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Pesticide Residues in Marketed Raw Milk in El-Bayda City, Libya: A Cross-Sectional Screening Study and Analytical Quality Framework

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Abstract:

Milk can carry pesticide residues through contaminated feed, water, pasture, or veterinary and agricultural use. This cross-sectional screening study examined 60 raw milk samples marketed in El-Bayda City, Libya (30 cow and 30 goat milk) for organophosphorus, pyrethroid, and organochlorine pesticide residues using QuEChERS extraction followed by GC–MS. Basic milk-quality parameters were also reported. Pesticide residues were detected in 26/60 samples (43.3%): organophosphorus compounds in 12/60 (20.0%), pyrethroids in 8/60 (13.3%), and organochlorines in 6/60 (10.0%). Detection frequency was 46.7% (14/30) in cow milk and 40.0% (12/30) in goat milk; the difference was not statistically significant using the reported 2×2 data (χ^2=0.27, p=0.60). Samples classified as residue-detected had lower reported mean fat and protein values and higher titratable acidity than residue-free samples, but raw data were unavailable and a causal effect cannot be inferred. Four analyte means were supplied (chlorpyrifos, diazinon, cypermethrin, and DDT), but regulatory exceedance was not evaluated because the applicable residue definitions, regulatory source/date, sample-level concentrations, limits of detection and quantification, recoveries, and measurement uncertainty were not provided. The study therefore establishes a local screening signal that justifies validated quantitative surveillance rather than a compliance or health-risk conclusion. A strengthened monitoring framework is proposed, including matrix-matched calibration, recovery verification, traceable MRL selection, and linked farm-to-market sampling.

Keywords: raw milk; pesticide residues; QuEChERS; GC–MS; residue monitoring; maximum residue limits; food safety; El-Bayda; Libya

1. Introduction

Milk is widely consumed and nutritionally important, making chemical-residue monitoring a core food-safety responsibility. Pesticide residues may reach dairy animals through feed, water, pasture, environmental deposition, or direct ectoparasite treatment. Because the milk matrix contains fat, proteins, sugars, and water, both contamination pathways and analytical matrix effects must be considered when interpreting results (Claeys et al., 2013; Bhandari et al., 2022).

Organochlorine pesticides can persist and partition into fat; organophosphorus compounds and pyrethroids can also enter milk under particular agricultural or veterinary exposure conditions. The detection of any residue should not be interpreted in isolation. Compliance depends on the exact analyte or residue definition, commodity, method reporting limit, measurement uncertainty, and legally applicable maximum residue limit (MRL). Codex and national/regional MRL databases must be queried at the time of assessment rather than using generic limits (Codex Alimentarius Commission, 2025; European Commission, 2005).

QuEChERS is widely used for multiresidue extraction, but milk requires matrix-specific validation and appropriate clean-up because of its lipid and protein content. GC–MS can be suited to many volatile and semi-volatile pesticides; highly polar and thermolabile compounds may need complementary LC–MS/MS coverage. Validated methods should demonstrate selectivity, calibration, recovery, repeatability, LOQ, matrix effects, quality-control performance, and measurement uncertainty in the milk matrix (Anastassiades et al., 2003; Golge et al., 2018; European Union Reference Laboratories, 2026).

The present study aimed to describe pesticide-residue detection frequency in raw cow and goat milk marketed in El-Bayda City, report supplied milk-quality findings, and establish a defensible interpretation and reporting framework for future quantitative surveillance.

2. Materials and Methods

2.1 Study design and sampling: The study was designed as a cross-sectional market survey. Sixty raw milk samples were collected over six months: 30 cow and 30 goat milk. Samples were reportedly obtained from dairy farms, collection centres, retail shops, supermarkets, and traditional markets. Approximately 500 mL was collected into amber glass bottles, transported at 4 ± 1 °C, and analysed within 24 h. Before publication, the dataset should include sampling dates, source category, farm/lot code, milk species, packaging status, storage history, location, and a full chain-of-custody record.

