Development and validation of a method to determine pesticides in river water using QuEChERS combined with UHPLC-MS/MS

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ABSTRACT

The continuous increase in the use and release of pesticides is worrisome because water contamination can affect health and the environment. This study optimized and validated a multi-residue method in water. The method was developed using the QuEChERS method (Quick, Easy, Cheap, Effective, Rugged, and Safe) followed by ultrahigh- performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS). The validation was performed on the matrix (river water) regarding accuracy, precision, linearity, limits of detection (LODs) and limits of quantification (LOQs). LODs were below 3.03 µg L^{-1}and LOQs were from 6.25 to 9.18 µg L^{-1}. The accuracy (recoveries in the range of 80-117%) and for Inter-day precision, the coefficients of variation ranged from 0.35 to 15.71%, and for Intra-day precision were in the range of 0.48 to 7.02%.

Keywords: multi-residue analysis, pesticide, QuEChERS, water.

Desenvolvimento e validação de um método para determinação de pesticidas em água de rio por QuEChERS combinado com UHPLC-MS/MS

RESUMO

O aumento contínuo do uso e liberação de agrotóxicos tem tornado o cenário preocupante, pois a contaminação das águas pode afetar a saúde e o meio ambiente. Neste estudo, um método multiresíduo em água foi otimizado e validado. O método foi desenvolvido utilizando o método QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) seguido de cromatografia líquida acoplada a espectrometria de massa (UHPLC-MS/MS). A validação foi realizada na matriz (água do rio) avaliando à exatidão, precisão, linearidade, limites de detecção (LODs) e limites de quantificação (LOQs). Os LODs ficaram abaixo de 3,03 µg L^{-1} e os LOQs variaram de 6,25 a 9,18 µg L^{-1}. A exatidão apresentou recuperações de 80 a 117% e o coeficiente de variação para a repetibilidade foi de 0,35-15,71% e de 0,48-7,02% para a precisão intermediária.

Palavras-chave: água, análise multiresíduo, pesticidas, QuEChERS.

1. INTRODUCTION

Pesticides have a high potential for contamination of surface waters and groundwater. The degree of this contamination varies with parameters such as water solubility, and soil mobility, among others. The constant increase in the use of pesticides in agriculture increases the levels of contamination in food and the environment, thus harming health (da Silva Sousa *et al.*, 2021)

Brazil has become one of the largest consumers of pesticides in the world due to growing agricultural activity. This increase has negative implications for human health and the environment (Lopes-Ferreira *et al.*, 2022) There was a setback in the country's conservation policy, which generated pressure for the expansion of agricultural frontiers and changes in agricultural production. In the last 4 years, 551 pesticides have been released, 30 to 35% have been evaluated as potentially carcinogenic by international regulatory agencies and banned by the European Union. In addition to the damage to health, this high toxicity increases the concentration of harmful substances in bodies of water and soils (Barbosa *et al.*, 2021).

The toxicity of pesticides is associated with their chemical groups. Organochlorines, organophosphates, carbamates, pyrethroids, and neonicotinoids are among the most frequent. Carbamates and organophosphates are related to infertility, teratogenic, cytotoxic, and genotoxic effects (Liu *et al.*, 2020; Gomes *et al.*, 2020).

The work developed by Panis *et al.* (2022) analyzed 11 pesticides (glyphosate-AMPA, mancozeb-ETU, molinate, trifluralin, alachlor, aldrin-dieldrin, atrazine, chlordane, DDT-DDD-DDE, diuron, and lindane). These related or proven carcinogens, the research was carried out in 127 municipalities in the state of Paraná, Brazil. The minimum number of cancer cases related to drinking water contamination was estimated at 542 cases. They estimated using the average concentration of pesticides in water (ppb), the respective exposed population of each municipality, and the reference value for the risk of cancer from pesticides. The concentrations found reached significantly higher levels than those prescribed by the European Union (Panis *et al.*, 2022).

