOQ	–	–
Fenthion oxon sulfoxide	<LOQ	<LOQ	–	–	<LOQ	–	–
Fluopyram	16.5 ± 1.42^{a}	9.32 ± 1.66^{b}	0.57	43.4	6.06 ± 0.06^{c}	0.37	63.2
Fluquinconazole	14.9 ± 1.34	<LOQ	–	> 32.9	<LOQ	–	> 32.9
Flutriafol	16.50 ± 1.42^{a}	10.8 ± 1.16^{b}	0.59	40.3	9.06 ± 0.47^{b}	0.50	49.7
Fonofos	<LOQ	<LOQ	–	–	<LOQ	–	–
Fosthiazate	15.3 ± 0.45^{a}	11.0 ± 1.16^{b}	0.72	28.3	9.06 ± 0.47^{b}	0.82	17.5
Hexythiazox	34.5 ± 0.33^{a}	23.7 ± 3.1^{b}	0.69	31.1	19.0 ± 1.58^{b}	0.55	44.8
Indoxacarb	16.9 ± 0.62	<LOQ	–	> 40.7	<LOQ	–	> 40.7
Isoprocarb	<LOQ	<LOQ	–	–	<LOQ	–	–
Isoprothiolane	<LOQ	<LOQ	–	–	<LOQ	–	–
Isoproturon	<LOQ	<LOQ	–	–	<LOQ	–	–
Kresoxim-methyl	<LOQ	<LOQ	–	–	<LOQ	–	–
Linuron	22.6 ± 0.43^{a}	18.7 ± 1.10^{b}	0.83	17.3	14.9 ± 0.11^{c}	0.66	34.1
Lufenuron	43.8 ± 0.05^{a}	31.4 ± 0.16^{b}	0.72	28.2	26.3 ± 0.85^{c}	0.60	40.0
Mepanipyrim	20.8 ± 0.55^{a}	12.8 ± 0.03	0.62	38.2	11.7 ± 0.19^{c}	0.56	43.9
Metaflumizone	<LOQ	<LOQ	–	–	<LOQ	–	–
Metalaxyl	7.09 ± 0.44	<LOQ	–	> 29.5	<LOQ	–	> 29.5
Metalaxyl-M	<LOQ	<LOQ	–	–	<LOQ	–	–
Metazachlor	<LOQ	<LOQ	–	–	<LOQ	–	–
Metconazole	20.0 ± 0.60^{a}	14.9 ± 0.26^{b}	0.74	25.7	13.9 ± 0.47^{b}	0.69	30.7
Methiocarb	16.6 ± 1.40	<LOQ	–	> 39.9	<LOQ	–	> 39.9
Metribuzin	10.8 ± 0.50	<LOQ	–	> 7.14	<LOQ	–	> 7.14
Oxadixyl	<LOQ	<LOQ	–	–	<LOQ	–	–
Paclobutrazole	27.6 ± 1.76^{a}	16.6 ± 0.96^{b}	0.60	39.9	13.0 ± 0.34^{c}	0.47	52.8
Parathion	<LOQ	<LOQ	–	–	<LOQ	–	–
Parathion-methyl	<LOQ	<LOQ	–	–	<LOQ	–	–
Penconazole	16.9 ± 1.02^{a}	11.9 ± 0.42^{b}	0.70	29.7	10.2 ± 0.05^{c}	0.60	39.7
Pencycuron	<LOQ	<LOQ	–	–	<LOQ	–	–
Pirimiphos-ethyl	<LOQ	<LOQ	–	–	<LOQ	–	–
Pirimiphos-methyl	27.5 ± 2.54^{a}	15.4 ± 1.72^{b}	0.56	44.0	11.62 ± 0. 55^{b}	0.42	57.8
Prochloraz	<LOQ	<LOQ	–	–	<LOQ	–	–
Profenofos	14.8 ± 1.75	<LOQ	–	> 32.6	<LOQ	–	> 32.6
Propiconazole	35.4 ± 2.56^{a}	21.4 ± 1.83^{b}	0.60	39.6	15.6 ± 0.61^{c}	0.44	56.0
Propyzamide	12.3 ± 0.53	<LOQ	–	> 18.4	<LOQ	–	> 18.4
Prothioconazole desthio	35.8 ± 1.65^{a}	21.2 ± 2.03^{b}	0.59	40.6	14.8 ± 0.34^{c}	0.41	58.6
Pyrazophos	14.6 ± 0.24^{a}	11.5 ± 0.04^{b}	0.79	20.8	11.8 ± 0.22^{b}	0.81	19.2

