Application of bar adsorptive microextraction (BA μ E) for the determination of pesticides and emerging contaminants in water used for rice cultivation in southern Brazil

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Abstract

Brazil is among the ten largest rice producers in the world, concentrating its production in the southern region. Anthropogenic activities, such as the disposal of chemicals in the ecosystem and consequently in the aquatic environment, end up harming the availability and quality of the water. Here, we developed an analytical method based on BA μ E with WAX as an extraction phase for the determination of 5 pesticides and 2 emerging contaminants in water samples used in rice cultivation by HPLC–DAD. The method was fully optimized through univariate and multivariate approaches. The optimized condition was obtained with 145 min of extraction time, without salt addition and 35 min of desorption time using 250 μ L of MeOH:AcEt (60:40, v/v). A reduced mass of extraction phase (around 4 mg) and sample and solvent volumes (15 mL and 300 μ L, respectively) were used. The bars have a low cost and can be used up to 20 times without loss of extraction efficiency. Furthermore, the developed method presented high-throughput, because it uses a Voltage Regulator Variac system that allows the coupling of six magnetic stirrers simultaneously. The LODs ranged from 1.67 to 2.50 μ g L⁻¹ and the LOQs ranged from 5.00 to 7.50 μ g L⁻¹; both were below the VMP established by Ordinance 2.914/2011/MS for drinking water. Relative recoveries applied to the sample ranged from 80 to 121%. The intra-day and inter-day precision were up to 14% and 19%, respectively. The results were satisfactory, in accordance with the validation guidelines of the AOAC. Twenty-four samples collected in the Camboriú River Basin, which is influenced by rhiziculture, were analyzed and the analytes were not detected, as they are below the limits obtained in this method.

Keywords BA μ E · Rhiziculture · Pesticides · Emerging contaminants · Sample preparation · High performance liquid chromatography

1 Introduction

Sample preparation is a critical step in an analytical methodology because it is where contamination and analyte losses can occur, leading to analysis errors [9]. Therefore, robust sample preparation techniques are always being developed to minimize human manipulation and to isolate

and preconcentrate the compounds of interest quickly and efficiently [18]. Besides, each matrix presents particular characteristics, which makes it difficult to develop a universal method. Even with the advancement of technology, direct analysis is generally restricted, either by the constitution of the sample or even by the low concentration of

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the analytes, leading to possible quantification and detection errors [10, 13].

Many techniques of extraction and preconcentration are described for several compounds in the most different matrices. New methods have been studied to overcome disadvantages, such as the use of solvents that are harmful to human health and the environment, the use of large volumes of these solvents, long times of preparation and high cost [34]. Microextraction techniques have been applied in order to improve these limitations, besides allowing the use of extraction phases of different compositions, allowing greater versatility and efficiency for the extraction of different organic and inorganic compounds [16, 25].

Solid-phase microextraction (SPME) is one of the pioneer techniques in this context. It was introduced in the 1990s [32], allowing the development of new techniques based on sorption, such as stir bar sorptive extraction (SBSE) [5]. These techniques, despite their broad applications, still have aspects that limit their use, such as the fragility of the fibers in SPME and the loss of sorbent material in SBSE caused by the contact of the device with the glass flask in the stirring step of the sample. To overcome some of these problems, bar adsorptive microextraction (BA μ E) was developed [26, 27].

BA μ E is a technique based on a cylindrical device, usually made of polypropylene, which allows its sampling to occur by flotation. The extraction phase is fixed in this device to perform the extraction of the analytes from the matrix. With this configuration, the material does not have contact with the sample vial wall, avoiding losses of the extraction phase, besides the device being less fragile than the fibers in SPME. Another advantage associated with this technique is the versatility to choose the extraction phase according to the type of matrix and the physicochemical characteristics of the analytes [13, 26, 27]. Although the flotation method is an advance in the technique, there is still the difficulty of keeping the bar under constant stirring in the vortex. In this way, a new configuration using a stainless steel rod was proposed for the first time in our group, to keep the bar balanced [30]. Recently, our group also proposed the coupling of several agitators to allow the simultaneous use of several adsorptive bars to improve the high-throughput aspects of the technique [23]. The applicability of BA μ E has already been successfully demonstrated for the extraction of different analytes in several matrices, among them aqueous matrices [1, 13, 21].

In rice cultivation, many compounds are used, such as pesticides, with about 100 active ingredients for use in rhiziculture in Brazil, according to the “Agência Nacional de Vigilância Sanitária (ANVISA)” [8]. For this study, carbofuran, methyl parathion, tebuconazole, trifluralin, and pendimethalin, which are the most frequently used in

rhiziculture in Brazil, were selected. For many of these substances there are already several studies indicating their toxicity to human health and the environment [3, 22, 29, 31]. In contrast, other substances are also constantly dumped into the environment, like caffeine and benzophenone, two emerging contaminants widely used in products, such as beverages and food, and UV filters, respectively. These compounds often reach aquatic environments through the inadequate disposal of domestic sewage. In general, these compounds act in the endocrine, nervous and cardiovascular system of the human being [25, 28].