Several studies indicate the presence of pesticides in Brazilian surface waters. A review study carried out by De Souza *et al.* (2020) demonstrates the presence of different classes of pesticides (herbicides, insecticides, fungicides) in different countries, including Brazil. The concentrations of these compounds in surface waters range from 0.00 to 61200.00 ng L^{-1}.

Studies have detected atrazine in surface waters in reservoirs in Ceará State at 15 µg L^{-1}, in Rio Grande do Sul concentrations of 0.48 and 0.82 µg L^{-1}, and also in the State of Mato Grosso concentrations of 0.68 and 0.70 µg L^{-1} in surface waters and groundwater (Bortoluzzi *et al.*, 2007; Nogueira *et al.*, 2012; Sousa *et al.*, 2016).

Albuquerque *et al.* (2016) demonstrated in their study the presence of pesticides in Brazilian freshwater at concentrations of 0.002 to 26 µg L^{-1}. Seven pesticides were detected in the Camanducaia River, which is part of the Piracicaba Hydrographic Basin, which pumps water to the Cantareira system, an important source of water for the metropolis of Paulista and Campinas, Brazil. Atrazine was the most frequent, at concentrations of 0.3-1.4 µg L^{-1} (Barizon *et al.*, 2020)

To quantify pesticides in water is necessary to develop methods with good selectivity and precision that can analyze several compounds at once, with multi-residue methods being advantageous (Belmonte *et al.*, 2022). Among the existing methods, liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) has stood out for the determination of pesticides. LC-MS/MS can be applied to complex matrices in addition to allowing separation, detection, and confirmation steps to occur in a single run (Abdel Ghani and Hanafi, 2016). For the analysis, sample preparation is essential, and liquid-liquid extraction is widely used; but it

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involves the use of toxic solvents and has limitations regarding reproducibility and sensitivity. Another method that has been used is QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe), widely used to extract pesticides in food and some environmental samples (Abdel Ghani and Hanafi, 2016; Zaidon *et al.*, 2019). Although the QuEChERS method is widely explored in food samples, in water it is underexplored.

Therefore, efficient validated methods are increasingly needed to quantify pesticides in water. In this study, we propose the modification of the QuEChERS method for application in water, and we optimize and validate a multi-residue method by (UHPLC-MS/MS) for the determination of the pesticides methomyl, diflubenzuron, imidacloprid, pyraclostrobin, and atrazine, all in active use in Brazil, involving different classes of pesticides: insecticides, fungicides, and herbicides.

2. MATERIALS AND METHODS

2.1. Chemicals and reagents

Pesticide reference standards (Atrazine, methomyl, pyraclostrobin, diflubenzuron, imidacloprid) and formic acid (98% purity), and methanol were purchased from Sigma-Aldrich Co. (St Louis, MO, USA). Acetonitrile (ACN) HPLC grade was purchased from TEDIA (USA). For the QuEChERS method, magnesium sulfate ($MgSO_4$) was obtained from Reatec and sodium chloride (NaCl) (Vetec). The Primary- Secondary Amine (PSA) was purchased from Supelco Sigma-Aldrich (St Louis, MO, USA) for the cleaning step. The water purification system used was MilliQ (Millipore Ltd.). The syringe filter used was a $0.22\,\mu m$ nylon filter. An individual stock solution of analytes was prepared at a concentration of $0.2\,g\,L^{-1}$, and a solution containing all target compounds was prepared at a concentration of $1\,mg\,L^{-1}$, and used for the necessary dilutions. The water for the validation study was collected in Rio das Mortes, located in the municipality of Guarapuava, in the State of Paraná (PR) – Brazil. The water was collected in amber glass bottles and stored under refrigeration.