2.2 Physicochemical quality measurements: Fat, protein, pH, and titratable acidity were measured using the stated Gerber, Kjeldahl, calibrated pH-meter, and titration procedures. The final protocol must give the exact AOAC method numbers, acid concentration and butyrometer conditions, Kjeldahl digestion/distillation details, pH meter calibration acceptance criteria, titration endpoint, analysts, duplicates, and quality-control results. ISO 8968-1 is an appropriate reference for Kjeldahl nitrogen/protein determination in milk.

2.3 QuEChERS extraction and GC–MS: The intended target list included organochlorines (DDT/DDE, aldrin, dieldrin, lindane, endosulfan), organophosphorus compounds (chlorpyrifos, diazinon, malathion, dimethoate), and pyrethroids (cypermethrin, deltamethrin, permethrin). The supplied method specifies a DB-5MS column, EI ionization, and SIM acquisition. To be reproducible, it must also state test portion mass, acetonitrile composition, salt and sorbent quantities, extraction/centrifugation conditions, internal standards, detailed oven programme, target/qualifier ions,

retention windows, matrix-matched calibration, blank criteria, and all validation results. GC–MS should be complemented or justified for analytes outside its validated scope.

2.4 Validation and regulatory comparison: Quantitative pesticide data must be validated in milk according to an applicable current quality-control guideline. At minimum, report analyte-specific calibration, LOQ, recovery at relevant fortification levels, precision, identification criteria, matrix effect, procedural blanks, ongoing QC, and expanded uncertainty. MRL comparisons should use the current Codex or applicable national/regional database for the exact residue definition and milk commodity. The source dataset did not supply these elements; consequently, this revision does not report MRL exceedance.

2.5 Statistical analysis: Descriptive frequencies and Wilson 95% confidence intervals were calculated for reported detection proportions. The cow-versus-goat 2×2 table was re-evaluated with Pearson χ^2. Supplied t-tests and correlation coefficients were not retained because their values conflict with the reported summary statistics or cannot be evaluated without raw observations and a defined total-residue metric. Future models should specify whether concentration is individual-analyte, summed residue burden, or another pre-specified metric, and control for milk species, farm/source, season, storage time, and relevant quality variables.

3. Results

3.1 Detection frequency by pesticide group: Pesticide residues were reported in 26/60 samples (43.3%). The supplied group frequencies were 12/60 for organophosphorus compounds (20.0%; 95% CI 11.9–31.8%), 8/60 for pyrethroids (13.3%; 95% CI 6.9–24.2%), and 6/60 for organochlorines (10.0%; 95% CI 4.7–20.2%) (Table 1; Figure 1). The group counts sum to 26 and are displayed as mutually exclusive classifications. This assumption must be verified from the analytical data because a sample may contain multiple pesticide residues.

Pesticide group	Positive samples	Percentage	95% Wilson CI
Organophosphorus	12/60	20.0%	11.8–31.8%
Pyrethroids	8/60	13.3%	6.9–24.2%
Organochlorines	6/60	10.0%	4.7–20.1%

Table 1. Reported pesticide-group detection frequency. No χ^2 test is displayed because group mutual exclusivity/co-occurrence was not documented.

