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Unified method for multiresidue pesticide analysis in corn and sediment

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Abstract: Due to Brazil's significant role as a major global corn producer and the impact of pesticide accumulation in sediments on the health of aquatic ecosystems, this study addresses the need for a simplified method to assess pesticide residues in both matrices, corn and sediments. A modified QuEChERS method combined with gas chromatography-mass spectrometry, was validated for the analysis of seven common pesticides in Paraná State, Brazil: desisopropylatrazine (DIA), deethylatrazine (DEA), diazinon, methyl parathion, pirimiphos methyl, malathion and pirimiphos ethyl. Following the guidelines of INMETRO and SANTE 12682/2019, the method achieved quantification limits (8.40–15.00 μg kg^{-1} for sediment and 8.80–13.00 μg kg^{-1} for corn) below the maximum residue limits (M*RL*) established by EC 396/2005 for corn. The procedure demonstrated excellent linearity ($R^2 > 0.99$), recovery rates (70–120 %) and precision (relative standard deviations ≤ 20 %). This validated method provides a unified, reliable, and sensitive approach for the multiresidue analysis of pesticides in corn and sediment, which is beneficial for environmental monitoring and food safety, particularly in essential agricultural regions like Brazil.

Keywords: agricultural impact; food; environmental matrices; detection and quantification; environmental monitoring.

INTRODUCTION

Pesticide contamination of food and water resources poses a significant threat to human health and ecosystems integrity.[1–3] Researchers have extensively studied pesticide residues in various food products and environmental matrices.[4] These residues can persist in harvested crops, such as corn grains, and can also contaminate environmental matrices, like sediments.[5,6] Sediments play a crucial role in the study of pesticide residues, as they act as reservoirs, accumulate contaminants

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transported from agricultural areas via runoff or leaching.[4–6] This issue is particularly concerning in regions with intensive agricultural activity.[7,8]

Corn production in Brazil has experienced significant growth, making the country the third-largest producer of this cereal in the world.[9,10] Within Brazil, the state of Paraná ranks as the second-largest agricultural producer, accounting for approximately 13 % of the nation's total corn and soybean production, based on the three-year average from 2021 to 2023.[9,11] This increase in crop production has led to the extensive use of pesticides, primarily herbicides, fungicides and insecticides.[8,11]

Many pesticides are classified as persistent organic pollutants due to their prolonged presence in the environment and the potential risks they pose to human health and ecosystems.[6,7,10] Several commonly used pesticides in corn and soybean cultivation, including atrazine, diazinon, malathion, ethyl parathion, pirimiphos ethyl, methyl parathion and pirimiphos methyl, fall into this category.[8] The classification of these substances as chronic residues by Brazil's National Health Surveillance Agency (ANVISA) underscores the urgent need for strict monitoring and management practices to mitigate risks to food safety and environmental health.[8,12]

Current methods for analyzing pesticide residues often require separate, time-consuming procedures for different matrices.[4,13] QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe), developed by Anastassiades *et al*. in 2003,[14] is an accessible, cost-effective extraction method with reduced solvent consumption, widely used for extracting organic and inorganic residues from various matrices.[4,14] Its consistent application in food matrices has led to official validation by AOAC International and the European Committee for Standardization (CEN), underscoring its reliability for detecting pesticide residues in fruits and vegetables.[13–15]

In recent years, the QuEChERS approach has been the focus of extensive research aimed at evaluating a variety of food and environmental samples.[4] Numerous studies in Brazil have explored the application of QuEChERS for detecting pesticide residues in various materials, including rice,[3] soy-based beverages,[16] water,[17] crop plants,[18] soil[19] and sediments.[6] These studies underscore the importance of this methodology in ensuring food safety[2,3,13,16] and promoting environmental conservation.[6,17–19] However, there is a growing demand for more efficient and compatible methods capable of simultaneously assessing pesticide contamination in both food and environmental samples.[4,10,15,20]

Although some studies have utilized QuEChERS methods to analyze individual matrices, such as food and environmental samples,[4] the development and validation of a unified approach applicable to both corn and sediments remain limited.[6,15,18] Establishing a standardized analytical method is crucial, as it enhance the efficiency of monitoring of these matrices.[6,18]

