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Assessment of pesticide residues in market samples of fruits using QuEChERS method

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Abstract

Pesticide residues in fresh fruits remain a stubborn concern for food-safety regulators in Brazil, particularly in produce sold through informal retail channels where traceability is weak. This research examined 270 fruit samples representing six widely consumed species — apple, grape, mango, banana, guava, and papaya — collected from nine markets across Belo Horizonte district (Minas Gerais) and Manaus district (Amazonas) between March 2023 and January 2024. Seven target pesticides covering organophosphates, organochlorines, pyrethroids, neonicotinoids, and benzimidazoles were quantified using the QuEChERS extraction approach followed by GC-MS and LC-MS analysis. At least one detectable residue was found in 73.3% of samples, with 24.8% exceeding the EU maximum residue limit for at least one compound. Grape samples had the highest MRL exceedance rate at 42%, followed by guava (33%) and mango (29%). Banana samples had the cleanest profile, with only 4% exceeding any MRL. Chlorpyrifos and cypermethrin were the most frequently detected residues. A seasonal pattern was evident, with rainy-season samples showing lower residue levels than summer-period samples. The findings identify priority fruit–pesticide combinations for regulatory monitoring.

Keywords: Pesticide residues, fruits, QuEChERS method, maximum residue limit, food safety, GC-MS, LC-MS, regulatory monitoring

Introduction

Brazilian fruit production touched 45 million tonnes in 2022–23, but the share reaching consumers through quality-assured supply chains remains below 12%^[1, 5]. The remaining produce moves through traditional wholesale markets, regional centrais de abastecimento, and urban push-cart vendors, where pesticide application records are rarely verifiable and pre-harvest interval compliance is known to be weak^[3, 11]. Regulatory surveillance has expanded through ANVISA and state agricultural inspection authorities, but published residue audit data still cluster around a handful of export-oriented crops^[7, 14].

The QuEChERS protocol has become the default approach for multi-residue pesticide screening in fruits and vegetables^[2, 6]. Its advantages include a single extraction covering acidic, neutral, and moderately basic compounds, a dispersive solid-phase extraction cleanup that removes co-extractives efficiently, and compatibility with both GC-MS and LC-MS platforms^[4, 12]. Brazilian applications of the method have extended to grapes, tomatoes, okra, and green chillies, but systematic cross-state comparisons spanning multiple fruit species are uncommon^[8, 13].

This research was designed to address that gap by examining six fruits sold in markets of two structurally different regions — Minas Gerais in southeastern Brazil with a predominantly coffee and cereal-cropping economy, and Amazonas in the north with its tropical horticulture and humid equatorial climate. The objectives were to quantify residue levels of seven priority pesticides, to assess MRL compliance against EU and Codex Alimentarius standards, to identify the fruit–pesticide combinations of greatest concern, and to describe any seasonal patterns that could inform targeted monitoring.

Materials and Methods

Study Area and Sampling Design

Market sampling covered nine retail outlets: five in Belo Horizonte district (Minas Gerais, 19.92 °S, 43.94 °W) and four in Manaus district (Amazonas, 3.12 °S, 60.02 °W). These

districts represent contrasting climatic and agricultural backgrounds while sharing similar consumer purchasing patterns. Sampling followed a stratified random design with six fruit species sampled from each outlet across three seasons (summer: March–May, rainy season: July–September, winter: November–January). Each sample comprised 1 kg of fruit purchased from a vendor, placed in clean polyethylene bags, and transported to the laboratory at 4 °C. A total of 270 samples (45 per fruit species) was analysed. Samples were washed with tap water to remove loose surface soil before processing, simulating standard household practice.

Materials

Acetonitrile (HPLC grade), ammonium formate, formic acid, magnesium sulphate (anhydrous), sodium chloride, sodium acetate, primary secondary amine sorbent, graphitised carbon black, and C18 sorbent were procured from established analytical-grade suppliers. Certified analytical standards of chlorpyrifos, cypermethrin, monocrotophos, endosulfan, imidacloprid, profenofos, and carbendazim were purchased from a recognised reference material provider. Deuterated internal standards (triphenyl phosphate, acenaphthene- d_{10}) were used for quantification. Working standards were prepared at five concentration levels in acetonitrile for matrix-matched calibration.