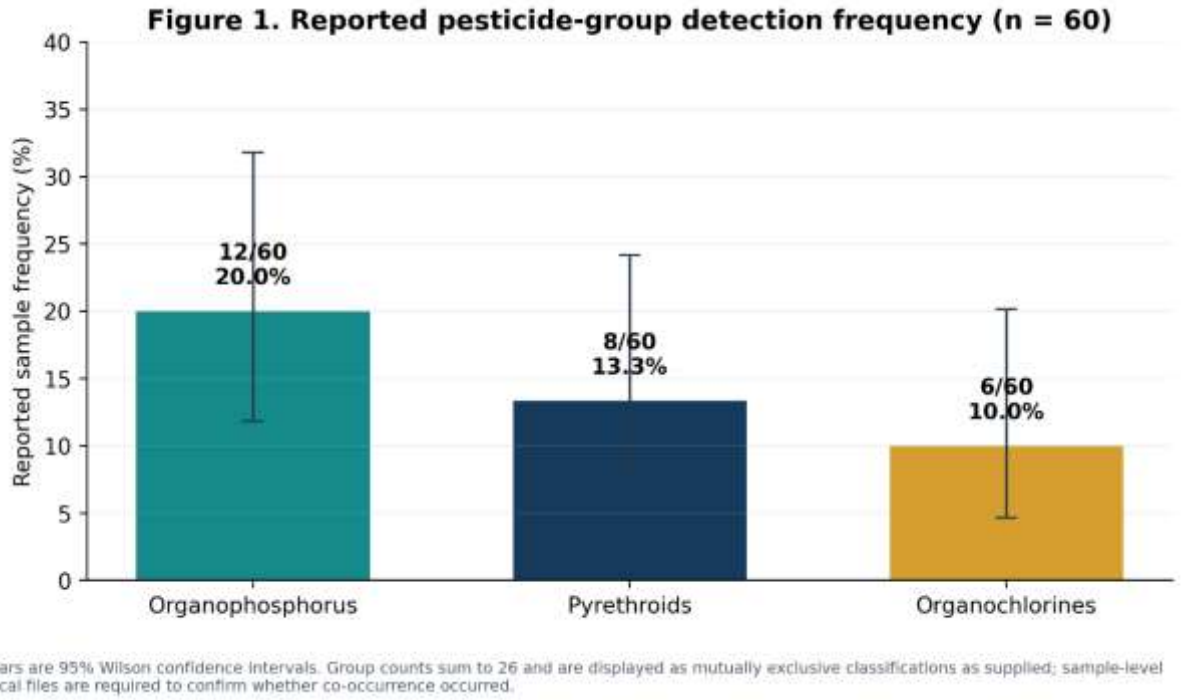

Figure 1. Reported pesticide-group detection frequency.

3.2 Comparison by milk species: Residues were reported in 14/30 cow-milk samples (46.7%; 95% CI 30.2–63.9%) and 12/30 goat-milk samples (40.0%; 95% CI 24.6–57.5%) (Table 2; Figure 2). The reported counts give Pearson $\chi^2(1)=0.27$ and $p=0.60$, indicating no statistically demonstrable difference between milk species in this sample. The original $\chi^2=5.45$, $p<0.01$ entry is inconsistent with the stated counts and has been corrected.

Milk type	Positive samples	Percentage	95% Wilson CI	Corrected comparison
Cow milk	14/30	46.7%	30.2–63.9%	$\chi^2(1)=0.27$; $p=0.602$
Goat milk	12/30	40.0%	24.6–57.5%	No significant difference from counts shown.

Table 2. Comparison of reported detection frequency by milk species. The χ^2 was recalculated from the displayed 2×2 data.