(*continued on next page*)

Table 3 (*continued*)

Pesticides	Unprocessed Samples	Washing			Washing with Vinegar		
	Concentration ± SD	Concentration ± SD	PF	Reduction (%)	Concentration ± SD	PF	Reduction (%)
Pyrimethanil	18.8 ± 0.60[a]	13.3 ± 0.0.64[b]	0.71	29.4	11.9 ± 0.08[c]	0.63	36.7
Quinoxyfen	25.7 ± 0.48[a]	21.9 ± 0.70[b]	0.85	14.7	21.5 ± 0.07[b]	0.84	16.3
Rotenone	11.9 ± 0.82	<LOQ	–	> 15.9	<LOQ	–	> 15.9
SpinosadA	26.8 ± 1.63[a]	13.0 ± 0.0.30[b]	0.49	51.3	11.7 ± 0.07[b]	0.44	56.4
SpinosadD	23.4 ± 1.55[a]	14.6 ± 1.12[b]	0.63	37.7	11.4 ± 0.21[c]	0.48	51.6
Spiroxamine	27.1 ± 1.07[a]	13.4 ± 0.20[b]	0.49	51.3	11.7 ± 0.37[c]	0.44	56.4
Tebuconazole	<LOQ	<LOQ	–	–	<LOQ	–	–
Tebufenpyrad	<LOQ	<LOQ	–	–	<LOQ	–	–
Terbuthylazine	19.1 ± 0.70	14.7 ± 0.30[b]	0.77	23.1	13.0 ± 0.31[c]	0.68	31.8
Tetraconazole	21.3 ± 2.84	<LOQ	–	> 53.1	<LOQ	–	> 53.1
Thiabendazole	<LOQ	<LOQ	–	–	<LOQ	–	–
Thiacloprid	18.9 ± 0.39[a]	13.4 ± 0.94[b]	0.70	29.2	11.0 ± 0.37[c]	0.58	41.7
Triadimefon	25.8 ± 0.63[a]	20.7 ± 0.04[b]	0.80	19.8	18.0 ± 0.33[c]	0.70	30.4
Tricyclazole	14.0 ± 0.13	<LOQ	–	> 28.7	<LOQ	–	> 28.7
Triflumuron	45.4 ± 2.53[a]	36.9 ± 1.94[b]	0.81	18.9	28.1 ± 0.26[c]	0.62	38.1
Zoxamide	20.4 ± 0.31[a]	19.7 ± 0.28[a]	0.97	3.32	17.4 ± 0.73[b]	0.85	15.0
Fludioxonil	23.0 ± 0.76[a]	22.7 ± 0.78[a]	0.97	2.90	15.2 ± 1.71[b]	0.65	35.0

Legend: DMST- *N,N*-dimethyl-N′-p-tolysulphamide; EPN- O-ethyl O-4-nitrophenyl phosphonothiate.