The type of matrix used significantly influences the extraction efficiency of the QuEChERS method.[6,15,18] In environmental matrices, such as soil and sediment, factors like organic matter and clay content can influence extraction performance.[6,19] In food matrices, extraction efficiency may be impacted by water content, as well as the presence of fats and sugars.[2,15,18,21] While matrix-matched calibrations are often recommended for various methodologies,[6,15] a more straightforward approach can be applied to complex matrices.[18] This involves using a single level standard addition in the sample (SLSAS),[18] which is based on the standard addition method outlined in official guidelines (SANTE 12682/2019).[22] To address these challenges, it is essential to continue applying the QuEChERS approach while enhancing its validation across different contexts (matrices and detection techniques). This will enable more efficient analysis and monitoring of pesticide residues.[1,4]

This research aims to develop and validate a modified QuEChERS method combined with gas chromatography-mass spectrometry for the analysis of multiple pesticide residues in corn and sediment samples from the Paraná State in Brazil. The study addresses a critical gap in current analytical practices, which often depend on separate methods tailored to each matrix.[1,4,18] It underscores the urgent need for a reliable and sensitive technique capable of simultaneously quantifying multiple pesticide residues in both food and environmental matrices. By integrating this approach, the study seeks to enhance monitoring capabilities in agricultural regions.

EXPERIMENTAL

Reagents

High-performance liquid chromatography (HPLC)-grade acetonitrile (MeCN) and the sorbents, primary secondary amine (PSA) and octadecylsilane (C18) were acquired from Supelco (Germany). Ethyl acetate (EtOAc) and dichloromethane (DCM) also HPLC grade, were acquired from Honeywell (USA). Glacial acetic acid (HAc) was sourced from Dinâmica (Brazil), heptahydrated magnesium sulfate from Vetec (Brazil), and sodium chloride from Synth (Brazil). Ultrapure water was acquired using a Purelab® ultra-purifier (Options-Q). All pesticide standards were obtained from Sigma–Aldrich with a purity of > 96.7 %. Individual pesticide standard solutions: desisopropylatrazine (DIA), deethylatrazine (DEA), atrazine-D5 (ATZ-D5), diazinon, methyl parathion, pirimiphos methyl, malathion and pirimiphos ethyl were prepared in EtOAc at a concentration of 1000 mg L^{-1}. An intermediate working standard was then prepared in MeCN at 10 mg L^{-1}. The solutions used for analyte addition to the samples were formulated from the separate intermediate solutions, creating a mixed standard in MeCN. The mixed standards were prepared at concentrations of 350, 450, 550, 650, 750, 850, 950 and 1050 μg L^{-1}. All solutions were stored at –18 °C until used.

According to recent studies, atrazine (ATZ) exhibits high water solubility, low sediment solubility and rapid degradation, forming its metabolites, as DIA and DEA under environmental conditions. This degradation is largely influenced by the high organic matter content and humidity associated with sediments, which promote increased microbial activity.[23-26] These characteristics influence the detection and analysis of atrazine in environmental studies, shifting

the focus toward its more persistent metabolites. ATZ-D5 was selected as the internal standard, while ATZ was excluded due to the unavailability of the standard in the laboratory.

To monitor the primary pesticides used in corn cultivation, analyses were conducted on the following compounds: DIA, DEA, diazinon and methyl parathion. Additionally, to assess the methodology's effectiveness in sediment analysis, the following pesticides were selected: DIA, DEA, diazinon, malathion and ethyl parathion. The latter two are particularly significant due to their higher affinity for sediments (as organophosphates) and their widespread use in large-scale crops such as soybeans.[27,28]

Sampling and localization

The corn grains samples were obtained from traditional cultivation, in the municipalities of São Miguel do Iguaçu (M1, M7, M8 and M9); Missal (M2, M3, M4 and M6); Foz do Iguaçu (M5, M10), in the Parana State, Brazil. However, sample M5 was sourced from a certified organic cultivation. In total, 10 different samples were collected. All methodology validation tests were conducted using sample M10. The samples were harvested between January and February 2021, with the grains in the milky stage, the optimal phase for fresh consumption (in natura). The collected samples correspond to the first annual harvest in the region.[9]

Quartering was employed for sample collection.[29] At each collection point, the grains were mixed separately in a clean container to create a homogeneous sample. The mixed sample was then divided into four equal parts. Two opposite quadrants were discarded, while the remaining two quarters were combined to form a composite sample. Small portions were taken from this composite until each sample reached a weight of 500 g. These 500 g samples were placed in airtight plastic bags and stored at –18 °C until analysis. While still frozen, the samples were crushed for 1 min using a Hamilton Beach® food processor.