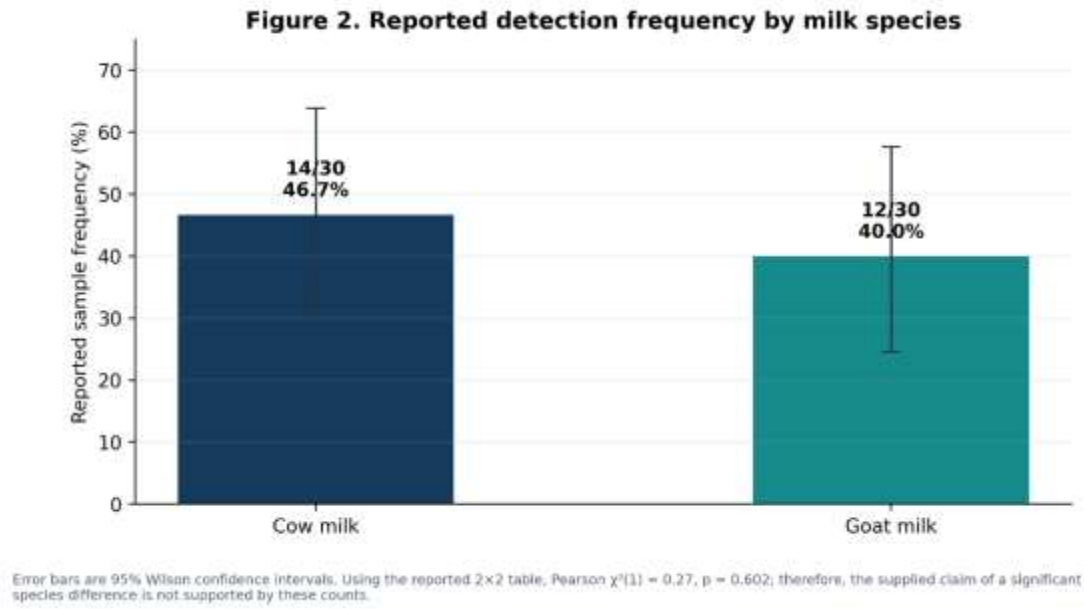

Figure 2. Reported detection frequency by milk species.

3.3 Reported milk-quality values: Milk classified as residue-detected had lower reported mean fat (3.45 ± 0.21% vs 3.78 ± 0.25%) and protein (3.12 ± 0.18% vs 3.40 ± 0.20%) and higher titratable acidity (0.19 ± 0.02% vs 0.17 ± 0.01%) than residue-free milk. Reported pH was 6.55 ± 0.10 and 6.68 ± 0.12, respectively (Table 3; Figure 3). These are descriptive group differences only. The source t values and p values were not retained because they do not match the supplied means, standard deviations, and group sizes under a conventional independent-samples calculation, and cross-sectional grouping cannot establish a pesticide-caused effect.

Parameter	Residue-detected milk (n=26)	Residue-free milk (n=34)	Interpretation
Fat (%)	3.45 ± 0.21	3.78 ± 0.25	Descriptive comparison; original p value not retained.
Protein (%)	3.12 ± 0.18	3.40 ± 0.20	Descriptive comparison; original p value not retained.
pH	6.55 ± 0.10	6.68 ± 0.12	Descriptive comparison; original p value not retained.
Acidity (% LA)	0.19 ± 0.02	0.17 ± 0.01	Descriptive comparison; original p value not retained.

Table 3. Reported physicochemical quality values. Inferential tests are withheld pending raw data verification.