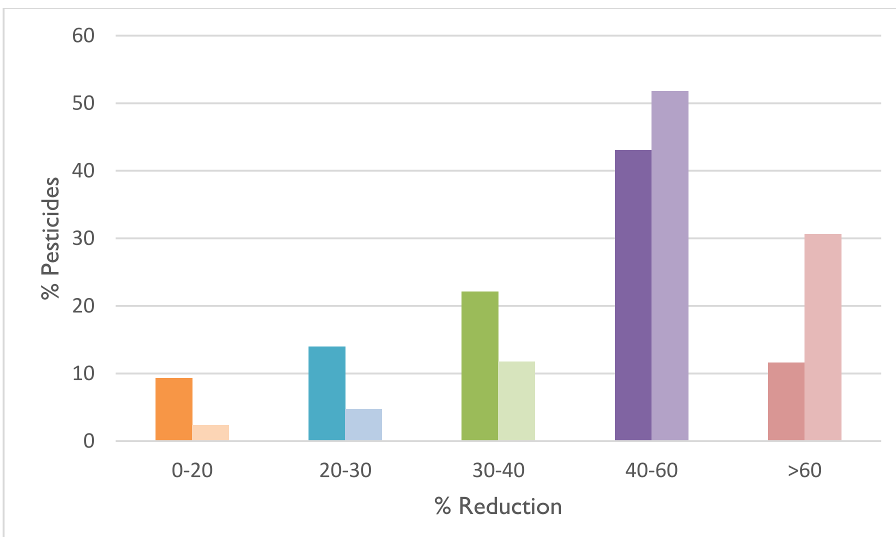

Fig. 1. Comparison of the effect of washing with vinegar (5 %, v/v) and washing just with water in reducing the initial concentration of pesticides in contaminated rice samples (50 μg/kg).

(a neonicotinoid), cadusafos (an organophosphate), carboxin (a carboxanilide), fluquinconazole (a triazole), indoxacarb (an oxadiacin), metalaxyl (an acylanine), and tricyclazole (a triazolobenzothiazole). More than 30 % of the pesticides presented a reduction between 30 and 40 % and 20 % between 40 and 60 % after washing with mineral water (Figure S6).

At the contamination level of 20 μg/kg, after washing with vinegar (5 %, *v*/v), all the pesticides were below their LOQ, except for diazinon (organophosphate) and zoxamide (benzamide), with a 2.8 and 7.7 % reduction, respectively.

At the contamination level of 50 μg/kg, the percentage reduction after washing with vinegar (5 %, *v*/v) varied from 16.3 to 63.2 % for pesticides above their LOQ. The highest reduction occurred for the pesticide fluopyram (benzamides-pyridines). As found when washing the samples with mineral water, concentrations of pesticides below the LOQ were also found after washing with vinegar. In addition to those mentioned above, more pesticides were below the LOQ, such as azoxystrobin (strobilurin), ethoprophos (organophosphate), and tricyclazole (triazolobenzothiazole), among others.

Figure S7 shows that there is more than 30 % of the pesticides presented a reduction between 30 and 40 %, and more than 5 % of pesticides presented a reduction higher than 60 % after washing with vinegar (5 %, v/v).

4. Discussion

When examining the contamination level of 20 μg/kg across the various rice types, it is observed that most of the 121 pesticides in the contaminating mixture felt below the LOQ. Notably, long-grain rice exhibits a higher quantity of pesticides than other types. In the case of Basmati rice, all pesticides are below the LOQ except for the 10 previously mentioned. Furthermore, at this contamination level, the reductions achieved through washing with mineral water and washing with a solution of mineral water and vinegar (5 %, v/v) are minimal.

The washing effect was particularly pronounced at 50 μg/kg. Long-grain rice, once again, showcased superior outcomes, enabling the quantification of 97 pesticides out of the total 121. This surpassed integral and basmati varieties, where only 88 pesticides were quantifiable. Basmati rice exhibited the highest number of pesticides falling below the LOQ. These findings can be attributed to the unique chemical