2.2. UHPLC-MS/MS Analysis

Chromatographic separation was performed on an ACQUITYTM UPLC system with a quaternary pump, vacuum degasser, and auto sampler (Waters, Milford, USA). Equipped with ACQUITY UPLC BEH C18 column (100 mm×2.1 mm, I.D., 1.7 µm, Waters Corp., Milford, USA). Different mobile phases were evaluated. The mobile phase was 0.1% formic acid in water (solvent A) and ACN (solvent B). The chromatographic conditions were optimized to obtain a good resolution and better signal from the analytes and minimize the analysis time. The column was maintained at 40°C, and the injection volume was 2 µL. The gradient elution started with a flow rate of $0.2\,mL\,min^{-1}$: 0 min, 30% B; $0.3\,mL\,min^{-1}$:4 min, 70% B; 6 min, 70% B; 7 min, 99% B; 8 min, 30% B; $0.2\,mL\,min^{-1}$: 10 min, 30% B.

The determination of Pesticides was carried out with a triple-quadrupole Xevo-TQD mass spectrometer (Waters, Milford, USA). With an electrospray source (Z-spray TM) operated in positive ionization mode (ESI+). The instrument control software was MassLynxTM 4.1 (Milford, USA). The capillary voltage was 3.2 kV, desolvation temperature at 500ºC, desolvation gas flow $1000\,L\,h^{-1}$, and cone gas flow at $50\,L\,h^{-1}$. Pesticide (analyte) fragmentation, collision energy, and cone were optimized. For the optimization of MS/MS parameters, $1\mu g\,mL^{-1}$ solution was used for, each analyte. We selected two product ions for each precursor ion, defining the most sensitive transition as a quantifier and a second as a confirmation. Along with other parameters, such as collision energy, cone voltage was also optimized and is presented in Table 1. Pesticides were selected as a function of use in Brazil and also due to the lethality observed in worker bees.

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Table 1. Mass spectrometric parameters for each pesticide.

Pesticide	Chemical structure	Rt (min)	Cone (v)	MRM transition	CE (eV)
Imidacloprid		2.00	36	255.99>175.10 255.99 >209.06*	14/14
Atrazine		3.98	40	216.10>174.10* 216.10 > 95.93	18*/22
Diflubenzuron		5.28	20	311.00>158.00* 311.00> 141.00	15*/30
Pyraclostrobin		6.21	32	388.07>194.02* 388.07 > 163.02	12*/31
Methomyl		1.53	15	163.21 > 87.90* 163.21 > 105.90	10/10
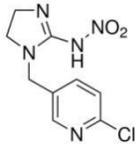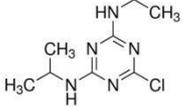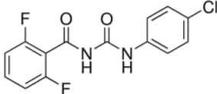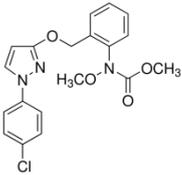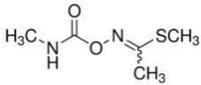
The asterisk * in the MRM transition indicates the quantifier ion.
CE: Collision Energy.
MRM: Multiple reaction monitoring.

2.3. Sample preparation

The QuEChERS method consists of liquid partitioning with ACN and a dispersive solid-phase extraction (D-SPE) cleanup step (Cerqueira *et al.*, 2014). In this study, an adaptation of the QuEChERs extraction procedure was performed. The validation process of the proposed method was performed by doping natural water (class 2) (CONAMA, 2005; 2008), samples with pesticides for each point of the calibration curve, 20 to 100 µg L^{-1}, in triplicate. 10 mL of sample (doping natural water) was added to 5 mL of ACN and acidified with 200 µL of acetic acid, then refrigerated for 10 min. 4 g of MgSO$_4$ and 1 g of NaCl were added, and the sample was vortexed and centrifuged for 8 min (4500 g, 0.5°C). 3 mL of supernatant was removed and added to the tube with 300 mg MgSO$_4$ and 125 mg PSA. Again, the tube was vortexed followed by centrifugation, and finally, 2 mL of extract was transferred, passed through the filtration membrane, and analyzed by UHPLC-MS/MS.

2.4. Validation Method

The matrix effect was obtained by comparing the angular coefficients of the calibration curves in the solvent and the matrix (freshwater) (Guedes *et al.*, 2016; Salvia *et al.*, 2013). Matrix effect = (slope of calibration curve in the extract - slope of calibration curve in solvent / slope of calibration curve in solvent) x 100.