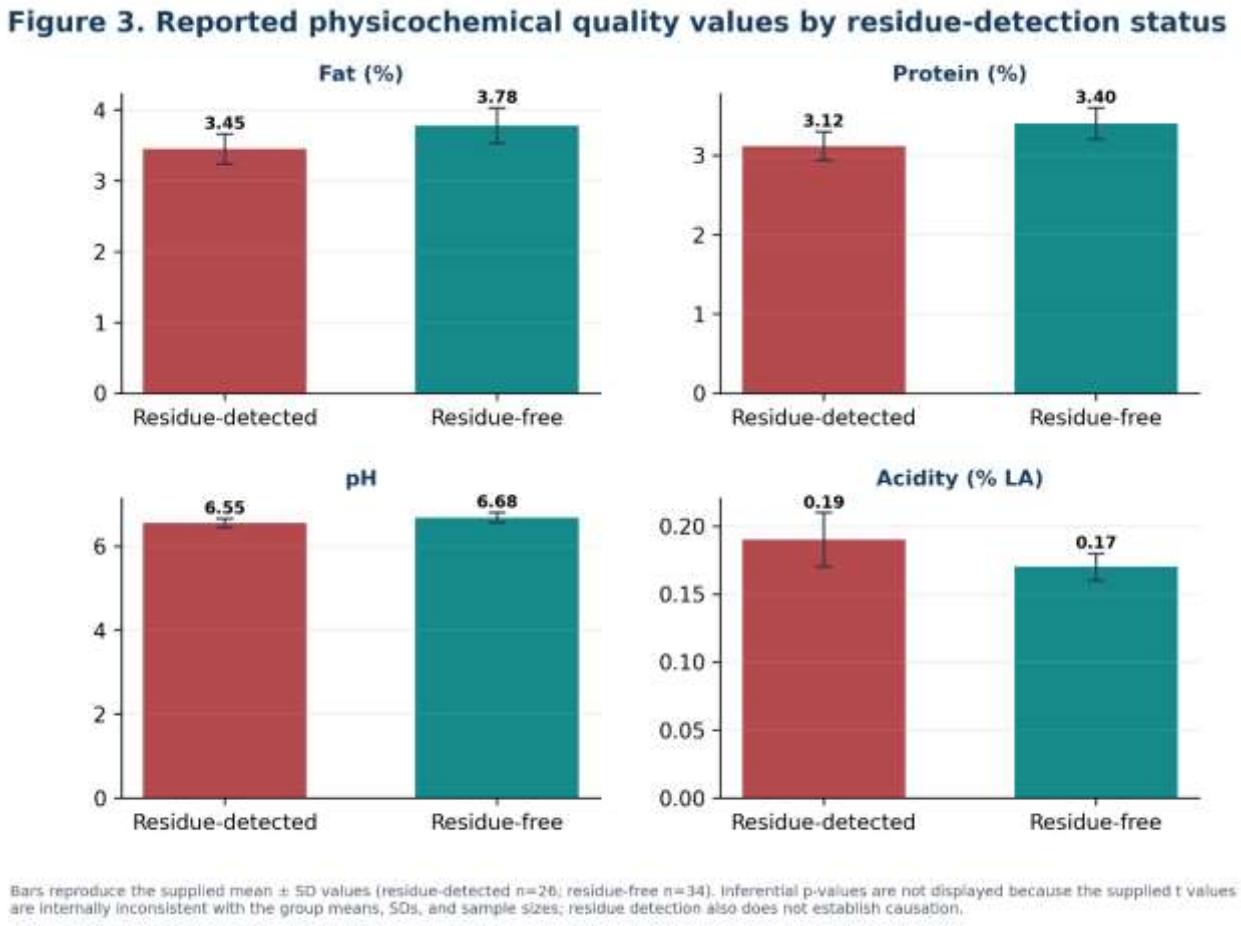

Figure 3. Reported physicochemical quality values by residue-detection status.

3.4 Reported analyte concentrations: The supplied data report means ± SD concentrations of chlorpyrifos (0.045 ± 0.012 mg/kg), diazinon (0.038 ± 0.010 mg/kg), cypermethrin (0.020 ± 0.006 mg/kg), and DDT (0.015 ± 0.005 mg/kg) (Table 4; Figure 4). The denominator for these means—whether all samples or only positive samples—was not specified. MRL lines and percentage-exceedance claims are not reported in this revision because the regulatory source, exact residue definition, date, and sample-level analytical data were not documented. In addition, the supplied DDT exceedance percentage (15% of 60 = 9 samples) is incompatible with the reported organochlorine group count (6/60).

Analyte	Reported mean ± SD (mg/kg)	Compliance interpretation
Chlorpyrifos	0.045 ± 0.012	Not assessed: verify residue definition, MRL source/date, individual result, LOQ, recovery, and uncertainty.
Diazinon	0.038 ± 0.010	Not assessed: verify residue definition, MRL source/date, individual result, LOQ, recovery, and uncertainty.
Cypermethrin	0.020 ± 0.006	Not assessed: verify residue definition, MRL source/date, individual result, LOQ, recovery, and uncertainty.
DDT	0.015 ± 0.005	Not assessed: verify residue definition, MRL source/date, individual result, LOQ, recovery, and uncertainty.

Table 4. Reported analyte concentrations. Compliance cannot be assessed from the supplied summary data.