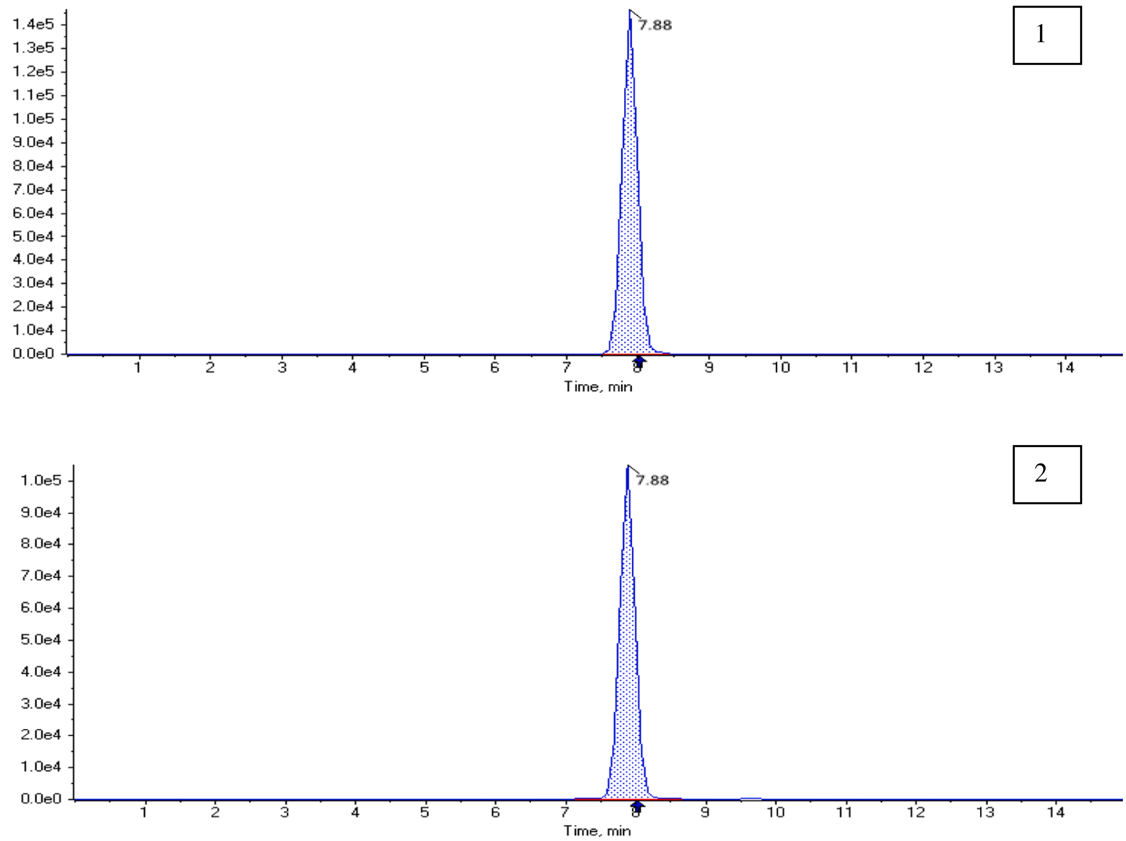

Fig. 2. Chromatograms of different samples: washed (1) and washed with vinegar (2) for Bixafen. A- Long grain rice; B- Brown rice; C- Basmati rice. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

composition of basmati grain types, characterized by higher protein and fiber contents when compared to other long rice varieties. This distinction is further supported by their maintained grain integrity after cooking, as highlighted in the study conducted by Pereira et al. (2024) (Pereira et al., 2024).

Fig. 3A shows that long-grain rice achieved the most significant reductions, with most pesticides registering between 40 and 60 %, while basmati rice reductions ranged from 30 to 40 %, and integral rice showed reductions between 0 and 20 %.

Fig. 3B reaffirms that long-grain rice exhibited the most substantial reductions, with approximately 30 % of pesticides reduced by more than 60 %, whereas brown and basmati rice did not surpass the 10 % reduction mark.

Pesticide reduction is affected by various factors such as solubility, pH, temperature, and the pesticide's mode of action. The mode of action is particularly important when considering residue removal through washing processes. Pesticides can be categorized as systemic or contact (non-systemic). Contact pesticides, such as carbaryl, cadusafos, and triflumuron, are typically applied to the surfaces of commodities and can be effectively removed by washing because they do not penetrate the product. In contrast, systemic pesticides, like bupirimate, propyzamide, and thiacloprid, are absorbed by the plant's vascular system, moving from the leaves and stems to other parts of the plant. Consequently, washing techniques are often ineffective at removing systemic pesticides (Tiryaki & Polat, 2023).

When comparing the reduction of pesticide residues in rice, cadusafos (a non-systemic pesticide) showed greater reductions than propyzamide (a systemic pesticide) across all rice types. For example, washing long-grain rice with water resulted in a 65.8 % reduction for cadusafos, and a 72.3 % reduction with water and vinegar. However, propyzamide decreased only 13.3 % when washing with water and 19.5 % % when washing with water and vinegar. Finally, in basmati rice, cadusafos achieved reductions of more than 75.6 % in both washings, and propyzamide achieved reductions of more than 18.4 %.

In Portugal, there is a list of pesticides authorized on rice plantations. From this list, we have 3 pesticides in common with our results: acetamiprid, azoxystrobin, and difenoconazole, all systemic pesticides.