Sediment samples were collected in the Tamanduá River basin, which supplies part of the municipality of Foz do Iguaçu, in the Parana State of Brazil. The five sediment collection points were in the Dourado stream; with points 1 and 2 (P1, P2) corresponded to the stream's springs, point 3 (P3) was situated upstream of the former municipal landfill, point 4 (P4) was downstream of the former landfill area and point 5 (P5) was at the intersection with the Tamanduá River (for details, see Supplementary material to this paper). The collected samples correspond to those cited in Da Silva *et al*.[30] At each collection point, 500 g of composite samples were obtained each consisting of a mixture of 16 subsamples.[27,29] After collection, the samples were placed in stainless steel trays, dried at 40 °C in a Limatec® (Brazil) forced-air oven, for 24 h and then macerated and sieved through a 28 mesh.[28] All methodology validation tests were conducted using sample P3. The maps displaying the locations of the collection points for both matrices are provided in Figs. S-1 and S-2 of the Supplementary material.

QuEChERS Method

The methodology is based on the QuEChERS approach developed by Anastassiades *et al*.,[14] with modifications to enhance its applicability for both corn and sediment matrices. One of the simplest strategies involves reducing the sample size.[14] Additionally, acidifying the extraction solvent with acetic acid (HAc) helps prevent pesticide hydrolysis in a basic pH environment.[15] Increasing both the duration and speed of the mixing and separation stages can further improve extraction efficiency and enhance phase separation during these processes.[14] Moreover, using a larger quantity of salts and adsorbents, along with the incorporation of a C18 adsorbent during the cleaning stage can significantly enhance the method's effectiveness.[15] All these strategies were implemented to improve the overall efficiency of the process.

Similar analysis methodologies have been proposed for the matrices analyzed, specifically corn[15] and sediments.[6] These studies have confirmed the existence of a matrix effect in the validation of pesticide quantification methods. In both cases, matrix-matched calibrations were employed.[6,15,22]

The use of the matrix-matched calibration is advantageous, as it enhances signal detection during the analysis stage, particularly in gas chromatography–mass spectrometry (GC––MS).[2,6,15,31] When validating methods that involve complex matrices, and a blank or reference material is unavailable to prepare matrix-matched standard solutions, the standard addition approach can be employed.[22] To address this limitation , Viera *et al*.[18] proposed the single level standard addition in the sample (SLSAS) technique for analyzing pesticide residues in crops. This method enables validation to be carried out on a sample without requiring a specific target sample.[18] The same approach was applied in the methodology validation stages using samples M10 for corn and P3 for sediments.

To construct the analytical curve, 5.00 g of corn grains or sediment samples were weighted in triplicate in a 50 mL polypropylene centrifuge tube. Subsequently, 9.0 mL of 1 vol. % MeCN acidified with HAc was added, followed by 1.0 mL of a standard solution containing the analytes in MeCN, resulting in a total solvent volume of 10 mL. The mixture was then homogenized for one minute using a Phoenix® (Brazil) vortex.

Subsequently, 4.00 g of $MgSO_4$ and 1.00 g of NaCl were added to the 50 mL polypropylene tube, followed by vortex mixing for 1 min and centrifugation at 4000 rpm for 15 min. After centrifugation, 2.0 mL of the supernatant was removed and transferred to a 15 mL polypropylene tube, where 300 mg of $MgSO_4$, 50 mg of PSA and 100 mg of C18 were added. The mixture was vortexed for 30 s and centrifuged at 4000 rpm for 15 min. Next, 1 mL aliquot of the supernatant was extracted and evaporated under a nitrogen stream using an evaporator. The dried residue was reconstituted in 400 μL of DCM for injection into the GC–MS system.