We validate the method using the RDC 166 (Anvisa, 2017). The parameters evaluated in river water doped with pesticides were linearity, selectivity, accuracy, intra-day precision, inter-day precision, LODs and LOQs. The LODs and LOQs were obtained from the standard deviation of the intercept with the Y-axis of three calibration curves containing analyte concentrations (5-50 µg L^{-1}) close to the supposed detection limit. The linearity study was performed with a calibration curve in the matrix at concentration levels (20-100 µg L^{-1}).

Accuracy (expressed by recovery) and precision (expressed by relative standard deviation) were performed in quadruplicate and at three concentration levels: 30, 50, and 100 µg L^{-1}. Intra-day precision at different times on the same day and Inter-day precision on three different days.

3. RESULTS AND DISCUSSION

3.1. UHPLC-MS/MS optimization

We evaluated the selectivity by injecting the mixture of standards at a concentration of 30 µg L^{-1}, obtained in the SEM mode, to verify the chromatographic separation. Samples were prepared in solvent and matrix (natural water). The matrix was submitted to the QuEChERS method (adapted) to assess whether the selectivity would remain. The chromatograms in the solvent and the fortified matrix are demonstrated in Figures 1 A and 1 B. It can be verified that the intensity of pesticide signals in ACN were almost twice that of the signals obtained in natural water, evidencing interferences of the constituents of the matrix.
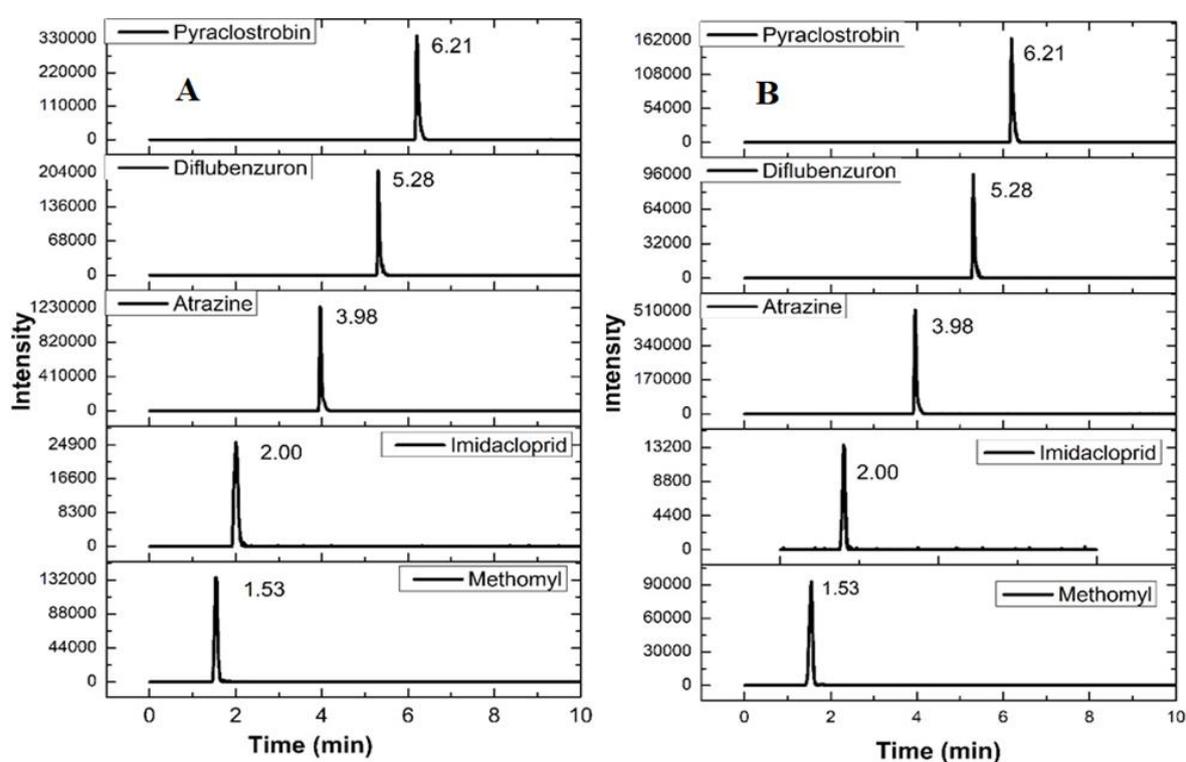
Figure 1. Selectivity of pesticides (30 µg L^{-1}) in (A) ACN and (B) in natural water SRM mode.