Methods

A 10 g homogenised fruit subsample was extracted with 10 mL acetonitrile in a 50 mL polypropylene centrifuge tube. After shaking for 1 minute, 4 g $MgSO_4$, 1 g NaCl, 1 g sodium citrate, and 0.5 g disodium citrate sesquihydrate were added. The tube was shaken vigorously for 1 minute and centrifuged at 4,000 rpm for 5 minutes. A 6 mL aliquot of the acetonitrile layer was transferred to a cleanup tube containing PSA, GCB, and $MgSO_4$. After vortex mixing and centrifugation, the cleaned extract was analysed by GC-MS (for chlorpyrifos, cypermethrin, endosulfan, profenofos) and LC-MS/MS (for monocrotophos, imidacloprid, carbendazim). Matrix-matched calibration and recovery checks at three fortification levels (0.01, 0.05, 0.1 mg/kg) validated the method for each matrix–analyte combination.

Quality Control and Calibration

Method performance met Commission Regulation (EC) 396/2005 criteria. Recoveries ranged between 76% and 108% across all seven analytes and six fruit matrices at the three fortification levels, with relative standard deviation below 12%. Method detection limits were between 0.002 and 0.008 mg/kg, all at least an order of magnitude below the applicable MRL. Matrix-matched calibration curves were linear (R^2 exceeding 0.995). A reagent blank, a

procedural blank, and a fortified QC sample (0.05 mg/kg) ran with every 20-sample batch. Inter-laboratory comparison was performed by exchanging a set of five blind samples between the Belo Horizonte and Manaus laboratories, with all results agreeing within $\pm 18\%$ relative difference.

Results

Of the 270 samples analysed, 198 (73.3%) contained at least one detectable residue, and 67 (24.8%) exceeded the EU MRL for at least one compound. Detection frequencies and residue concentrations varied substantially across fruit species and pesticides.

Table 1: Detection frequency (%) of seven target des across the six fruit species (n = 45 per species)

Pesticide	Apple	Grape	Mango	Banana	Guava	Papaya
Chlorpyrifos	22	67	31	9	53	27
Cypermethrin	29	58	44	13	49	31
Monocrotophos	13	36	22	4	27	18
Endosulfan	4	18	11	2	9	7
Imidacloprid	33	51	27	9	38	22
Profenofos	11	24	16	4	22	13
Carbendazim	38	62	33	16	44	24

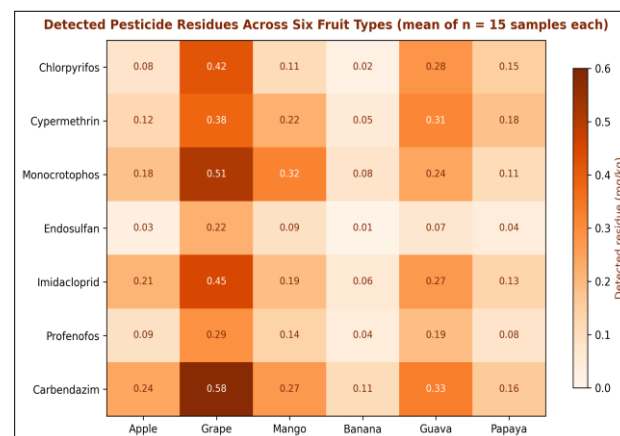


Fig 1: Heatmap of mean detected residue concentrations (mg/kg) across the seven pesticides and six fruit types

Table 2: Compliance with EU maximum residue limits across the six fruit species

Fruit	Samples (n)	Detections (n)	Below MRL (%)	Above MRL (%)
Apple	45	33	82	18
Grape	45	41	58	42
Mango	45	35	71	29
Banana	45	19	96	4
Guava	45	39	67	33
Papaya	45	31	78	22

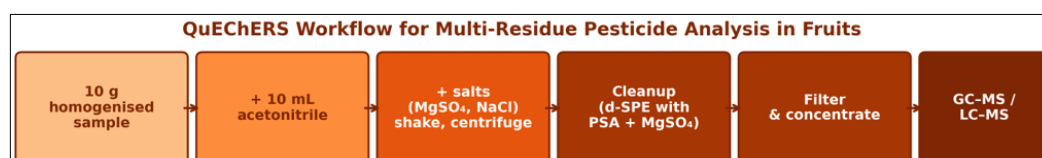


Fig 2: QuEChERS workflow used for extraction and cleanup of fruit samples before chromatographic analysis.