GC–MS Analysis

Chromatographic analyses were performed using a TRACE 1300 GC system equipped with a TriPlus RSH automatic sampler and coupled to an ISQ single quadrupole MS mass analyzer, all from Thermo Scientific (USA). The compounds were separated in a TR-5MS capillary column (30 m×0.25 mm×0.25 mm), also from Thermo Scientific (USA), with a stationary phase composed of 5 % phenyl polysilphenylene–siloxane. The injector temperature was set at 250 °C and the samples were injected (1 μL) in splitless mode. The temperature program used was from 50 °C (holding for 1 min) to 180 °C at a rate of 25 °C min^{-1} and increased to 280 °C at 3 ºC min^{-1}. The carrier gas used was helium, of chromatographic purity, with a constant flow of 0.500 mL min^{-1}. Furthermore, in the mass spectrometry system, the ion source temperature was set at 280 °C and the transfer line temperature was set at 270 °C. The system was operated in the selective ion monitoring (SIM) mode using one target and three qualifier ions, as listed in Table I. Data processing was carried out using Thermo Xcalibur software, version 2.2, Thermo Scientific (USA).

TABLE I. Retention time, corresponding ions, CAS, molecular formula and log K_{ow} of the pesticides analyzed

Pesticide	Retention time, min	Ions (*m*/*z*)	CAS[a]	Formula[a]	log K_{ow}[a]
DIA	12.70	173, 158, 145	1007-28-9	$C_5H_8ClN_5$	–
DEA	13.53	172, 174, 187	6190-65-4	$C_6H_{10}ClN_5$	1.51
ATZ-D5	15.10	205, 178, 220	163165-75-1	$C_8H_{14}ClN_5$	–

TABLE I. Continued

Pesticide	Retention time, min	Ions (*m*/*z*)	CAS[a]	Formula[a]	log K_{ow}[a]
Diazinon	17.87	179,137, 152	333-41-5	$C_{12}H_{21}N_2O_3PS$	3.81
Methyl paration	18.85	109, 125, 263	298-00-0	$C_8H_{10}NO_5PS$	2.86
Pirimiphos methyl	20.92	290, 276, 305	29232-93-7	$C_{11}H_{20}N_3O_3PS$	4.12
Malathion	22.01	173, 125, 93	121-75-5	$C_{10}H_{19}O_6PS_2$	2.36
Pirimiphos ethyl	23.19	318, 304, 168	23505-41-1	$C_{13}H_{24}N_3O_3PS$	5.00

[a]Data extracted from PubChem[32]

Internal standard

The internal standard (IS) was introduced in the step preceding injection to compensate for minor variations in injection volume and instrument performance, ensuring the normalization of relative peak areas of each pesticide.[22,33] ATZ-D5 was selected as the internal standard due to its expected absent in the sample.[23-26] The internal standard, maintained at a fixed concentration (10.00 μg L^{-1}), was added to each calibration solution. The response factor, based on the detector response of the analyte relative to the internal standard at each injected concentration, was plotted against the pesticide concentration. The adjusted analytical curve was determined using linear regression. Additionally, ATZ-D5 was incorporated into all final extracts as a quality control measure.

Method validation

The parameters evaluated for the quantitative analytical method were linearity, limit of detection (*LOD*), limit of quantification (*LOQ*), repeatability (in terms of relative standard deviation, *RSD*, %) and recovery. The criteria used to assess validation performance were those stablished in SANTE 12682/2019[22] and by the National Institute of Metrology, Quality and Technology (INMETRO, Brazil).[33]

The assessment of validation parameters, such as *LOD* and *LOQ* was conducted using the spreadsheet validation method developed by Ribeiro *et al*.[34] After obtaining the area ratios of the peaks for each pesticide relative to the internal standard peak (A_P/A_{IS}) at various concentrations during the linearity test (calibration solutions were injected in triplicate, $n = 3$), the data was entered into the spreadsheet created by Ribeiro *et al*.[34] This spreadsheet uses specific equations to estimate the limits of detection and quantification:

$$LOD = 2\frac{s_y t}{a_1}\sqrt{\frac{1}{N}+1+\frac{(y_c-\bar{y})^2}{a_1^2\sum_{i=1}^{n}(x_i-\bar{x})^2}} \quad (1)$$

$$LOQ = \frac{y_h-a_0}{a_1}+\frac{s_y t}{a_1}\sqrt{\frac{1}{N}+1+\frac{(y_c-\bar{y})^2}{a_1^2\sum_{i=1}^{n}(x_i-\bar{x})^2}} \quad (2)$$