After washing with water, acetamiprid (*) was reduced by 34.7 % and 0.33 % in long-grain and brown rice, respectively. Azoxystrobin reduced 59.8 %, 25.0 %, and 39.1 % in long-grain, brown, and basmati rice. Difenoconazole reduced 61.0 %, 35.0 %, and 34.4 % in long-grain, brown, and basmati rice, respectively. After washing with water and vinegar (5 %, *v*/v), acetamiprid was reduced by more than 50.0 % in long-grain rice and 24.4 % in brown rice. Azoxystrobin reduced 65.6 %, 57.7 %, and over 50.4 % in long-grain, brown, and basmati rice, respectively. Difenoconazole reduced 68.4 %, up from 37.5 %, and 53.5 % in long-grain, brown, and basmati rice (*on basmati rice, difenoconazole is below the LOQ).

This study demonstrates that these two different washes without thermal processing can reduce contact and even systemic pesticides (which are more difficult to remove).

Lastly, the results reveal an absence of correlation between chemical structure and the levels of residue removed through washing. Limited comparative studies are available to analyze all 121 pesticides analyzed in the current study. For instance, diazinon exhibited a smaller percentage reduction on long-grain rice than others in the same chemical group (organophosphates), such as fosthiazate and EPN. This observation aligns with the results of Shakoori et al. (2018), who found no correlation between chemical structure and residue removal levels for 41 multi-class pesticides. Additionally, they demonstrated that water solubility does not correlate with residue removal. For instance, oxadiazon and spinosyn D, with water solubility of 0.70 and 0.33 g/mL, respectively, experienced reductions of 88.1 % and 57.6 %, while phosphamidon and monocrotophos, with water solubility of 1.00×10^6