3.2. Extraction Method

We use the QuEChERS method with some modified steps. The method has advantages of being fast, easy, economical and safe. Tests were performed to decrease the use of solvent (ACN), making the experiment more environmentally friendly. Ratios of 4:1 and 2:1 were tested for water and ACN, 4:1 was considered insufficient. For the 2:1 ratio, 20 mL: 10 mL and 10 mL: 5 mL were tested. We opted for the proportion of 10 mL: 5 mL (water/ ACN), thus reducing the use of solvent. To increase the volume of the final extract, the amount of acetic acid was optimized, which was changed from 100 µL to 200 µL, resulting in 3 mL of supernatant in the first stage and 2 mL of final extract, which was considered adequate to conduct the experiments. The result can be explained because acetic acid increases the stability of pesticides in ACN (Bordin *et al.*, 2017; Zaidon *et al.*, 2019).

Moreover, cooling steps were also added to prevent evaporation in the process and generate better reproducibility.

3.3. Validation Method

The matrix effect was evaluated by comparing the slopes of the calibration curve in the solvent and the matrix. When it results in a positive difference, there is an elevation in the signal and when there is a negative difference, there is a suppression in the same. These values are classified as no, medium, or strong matrix effects (Ferrer *et al.*, 2011).

As river water is a complex matrix, it is suggested that the present components affect the ionization of these compounds (Cotton *et al.*, 2016). The results were 18.7; 15.4; -16.4; 63.5, and 99.3% for atrazine, diflubenzuron, methomyl, imidacloprid, and pyraclostrobin, respectively. Only imidacloprid and pyraclostrobin showed a strong matrix effect (-50% or above +50%). Three of the five pesticides did not show a significant matrix effect (-20% to 20%).

Calibration and validation in the matrix (river water) was performed to minimize the matrix effect. The results of the linearity study are shown in Table 2. The linear range was 20-100 µg L^{-1} the method showed good linearity, which we confirmed by the coefficient of determination (R^2) with a significant regression F, and the F statistical test was also performed, where the F of lack of fit was lower than the critical F for all pesticides.

Table 2. Linear regression of pesticide analytical curves in natural water by UHPLC-MS/MS.

Calibration Equation		Parameters					
		R^2	$F_{(reg.)}$	p	$F_{lack-of-fit}$	$F_{critical\ value}$	p
Atrazine	y=43899485 + 173465x	0.995	4562.48	0.00	2.52	2.74	0.065
Imidacloprid	y=1856709 + 150242x	0.988	1826.02	0.00	2.21	2.77	0.098
Diflubenzuron	y = 3595875 + 351046x	0.971	781.26	0.00	0.70	2.77	0.628
Pyraclostrobin	y=23517408 + 992234x	0.993	3272.70	0.00	1.21	2.74	0.343
Methomyl	y= 3266270 + 464954x	0.994	3130.55	0.00	1.71	3.03	0.202

The limits of detection and quantification were 2.06; 2.33; 2.72; 2.44; 3.03 µg L^{-1} and 6.25; 7.06; 8.26; 7.40; 9.18 µg L^{-1} for atrazine, diflubenzuron, pyraclostrobin, methomyl, and imidacloprid, respectively. Intra-day precision and Inter-day precision in the matrix were evaluated at concentrations of 30, 50, and 100 µg L^{-1} in quadruplicate, and the values are shown in Table 3. For Inter-day precision, the coefficients of variation ranged from 0.35 to 15.71%, with the highest value for diflubenzuron at 30 µg L^{-1}. For Intra-day precision, the coefficients of variation were in the range of 0.48 to 7.02%. The recoveries ranged from 80 to 117%, with both minimum and maximum values related to imidacloprid, the others all above 90%. The results indicate good selectivity and sensitivity of the method developed to quantify these pesticides in water.