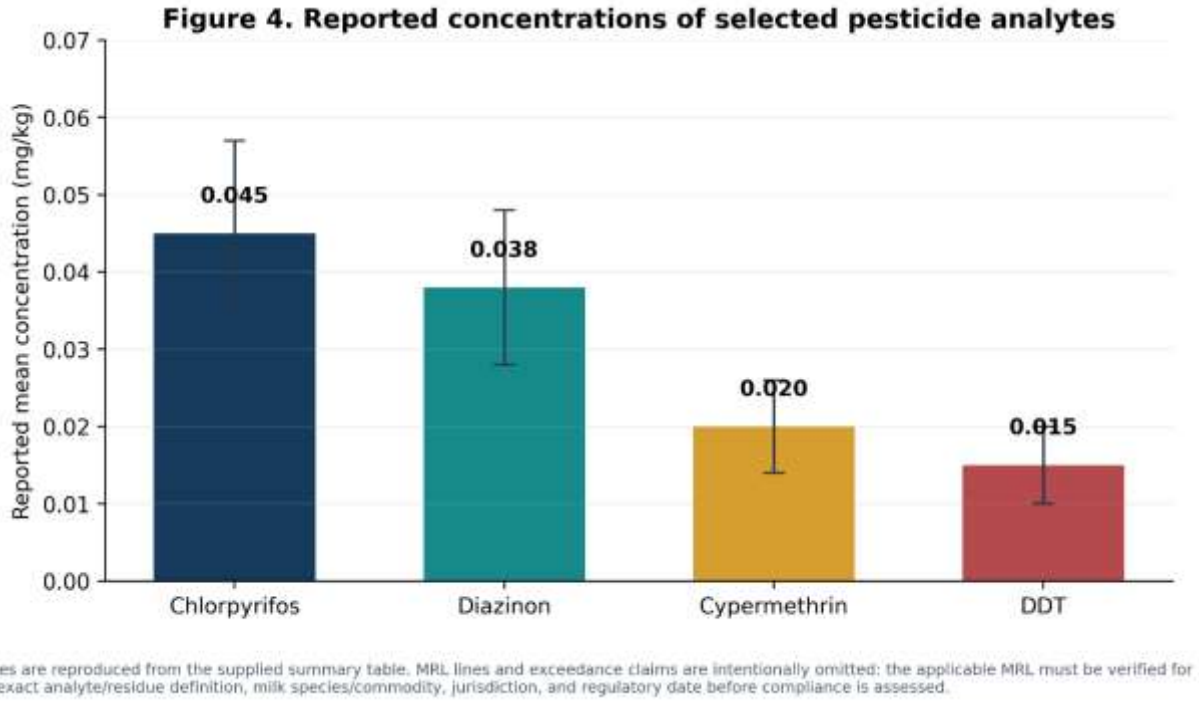

Figure 4. Reported concentrations of selected pesticide analytes.

3.5 Interpretation for surveillance: The aggregate dataset indicates a need for a documented milk-residue surveillance system in El-Bayda. It does not yet establish regulatory non-compliance, consumer exposure, or a causal mechanism for changes in milk composition. Figure 5 presents the traceability and analytical-quality chain required for a future defensible monitoring programme.

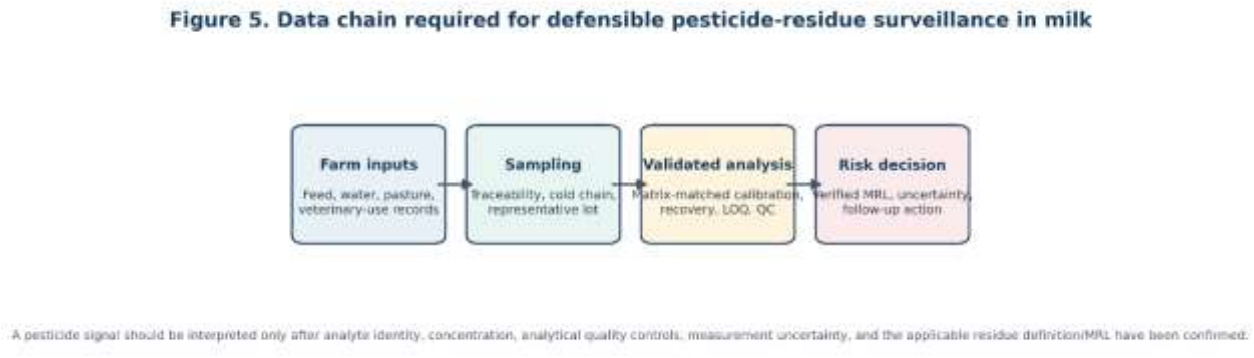

Figure 5. Data chain required for defensible pesticide-residue surveillance in milk.