Thus, the present work aimed at the development of an environmentally-friendly method with high-throughput aspects using BA μ E with WAX as extraction phase allied to the HPLC–DAD system for determination of 5 pesticides and 2 emergent contaminants in the water of the Camboiú River Basin (Santa Catarina state), Brazil, which may be influenced by rice cultivation as well as domestic sewage disposal.

2 Materials and methods

2.1 Reagents and solutions

High purity analytical standards (99%) of caffeine (CFN), benzophenone (BZP), carbofuran (CRB), methyl parathion (MPT), tebuconazole (TBZ), trifluralin (TFL), and pendimethalin (PDM) were purchased from Sigma-Aldrich (São Paulo, Brazil) with 99% of purity. The chemical structure and some physicochemical properties of the analytes are shown in Table 1. Ultrapure (UP) water was obtained from the Mega Purity water purification system (Billerica, MA, USA). HPLC grade acetonitrile (ACN) and methanol (MeOH) were purchased from JT Baker (Mallinckrodt, NJ, USA) and HPLC grade ethyl acetate (AcEt) was purchased from Sigma Aldrich (São Paulo, Brazil). Sodium chloride used to study of the salting-out effect was obtained from Vetec (Rio de Janeiro, Brazil). Individual stock solutions of each analyte were prepared at a concentration of 100 mg L⁻¹ and 10 mg L⁻¹ in MeOH. A working solution containing a mix of the analytes at a concentration of 2 mg L⁻¹ in MeOH was used for the fortification of the aqueous samples in the optimization and determination of analytical figures of merit of the method. As the extraction phase, a powdered solid material (WAX) obtained from pipette tips of DPX-WAX, acquired from DPX Labs (Columbia, SC, USA) was used.

Table 1 Chemical structure, pK_a and $\text{Log } K_{ow}$ of the analytes under study [11]

Analyte	Chemical structure	pK_a	$\text{Log } K_{ow}$
CFN		10.40	-0.55
BZP		-	3.43
CRB		14.76	2.05
MPT		-	2.60
TBZ		13.85	3.69
TFL		-	4.60
PDM		10.52	4.82

2.2 Instrumental and chromatographic conditions

In this study, the analyses were carried out in a liquid chromatograph model LC 20AT (Shimadzu, Kyoto, Japan) equipped with a diode array detector, model SPD-M20A Series, manual injector model Rheodyne 7725i (Rohmert Park, CA, USA) with a 20 μL loop. Separation was performed in reverse phase with a C18 column (Gemini, 250 mm length $\times$ 4.6 mm i.d., 5 μm film thickness; Allcrom, SP) and a flow rate of 1 mL min^{-1} . The gradient mode consisted of ACN (A) 20% and water (B) 80% from 0 to 6.5 min; from 6.5 to 15 min, the mobile phase A was increased from 20 to 80% and maintained until 20 min; from 20 to 25 min, the mobile phase A was decreased from 80 to 70%; and finally, at 25 min, the initial condition was returned and maintained up to 30 min. The monitored wavelengths were 200 nm for caffeine, carbofuran, methyl parathion, tebuconazole and trifluralin; 251 nm for benzophenone; and 240 nm for pendimethalin. Six magnetic stirrers (Fisatom, SP, Brazil) were coupled to a Voltage Regulator Variac TDGC2-1 1KVA/4MP (EZA, Instruments, SP) and to a line filter NBR 20605 (Power Line). The agitator's voltage was controlled by a Digital Multimeter ET-1002 (Minipa, SP, Brazil) and maintained at 155 V for all extractions. A portable salinity refractometer (Extech RF:20) was used to measure the salinity of the river water samples.

2.3 Preparation, conditioning, and morphology of the adsorptive bars

The first step for preparation of the adsorptive bars was performed according to the procedure of [Dias et al. [13]]. The bars are polypropylene with cylindrical shape and size of 15 mm in length and 3 mm in diameter.

These bars were coated with the extraction phase WAX obtained from DPX-tips (20 mg), fixed to the bar using double-sided adhesive tape of 10 mm width. In the second step, cleaning and conditioning were performed. The adsorptive bars were placed in contact with 250 μL of ACN in polypropylene flasks with glass insert with 300 μL capacity under ultrasonic agitation for 15 min. The adsorptive bars were then transferred to other glass insert polypropylene vials containing 250 μL of UP water under ultrasonic agitation for 30 min [13]. The temperature of the water in the ultrasonic bath was kept below 36 $^{\circ}\text{C}$, preventing the strips from detaching from the bars. Figure 1 shows the procedure for the preparation of adsorptive bars and conditioning.