The calculations for each term in these equations are detailed in the work of Ribeiro *et al*.[34] and are also included in the Supplementary material. The spreadsheet was chosen because it simplifies the calculation of this parameters using information from the calibration curve.[33,34]

To ensure repeatability, six concentration levels were established for each analyte, with three replicates for each level ($n = 3$). The assessment values for each analyte were adjusted according to the specific linearity of each pesticide. Repeatability was evaluated using the relative standard deviation (*RSD*, %), as detailed in Eq. (3) stablished by INMETRO:[33]

$$RSD = \frac{100s}{\bar{x}} \quad (3)$$

In this context, s represents the standard deviation, and $\bar{x}$ denotes the average of the measurements collected on the same day. This calculation helps evaluate the precision related to the repeatability of the applied methodology. Using the same levels evaluated for repeatability, a recovery study (representing accuracy) was conducted in accordance with INMETRO.[33] Eq. (4) was utilized for the quantification of recovery:

$$\text{Reovery} = 100\frac{C_1 - C_2}{C_3} \quad (4)$$

The terms used in the Eq. (4), are referred to: C_1, concentration of the analyte in the fortified sample; C_2, concentration of the analyte in the unfortified sample; C_3, as the concentration of the analyte added to the fortified sample.

RESULTS AND DISCUSSION

Linearity, LOD *and* LOQ *limits*

The results obtained were used to assess the linearity of the methodology for the analyzed pesticides, as shown in Tables II and III. Analytical curves were established within a concentration range of 17.50–52.50 μg kg^{-1} for the pesticides DIA, DEA, diazinon, methyl parathion, pirimiphos methyl, malathion and pirimiphos ethyl. The correlation coefficients (R^2) for the identified analytes exceeded 0.990, confirming that the analytical curves met the established criteria for validating methodologies for pesticide residue extraction and quantification.[2,22,33]

TABLE II. Values obtained from the assessment of linearity, limit of detection (L*OD*) and limit of quantification (*LOQ*) for sediments (n = 3)

Pesticide	Parameter				
	Range μg kg^{-1}	R^2 (A_P/A_{IS})[a]	Equation $y = ax \pm b$	*LOD* μg kg^{-1}	*LOQ* μg kg^{-1}
DIA	17.50–42.50	0.9961	$y = 0.0012x - 0.0019$	5.60	8.40
DEA	17.50–52.50	0.9902	$y = 0.0017x - 0.0014$	7.30	10.90
Diazinon	17.50–42.50	0.9901	$y = 0.0062x - 0.0468$	6.10	9.10
Malathion	17.50–42.50	0.9937	$y = 0.0038x - 0.0273$	5.80	8.60
Pirimiphos ethyl	17.50–42.50	0.9935	$y = 0.0029x - 0.0252$	9.70	15.00

[a]Standardized area with IS (Internal Standard, ATZ-D5)

The compiled data from Tables II and III, indicate that the *LOD* (5.60–9.70 μg kg^{-1}) and *LOQ* (8.40–15.00 μg kg^{-1}) obtained for sediments, closely align with values reported in the literature for Brazilian samples.[6] In contrast, the *LOD* (5.00––8.70 μg kg^{-1}) and *LOQ* (8.80–13.00 μg kg^{-1}) for corn grains, are comparable to those obtained for the same detection techniques.[15]

The maximum residue levels (*MRL*s) for the pesticides analyzed in corn, are established by the values specified in European Union Regulation EC 396/2005 for food and feed.[35] This regulation aims to ensure a high level of food safety and

protect consumers from potential health risks associated with pesticide residues. The *MRL* values for the pesticides of interest, applicable to both sweet corn and maize, are as follows: atrazine, related to DIA and DEA (50 μg kg^{-1}); diazinon (20 μg kg^{-1}); methyl parathion (20 μg kg^{-1}) and for pirimiphos methyl (500 μg kg^{-1}). Its is important to note that the *LOQ* must correspond to values ≤ *MRL* for each pesticide.[2,22] The *LOQ* for corn (8.80–13.00 μg kg^{-1}) obtained using this methodological approach, is considerably lower than the *LOQ* suggested by the *MRL* found for each pesticide.[15,22] Currently, no *MRL* values have been reported for sediments due to the exploratory nature of pesticide residue studies in this matrix.[6,7] However, the L*OQ*s obtained for the sediment matrix (8.40–15.00 μg kg^{-1}), are consistent with those obtained for the corn, demonstrating that the methodology is adaptable in both matrices.[6,15,22]