4. Discussion

The 43.3% reported detection frequency indicates that residue monitoring merits continued attention in the local milk supply. However, detection frequency is not equivalent to health risk. The toxicological and regulatory interpretation of a measured residue depends on its quantified concentration, the validated reporting limit, the uncertainty of measurement, the exact residue definition, and the current applicable MRL. This distinction is particularly important when more than one regulatory framework may be relevant (Codex Alimentarius Commission, 2025; European Commission, 2005).

Organophosphorus, pyrethroid, and organochlorine results should be discussed as analytical classes only after confirming that each category is mutually exclusive or, alternatively, reporting co-occurrence at the sample level. The count totals in the source data could represent a single predominant residue per sample, but that must be declared. A sample-by-analyte detection matrix would allow the study to describe mixtures and to identify whether residues originate from shared feed, water, pasture, or veterinary-use pathways.

The observed cow-versus-goat difference was small and not statistically significant when recalculated from the supplied counts. Differences in species exposure may still exist but require a study powered to evaluate them and detailed information on feed source, grazing system, housing, season, and farm. The statement that cow milk is more contaminated should therefore be avoided in the current paper.

The source data showed descriptive differences in fat, protein, pH, and acidity between residue-detected and residue-free groups. These values may be influenced by species, breed, feed, lactation stage, season, sample age, storage, and pre-existing microbial activity. They cannot demonstrate that pesticide residues themselves caused reduced nutritional quality. If individual concentration data become available, an adjusted regression model with pre-specified confounders may test associations; mechanistic causal claims require a different design.

In the final analytical method, milk-specific matrix validation is critical. Lipids and proteins can suppress or enhance analyte response and require matrix-matched calibration and suitable clean-up. The method

validation package should be filed with the manuscript or supplied as supplementary information. Recent raw-milk multiresidue methods demonstrate that QuEChERS-based workflows can be effective when recovery, precision, LOQ, and matrix effect are actually shown for the intended analyte panel and matrix (Tripathy et al., 2019; Wu et al., 2022).

Practical preventive action should connect farm and retail controls: documented pesticide use, feed-source verification, water management, veterinary treatment records, withdrawal periods, hygienic milking, refrigerated transport, retail storage, and traceable sample codes. Positive findings should trigger a targeted investigation, not merely disposal or broad attribution.

5. Conclusions

This survey reports pesticide-residue detection in 26 of 60 raw milk samples marketed in El-Bayda City, with comparable detection frequencies in cow and goat milk. The supplied group-level data suggest that organophosphorus-class detections were most frequent, followed by pyrethroid and organochlorine detections.

Yet the available evidence supports a screening conclusion only. It does not support the original MRL-exceedance claims, a statistically significant cow-versus-goat difference, the supplied t-test/correlation claims, or causal effects of pesticides on milk composition. A future publication should add sample-level concentrations, validated QC data, exact regulatory references, traceability variables, and an auditable statistical analysis. This will allow the study to progress from a useful local screening signal to a robust food-safety assessment.