To obtain the morphologies of the material, the micrographs were performed by scanning electron microscopy (SEM), performed in a new adsorptive bar and another one used 20 times.

2.4 Optimization procedure using BA μ E

To obtain the best analytical response, univariate and multivariate approaches were used [6, 20]. Initially, the optimizations were performed with UP water fortified with 100 $\mu\text{g L}^{-1}$ of each analyte in glass vials with capacity of 22 mL. The adsorptive bars were placed in the vial in contact with the fortified UP water and the extractions occurred under constant stirring for 60 min. Thereafter, the liquid desorption step was carried out in polypropylene flasks with glass insert with capacity of 300 μL . This step was performed using ACN as desorption solvent for 15 min and in an ultrasonic bath.

Fig. 1 Procedure for preparation and conditioning of the adsorptive bars with extraction phase WAX

2.4.1 Optimization of liquid desorption parameters

The liquid desorption time was evaluated at five levels, including 10, 20, 30, 35 and 40 min in univariate mode and triplicate. The study of the best solvent or mixture was performed by the simplex-centroid design with 12 experiments including a triplicate in the central point. The solvents studied were ACN, MeOH, and AcEt, chosen according to previous works [20, 35].

2.4.2 Optimization of extraction parameters

The extraction time and the amount of NaCl added in the sample were evaluated in a multivariate mode through the Doehlert design with nine experiments including a triplicate at the central point. The time ranged from 45 to 145 min and the amount of NaCl (m/v) ranged from 0 to 20%. The response surface was generated using the geometric means of the chromatographic peak areas of the analytes. Based on pKa of the analytes, the pH of the sample was not evaluated.

2.4.3 Optimization of a cleaning step

This step was performed with the objective of reusing the adsorbent bars. The number of cleaning cycles that would be necessary to avoid the carryover effect between the experiments using the condition optimized in liquid desorption step was evaluated.

2.5 Analytical figures of merit

Analytical curves were constructed using the standard addition method in the sample matrix. The concentrations of the analytes were between 5 and 250 $\mu\text{g L}^{-1}$; these concentrations were established according to the "VMP of Ordinance 2.914/MS - Brazil" [7] for pesticides in drinking water. The linear correlation coefficients (R) were obtained through the analytical curves. The first levels of concentration of the linear ranges were established as the limits of quantification (LOQs), and the limits of detection (LODs) were obtained by dividing the LOQ by 3.3. The precision of the method was evaluated through intra-day and inter-day assays, using the relative standard deviation (RSD, %). The accuracy of the method was evaluated through relative recovery (%). All experiments were performed in triplicate, fortified at three concentration levels (7.5, 50 and 125 $\mu\text{g L}^{-1}$), common to all analytes, using samples from point 1 of collection of the Camboriú River Basin. This point was chosen because

it is the place that receives the least anthropic interference among the sampling points.

2.6 Evaluation of the stability and reproducibility of the adsorptive bars

Three bars were used to evaluate the stability of the adsorptive bars under optimized conditions. The bars were denominated as bar 1 (used 5 times), bar 2 (used 10 times) and bar 3 (used 20 times). The reproducibility was evaluated through extraction efficiency comparing three bars used the same number of times. The results of both cases were assessed through the construction of a bar graph with the arithmetical means of the chromatographic peaks areas of each analyte.

2.7 Camboriú River Basin samples

The sampling points are localized in the municipality of Camboriú, SC, Brazil, shown in Fig. 2, and its coordinates are shown in Table 1-S of the Supplementary Material. The collection period was determined considering the stage of soil preparation, sowing, and rice harvest according to [Vieira et al. [36]]. Samples were collected in November, December and March at 8 sample points, in a total of 24 analyzed samples. For the determination of the sampling points, the following was considered: 5 collection points close to the rhiziculture may receive interference in the quality of the water, and the other 3 points do not undergo interference from the rhiziculture. Before analysis, the samples were filtered and kept under refrigeration at 4 °C in amber vials.

3 Results and discussion

3.1 Morphology of the extraction phase WAX in the adsorptive bar

The sorbent WAX was selected as the extraction phase due to the success demonstrated in pesticide extraction, as reported in previous work [12]. WAX is an extraction phase comprised of poly-amino groups with the potential for hydrogen interactions and hydrophobic interactions with the analytes under study (DPX [15]. Furthermore, a FTIR analysis showed absorption bands that can be attributed to ring stretching and to stretching of the C–H bond of unsaturated carbon, possibly at the aromatic ring, indicating an aromatic ring in the WAX structure that can interact with the analytes through π - π interactions [12].