The results shown in Table 4. demonstrate that the sensitivity developed in our study (LOQ below 9.18 ng mL^{-1} and LOD below 3 ng mL^{-1}) is compatible with the results developed in water using the Quechers.

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Table 3. Results of precision and accuracy for the determination of pesticides in natural water by UHPLC-MS/MS.

Pesticide	Concentration ($\mu g\ L^{-1}$)	Intra-day precision (% RSD)	Inter-day precision (% RSD)	Accuracy (%)
Atrazine	30	7.02	6.22	97.0
	50	3.35	12.29	98.3
	100	1.07	12.24	96.8
Imidacloprid	30	4.73	1.94	80.0
	50	2.96	5.95	117.2
	100	1.05	6.30	109.6
Diflubenzuron	30	3.88	15.71	91.5
	50	5.76	10.39	99.8
	100	4.35	8.14	96.0
Pyraclostrobin	30	2.39	2.82	93.9
	50	3.12	6.53	100.5
	100	3.07	6.00	97.5
Methomyl	30	3.75	0.35	103.4
	50	1.47	4.86	113.1
	100	0.48	4.22	103.9

Table 4. Comparative results from the literature.

Analytes	Sample	Method	LOD - LOQ	Ref
Methomyl Other pesticides (48)	Surface water	DI-SPME GC-ITMS/MS	1.09 - 1.43 $\mu g\ L^{-1}$ 0.001-0.458 $\mu g\ L^{-1}$ 0.04-1.43 $\mu g\ L^{-1}$	Jabali *et al.* (2019)
Imidacloprid	Water bodies of agricultural	HPLC/DAD	0.15 - 0.7 $\mu g\ mL^{-1}$	Hrybova *et al.* (2019)
Pesticides (55)	Agricultural water	QuEChERS LC-MS/MS	0.02 - 3.0 $\mu g\ L^{-1}$ 0.1 – 9.9 $\mu g\ L^{-1}$	Song *et al.* (2020)
Hormones, endocrine, disruptor, pesticides	Tap water and wastewater sample	DLLME GC-MS	0.09 - 3.36 $ng\ mL^{-1}$ 0.31 – 11.19 $ng\ mL^{-1}$	Chormey *et al.* (2017)
Pesticides (8)	River and well water samples.	QuEChERS GC-MS	0.3- 4 $\mu g\ L^{-1}$ 0.95- 13.69 $\mu g\ L^{-1}$	Abdel Ghani and Hanafi (2016)
Pesticides (30)	Drainage water	QuEChERS GC-MS	(LOQ) 4.59 – 15.91 $ng\ mL^{-1}$	Salama *et al.* (2022)

DI-SPME: Direct immersion solid-phase micro-extraction
GC-ITMS/MS: Gas chromatography-ion trap tandem mass spectrometry
HPLC/DAD: High-performance liquid chromatography with a spectrophotometric (diode array detector) detector
GC-MS: Gas chromatography–mass spectrometry.

4. CONCLUSIONS

The development of validated methods for quantifying pesticides in water is essential for their control and improvement of legislation, in addition to preventing severe risks to human

health and environmental damage.

The presented results demonstrated a method with good linearity, precision, and accuracy. Future work can develop the research in drinking water and explore other surface waters. The method developed can also be used to quantify pesticides in studies of the removal of these contaminants, which require methods already optimized for the development of research.

5. ACKNOWLEDGMENTS

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Rev. Ambient. Água vol. 19, e2940 - Taubaté 2024

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