TABLE III. Values obtained from the assessment of linearity, limit of detection (*LOD*) and limit of quantification (*LOQ*) for corn grains (n = 3)

Pesticide	Parameter				
	Range μg kg^{-1}	R^2 (A_P/A_{IS})[a]	Equation $y = ax \pm b$	*LOD* μg kg^{-1}	*LOQ* μg kg^{-1}
DIA	17.50–42.50	0.9914	$y = 0.0014x - 0.0112$	6.00	8.80
DEA	22.50–52.50	0.9952	$y = 0.0023x - 0.0273$	6.70	9.70
Diazinon	17.50–52.50	0.9928	$y = 0.0039x - 0.0029$	5.00	7.40
Malathion	22.50–52.50	0.9953	$y = 0.0095x - 0.0144$	7.10	10.40
Pirimiphos ethyl	17.50–47.50	0.9921	$y = 0.0028x - 0.0313$	8.70	13.00

[a]Standardized area with IS (Internal Standard, ATZ-D5)

Recovery and repeatability

Favorable findings regarding analyte recoveries are presented in Tables IV and V. The recovery percentages obtained are within the following ranges: for sediments, DIA (94.30–101.70 %), DEA (93.40–105.50 %), diazinon (88.10––109.80 %), malathion (95.00–108.30 %), pirimiphos ethyl (92.40–111.10 %); for corn, DIA (95.10–104.80 %), DEA (92.40–105.30 %), diazinon (88.40–106.60 %), methyl parathion (94.50–107.40 %), pirimiphos methyl (81.00–112.00 %).

Recoveries exceeding 100 % in pesticide residue analysis are often attributed to the matrix effect.[6,15,18,22] The matrix effect occurs when co-extracted compounds from the sample matrix, such as corn or sediment, enhance the ionization of target analytes (pesticides) during mass spectrometry analysis.[2,22,31] This enhancement can lead to an overestimation of pesticide concentration, resulting in a recovery rate greater than 100 %.[22] The recovery percentages obtained in both matrices fall within the recommended range of 70–120 % for each spike level tested[2,22,33] which ranged from 17.50 to 52.50 μg kg^{-1}, for the pesticides studied, as illustrated in Figs. 1 and 2. Importantly, the lowest recovery values exceed the recommended lower limit of 70 %.[22]

TABLE IV. Mean recovery (%) and relative standard deviation (*RSD*, %) for DIA, DEA, diazinon, malathion and pirimiphos ethyl in sediments (n = 3)

Fortification level, μg kg^{-1}	Parameter	Pesticide				
		DIA	DEA	Diazinon	Malathion	Pirimiphos ethyl
17.50	Recovery	96.90	93.40	99.30	95.40	92.40
	RSD	2.90	3.00	4.60	7.70	4.70
22.50	Recovery	101.70	107.50	109.80	98.50	103.90
	RSD	5.10	4.50	7.00	5.60	5.50
27.50	Recovery	96.20	105.60	96.80	108.30	99.40
	RSD	5.50	5.20	2.90	11.90	2.80
32.50	Recovery	97.00	98.00	100.60	105.70	111.10
	RSD	5.30	7.10	4.40	9.80	2.90
37.50	Recovery	94.30	95.60	88.10	95.00	101.60
	RSD	2.40	3.80	12.50	9.80	8.50
42.50	Recovery	97.10	98.00	97.80	95.70	97.90
	RSD	3.80	2.90	13.20	8.00	12.20

TABLE V. Mean recovery (%) and relative standard deviation (*RSD*, %) DIA, DEA, diazinon, methyl parathion and pirimiphos methyl in corn grains (n = 3)