References

Anastassiades, M., Lehotay, S. J., Štajnbaher, D., & Schenck, F. J. (2003). Fast and easy multiresidue method employing acetonitrile extraction/partitioning and dispersive solid-phase extraction for the determination of pesticide residues in foods. Journal of AOAC International, 86(2), 412–431. https://doi.org/10.1093/jaoac/86.2.412

Bhandari, G., Atreya, K., Scheepers, P. T. J., & Geissen, V. (2022). Pesticide residues in food and their implications for human health: A review. Environmental Research, 204, 112320. https://doi.org/10.1016/j.envres.2021.112320

Claeys, W. L., Cardoen, S., Daube, G., et al. (2013). Raw or heated cow milk consumption: Review of risks and benefits. Food Control, 31(1), 251–262. https://doi.org/10.1016/j.foodcont.2012.09.035

Codex Alimentarius Commission. (2025). Codex pesticides residues in food online database. https://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/en/

European Commission. (2005). Regulation (EC) No 396/2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin. https://eur-lex.europa.eu/eli/reg/2005/396/oj

European Food Safety Authority. (2025). The 2023 European Union report on pesticide residues in food. EFSA Journal, 23(5), e9398. https://doi.org/10.2903/j.efsa.2025.9398

European Union Reference Laboratories for Pesticide Residues. (2026). Analytical quality control and method validation procedures for pesticide residues analysis in food and feed (SANTE/11312/2021 v2026). https://eurl-pesticides.eu/docs/public/tmplt_article.asp?CntID=727

Golge, O., Koluman, A., & Kabak, B. (2018). Validation of a modified QuEChERS method for the determination of 167 pesticides in milk and milk products by LC-MS/MS. Food Analytical Methods, 11, 1122–1138. https://doi.org/10.1007/s12161-017-1066-0

International Organization for Standardization. (2014). ISO 8968-1: Milk and milk products—Determination of nitrogen content—Part 1: Kjeldahl principle and crude protein calculation. https://www.iso.org/standard/61020.html

Tripathy, V., Sharma, K. K., Yadav, R., Devi, S., Tayade, A., Sharma, K., Shakil, N. A., Pandey, P., Singh, G., Patel, A. N., & Gautam, R. (2019). Development, validation of QuEChERS-based method for simultaneous determination of multiclass pesticide residue in milk, and evaluation of the matrix effect. Journal of Environmental Science and Health, Part B, 54(5), 394–406. https://doi.org/10.1080/03601234.2019.1574169

Wu, X., Tong, K., Yu, C., Hou, S., Xie, Y., Fan, C., Chen, H., Lu, M., & Wang, W. (2022). Development of a high-throughput screening analysis for 195 pesticides in raw milk by modified QuEChERS sample preparation and LC-Q-TOF/MS. Separations, 9(4), 98. https://doi.org/10.3390/separations9040098

Zhang, Y., Liu, X., & Wang, S. (2012). Determination of pesticide residues in milk using a QuEChERS-based method developed by response surface methodology. Food Chemistry, 135(3), 1498–1504. https://doi.org/10.1016/j.foodchem.2012.05.052

Appendix A. Essential Analytical and Data Corrections

The original text included numerical claims that could not all be sustained by the supplied tables. This appendix records the corrections necessary before journal submission. It is intended to improve reproducibility, not to discard the value of the local surveillance study.

Issue	Correction required before submission
MRL compliance	Retrieve MRL/EMRL at the time of analysis for the exact analyte/residue definition and milk commodity from Codex or the applicable national/regional database; report the database date and unit.
Raw GC–MS data	Provide sample code, chromatogram, retention time, qualifier/quantifier ions and ratios, calibration, matrix blank, recovery, LOQ, precision, uncertainty, and concentration per sample.
Group counts	State whether the 12, 8, and 6 class counts are mutually exclusive. If not, report multiple-residue co-occurrence by sample.
Statistics	Re-run tests from individual values; specify total-residue metric for correlation/regression; report effect sizes and exact p values.
Concentration table	State whether means include all samples or detections only. Resolve the inconsistency between 15% DDT exceedance (9/60) and 6/60 organochlorine detections.

Table A1. Required corrections for an auditable pesticide-residue study.

Appendix B. Editable Charts and Reference Links

Milk_pesticide_data_editable_charts_and_references.xlsx contains the data entered from the supplied tables, native editable Excel charts, reference links, and integrity notes. Word charts are high-resolution images generated from those data; modify the Excel values and charts when verified laboratory data become available.