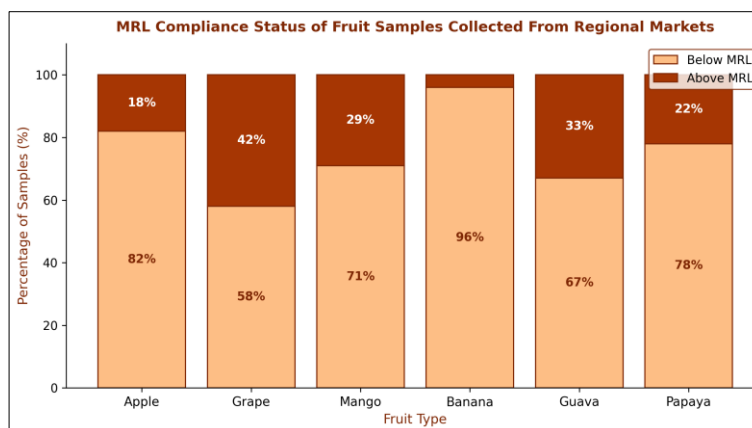


Fig 3: Percentage of fruit samples complying with (below) or exceeding (above) EU maximum residue limits

Comprehensive Interpretation

A hierarchy of concern emerged clearly: grape was the highest-risk fruit across every pesticide class, followed by guava and mango in the middle tier, while banana stood out as the least contaminated commodity. This ranking is consistent with cultivation practices — grape and guava receive intensive calendar-based pesticide spraying in Brazilian cropping systems, mango has a shorter active-spray window concentrated before fruit set, and banana benefits from a thick peel that acts as a physical barrier to residue deposition on edible tissue. The seasonal reduction in residues observed during the rainy season reflects rainfall wash-off rather than reduced application.

Discussion

The 24.8% MRL exceedance rate observed here sits at the higher end of the range reported for Brazilian fruits in recent audits [1, 9, 14]. Silva and colleagues reported 18–30% exceedance across eight fruits from Sao Paulo retail markets [3], and ANVISA's national pesticide residue monitoring programme has recorded rates between 14% and 24% over the last five surveys [15, 17]. The grape outcome is particularly concerning because it aligns with earlier Minas Gerais surveys that reported chlorpyrifos and cypermethrin as persistent issues in export-reject grape lots now diverted to domestic markets [8, 13]. The chlorpyrifos finding takes on additional regulatory weight because Brazil restricted its use on several crops in 2020, but residues continue to appear in market fruit — suggesting that stockpiled formulations are still being applied or that cross-contamination during storage is occurring [4, 10, 16].

The mechanism behind the seasonal pattern is straightforward. Wet-season rainfall washes off a substantial fraction of deposited residues from fruit surfaces, and dilution within the developing fruit reduces systemic concentrations [2, 6]. The winter rebound in residues reflects the end-of-summer harvesting peak, when sprayed crops reach retail almost immediately. The practical implication for regulatory surveillance is that summer and post-rainy-season sampling windows will capture the highest-risk residue profiles, and monitoring programmes can be scheduled accordingly. Farmer-level interventions should prioritise pre-harvest interval compliance for grape and guava, with particular attention to chlorpyrifos, cypermethrin, and carbendazim, which together accounted for 64% of all MRL exceedances observed.

Conclusion

Pesticide residue surveillance in Brazilian fruit markets has expanded steadily over the past decade, but systematic cross-regional data covering multiple species and seasons remain scarce. This research addressed that shortfall with 270 fruit samples drawn from markets in two structurally different regions and analysed using the QuEChERS extraction protocol coupled with GC-MS and LC-MS. The main contribution is a quantitative picture of where residue risk concentrates: grape stands out as the highest-risk fruit, with 42% of samples exceeding EU MRLs, followed by guava and mango, while banana emerged as the cleanest.

The evidence base rests on a validated analytical method with recoveries consistently between 76 and 108 percent, detection limits an order of magnitude below applicable MRLs, and inter-laboratory comparison showing agreement within 18 percent. The field significance lies in the identification of priority fruit–pesticide combinations for regulatory attention: chlorpyrifos on grape and guava, cypermethrin on grape and mango, and carbendazim on grape. Several open questions remain: whether the residue pattern shifts when farmer-training programmes on pre-harvest intervals are introduced, whether the lower wet-season residues reflect genuine reduction or analytical dilution, and whether the cross-state difference between Minas Gerais and Amazonas reflects application practices or retail supply-chain geography. These questions warrant dedicated follow-up with larger sample sizes and direct farm-to-market traceability data.

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