Fortification level μg kg^{-1}	Parameter	Pesticide				
		DIA	DEA	Diazinon	Methyl parathion	Pirimiphos methyl
22.50	Recovery	99.40	105.30	106.60	104.10	102.60
	RSD	1.90	1.50	6.80	0.50	2.80
27.50	Recovery	95.10	97.30	90.80	94.50	98.50
	RSD	1.20	0.80	5.20	1.10	3.60
32.50	Recovery	102.60	100.90	100.20	107.40	102.20
	RSD	5.90	5.10	3.20	2.50	8.90
37.50	Recovery	100.10	98.60	104.70	100.10	95.90
	RSD	3.00	3.40	3.80	4.00	7.50
42.50	Recovery	104.80	102.00	106.10	103.60	81.10
	RSD	5.10	4.70	2.30	3.70	3.10
47.50	Recovery	–	92.40	88.40	106.00	112.60
	RSD	–	3.50	1.60	3.00	3.60

Furthermore, the literature reviewed for similar studies reports comparable percentages, highlighting the effectiveness of the proposed methodology.[5,6,15,21] This methodology employs an efficient and simplified calibration technique (SLSAS), based on the work of Viera *et al.*[18] The relative standard deviation (*RSD*) for repeatability ranged from 0.80–13.20 %. A repeatability rate of less than 20 % is considered acceptable for multiresidue approaches.[2,22,33]

Matrix effect

The matrix effect of the applied method was evaluated by comparing the chromatograms of the selected sample for SLSAS calibration (M10 for corn and

P3 for sediments) with a spiked level from the pesticide analysis curve. This comparison was conducted for both matrices: corn and sediments (see Figs. S-4 and S-5 of the Supplementary Material). It was observed that there was an incremental effect in the signals (GC–MS) of the analytes when using the matrix in the calibration curve with SLSAS,[18] a finding that aligns with predictions from similar studies involving the analyzed matrices.[6,15] Due to this signal enhancement, it was not possible to validate the methodology for the pesticides malathion and ethyl parathion in the corn matrix, as well as for methyl parathion and pirimiphos methyl in the sediment matrix.

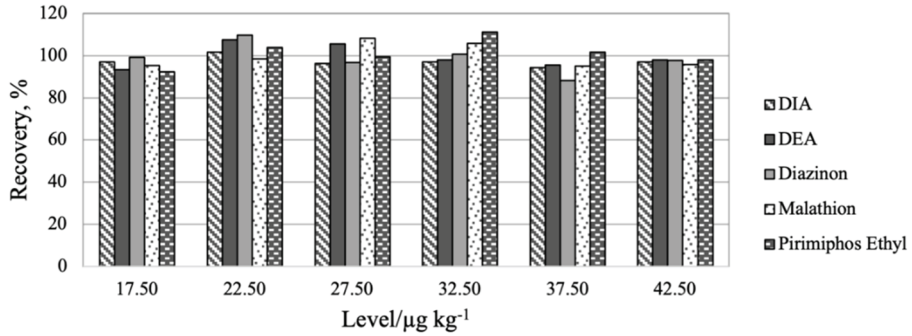

Fig. 1. Average recovery rates (%) for DIA, DEA, diazinon, malathion and pirimiphos ethyl, in sediments samples, obtained in triplicate (n = 3) for the modified QuEChERS/GC–MS method.

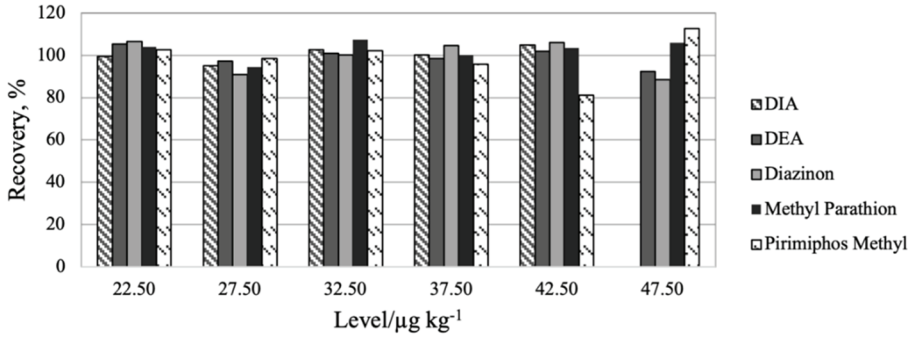

Fig. 2. Average recovery rates (%) for DIA, DEA, diazinon, methyl parathion and pirimiphos methyl, in corn grain samples, obtained in triplicate (n = 3) for the modified QuEChERS/GC–MS method.