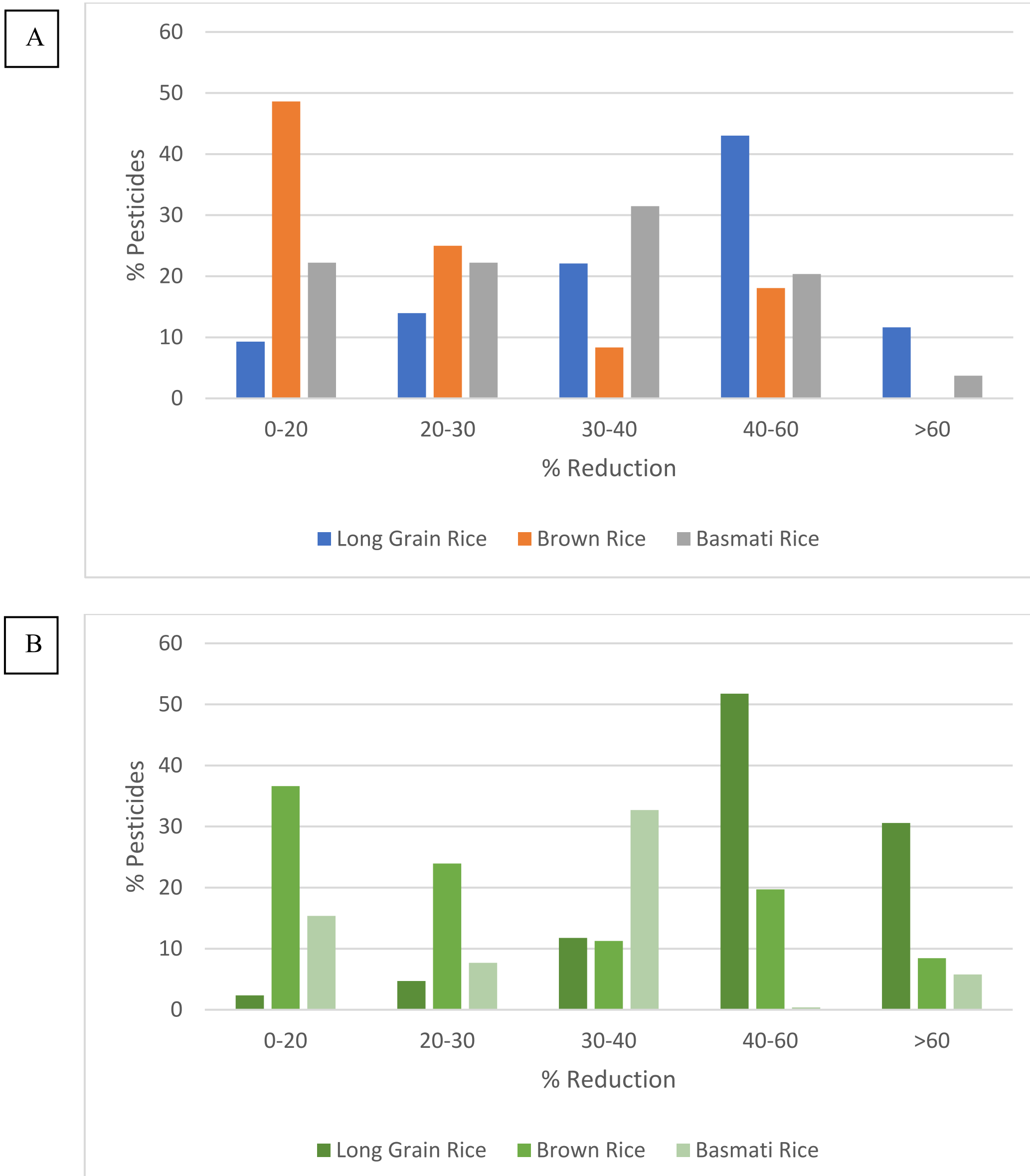

Fig. 3. 3A. Comparison of the effect of washing on the pesticide's reduction in contaminated long-grain rice, brown rice, and basmati rice samples (50 μg/kg); 3B. Comparison of the effect of washing with vinegar (5 %, *v*/v) on the pesticide's reduction in contaminated long-grain rice, brown rice, and basmati rice samples (50 μg/kg). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and 8.18×10^5 g/mL, were reduced by 25.7 % and 26.7 %, respectively (Shakoori et al., 2018). Other studies by Cabras et al. (1997) and Walter et al. (2000) also indicated that water solubility is not a predominant factor in removing pesticide residues through washing (Cabras et al., 1997; Krol et al., 2000).

As mentioned in the introduction, EFSA created a database (versions 2018 and 2022) with processing factors for various foods (fruits, vegetables, and cereal grains), including rice grains. However, in this database, in the 2018 version only six different pesticides are present (fluxapyroxad, imidacloprid, prochloraz, propanil, propiconazole, and tebufenozide); in the 2022 version, they evaluated 10 different pesticides (azoxystrobin, flutriafol, fluxapyroxid, imidacloprid, prochloraz, propanil, propiconazole, pyraclostrobin, spinosad, and tebufenozide). The rice samples were subjected to different processing operations, such as drying, polishing, fermentation, dehulling and germ removal by milling. Therefore, it is not possible to compare the PFs from our study with those from EFSA, as our study focused on washing long-grain, brown, and basmati rice. It should be noted that this study could contribute to the EFSA database, making it much more complete, as we have such a wide range of pesticides.

5. Conclusion

In conclusion, our study revealed that long-grain milled rice exhibited higher pesticide levels, having the fewest pesticides below the LOQ. Basmati rice, with the highest number of pesticides below the LOQ, displayed the lowest levels at both contamination levels. Generally, across all three rice types (long-grain, brown, and basmati), washing with vinegar yielded the best results. Future research could explore alternative washing methods, such as using substitutes like lemon juice or baking soda. However, these tests present complexity, particularly in managing the generated data. Factors such as the degree of pesticide adsorption by rice grains and the solubility of pesticide residues in water significantly influence the removal of pesticide residues during processing.

In fact, many nutritionists advise against washing rice before cooking due to the potential loss of nutrients in the washing process. Nevertheless, in populations where rice constitutes the primary dietary staple, the risk of chronic exposure to pesticide residues may outweigh the nutrient loss during washing, as other foods can fulfill nutritional requirements.

This study contributes substantially to analyzing changes in pesticide residues, providing robust references for the comprehensive risk assessment of pesticides in processed rice.

CRediT authorship contribution statement

Filipa Carreiró: Writing – original draft, Validation, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sílvia Cruz Barros:** Writing – original draft, Visualization, Validation, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Carla Brites:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition. **Patricia Cazón:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Duarte Torres:** Writing – review & editing, Validation, Supervision, Investigation. **Fernando Ramos:** Writing – review & editing, Validation, Supervision, Investigation. **Ana Sanches Silva:** Writing – review & editing, Visualization, Validation, Supervision, Project administration, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2025.102400.

Data availability

Data will be made available on request.

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