Application of the proposed method to real samples

To assess the performance of the method, it was applied to 10 different corn samples and 5 sediment samples. Each samples were analyzed in triplicate; however, the analytes of interest were not quantified in these samples. All results were

below the limit of detection (*LOD*) for the pesticides analyzed in both matrices (see Tables S-1 and S-2 of the Supplementary Material).

Given the validation quality of the approach developed in this study, it is considered a suitable alternative to conventional laboratory methods. The modifications to the methodology of Anastassiades *et al.*[14] enabled the simultaneous detection of seven pesticides: diazinon, malathion, pirimiphos ethyl, methyl parathion, pirimiphos methyl, DEA and DIA in two matrices with significantly different characteristics, corn and sediments. This was achieved using GC–MS/MS in selected ion monitoring (SIM) mode, a technique commonly employed for effectively analyzing pesticide residues in diverse matrices.[2,31] Furthermore, this adaptation aligns with other methodologies applicable to multiple matrices and meets the analytical control parameters necessary to establish it a viable option for use in sediment and corn within similar agricultural contexts and pesticide applications.

CONCLUSION

This study presents a methodology for analyzing seven pesticides in corn and sediment samples, specifically for application in the agricultural regions of Paraná State, Brazil. The QuEChERS/GC–MS methodology proved to be both simple and effective. It was validated with recovery rates ranging from 70 to 120 %. The validation parameters were appropriate for analyzing pesticide residues in both matrices – corn and sediments – with concentrations between 17.50 to 52.50 μg kg^{-1}. These concentrations resulted in quantification limits (*LOQ*) below the maximum residue limits established for the analyzed food matrix. The use of GC–MS with selective ion monitoring (SIM) and SLSAS calibration enhanced the method's sensitivity, further reinforced by the inclusion of an internal standard (ATZ-D5).

The proposed method was applied to corn and sediment samples from Paraná State, where no significant levels of the targeted pesticides were found in the samples. This method achieved satisfactory limits of quantification, precision (repeatability) and accuracy (recovery), demonstrating its suitability for multiresidue pesticide analysis in both corn and sediments, serving both regulatory and routine residue monitoring purposes. Given the widespread use of pesticides, this study encourages the application of this methodology to other matrices involved in the environmental degradation cycles of pesticides, as well as on a broader range of pesticides used in various agricultural practices and application patterns.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/13136, or from the corresponding author on request.

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ИЗВОД

ОБЈЕДИЊЕНА МЕТОДА МУЛТИРЕЗИДУАЛНЕ АНАЛИЗЕ ПЕСТИЦИДА У КУКУРУЗУ И СЕДИМЕНТИМА

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Због значајне улоге Бразила као главног светског произвођача кукуруза и утицаја акумулације пестицида у седиментима на здравље водених екосистема, ова студија се бави потребом за поједностављеном методом за процену остатака пестицида у матрицама као што су кукуруз и седименти. Модификована QuEChERS метода комбинована са гасном хроматографијом–масеном спектрометријом, валидирана је за анализу седам уобичајених пестицида у држави Парана, Бразил: дезизопропилатразин (DIA), деетилатразин (DEA), диазинон, метилпаратион, метилпиримифос, малатион и етилпиримиф. Пратећи смернице INMETRO и SANTE 12682/2019, методом су постигнуте границе квантификације (8,40–15,00 μg kg^{-1} за седимент и 8,80—13,00 μg kg^{-1} за кукуруз) испод максималних граница остатка (*MRL*) утврђених од стране ЕС 396/2005 за кукуруз. Процедура је показала одличну линеарност (R^2 > 0,99), стопе опоравка (70–120 %) и прецизност (релативне стандардне девијације ≤ 20 %). Ова валидирана метода пружа јединствен, поуздан и осетљив приступ за анализу остатака већег броја пестицида у кукурузу и седименту, што је корисно за праћење животне средине и безбедност хране, посебно у кључним пољопривредним регионима као што је Бразил.

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