In addition, the surface and the thickness of the extraction phase WAX, micrographs in different magnifications, as well as transverse micrographs for a BA μ E bar (new and

Fig. 2 Location of the sampling points in the Camboriú River Basin—SC, Brazil

Fig. 3 Micrographs obtained by SEM for the new BAμE bar. **a** Surface of the bar covered with extraction phase WAX magnified 100 times; **b** transverse bar micrograph enlarged 40 times; and **c** transverse bar micrograph with measurements, magnified 200 times

Fig. 4 Micrographs obtained by SEM for the BA μ E bar used 20 times. **a** Surface of the bar covered with extraction phase WAX magnified 100 times; and **b** transverse bar micrograph with measurements, magnified 200 times

used 20 times) were evaluated. The micrographs are presented in Figs. 3 and 4.

In Fig. 3a, b it can be observed that the coating of the extraction phase WAX on the surface of the bar is homogeneous, presenting particles of different sizes and a similar shape, forming a porous layer. In Fig. 3c, it is possible to observe the thickness of the layer of extraction phase, which is between 152 and 178 μm , with an average size of 165 μm . In Fig. 4a, a loss of extraction phase is observed after 20 extractions, which may be related to bar manipulation, stirring losses with the magnetic bar or the contact with the walls in the vial in the desorption stage. In Fig. 4b, it can be seen that the thickness of the extraction phase was reduced by an average of 53 μm . Although the loss of the extraction phase occurs, the efficiency is maintained for up to 20 extraction cycles, according to the RSDs obtained in the stability test. This may be explained because the saturation of the extraction phase does not occur, due to the large mass coating the adsorptive bar (around 4 mg), leaving sites available to perform the interactions with the analytes.

3.2 Optimization of the proposed method using BA μ E with WAX

3.2.1 Optimization of chromatographic separation

Seven analytes were suitably separated with the chromatographic conditions described in Sect. 2.2. The chromatographic separation is shown in Figure 1-S of the Supplementary Material.

3.2.2 Optimization of the desorption solvent

The desorption solvent is an important parameter to ensure the efficient desorption of the analyte from the extraction phase to a liquid matrix to be injected into the analytical equipment. Besides, it must ensure that

Fig. 5 Triangular surface obtained through simplex-centroid design using 15 mL of UP water, 60 min of extraction, no addition of NaCl, pH 6.00, 100 $\mu\text{g L}^{-1}$ of each analyte, 250 μL of desorption solvent and 15 min for desorption time

the analytes are efficiently desorbed from the adsorptive bars, allowing their reuse without a carryover effect. The solvents chosen were ACN, MeOH, and AcEt, which are compatible with the HPLC–DAD system and have groups that may interact with the analytes. Figure 5 shows the triangular surface constructed with a simplex-centroid design and a quadratic function.

On the triangular surface obtained with $R^2 = 0.9531$, it can be observed that the ACN region presents a weak response to desorption of the analytes. However, the best responses were obtained when a mixture between MeOH and AcEt was used, indicating a better interaction with the analytes. Thus, 250 μL of MeOH:AcEt (60:40, v/v) was used in further experiments.

Fig. 6 Bar graph obtained for optimization of liquid desorption time using 15 mL of UP water, 60 min of extraction, no addition of NaCl, pH 6.00, $100 \mu\text{g L}^{-1}$ of each analyte, 250 μL of desorption solvent MeOH:AcEt (60:40, v/v)

3.2.3 Optimization of the desorption time

In this step, the time required for the analytes to migrate from the extraction phase to the solvent mixture was optimized in univariate mode. As the amount of analyte is proportional to the volume of extraction phase in the bar, times of 10, 20, 30, 35 and 40 min were evaluated, and the results are shown in Fig. 6.

According to the bar graph, 35 min was the best desorption time for 6 of the 7 analytes. The time of 40 min was not chosen because a decrease in the area is perceptible, that is, the extractive phase may be re-extracting the analytes, which may imply a carryover effect in the experiments. Therefore, the time of 35 min was selected for further experiments.

3.2.4 Optimization of the extraction time and addition of NaCl in the sample

In the extraction step, a Doehlert design was applied to evaluate the extraction time and the amount of salt added to the sample to promote the salting-out effect of the analytes. The time range from 45 to 145 min was evaluated and for the added NaCl a proportion of 0–20% (m/v) was evaluated. The surface obtained is shown in Fig. 7.

The surface obtained with $R^2 = 0.9788$ showed a trend towards longer extraction times. However, no longer times were evaluated, so as not to impair the analytical frequency of the method, since 145 min is a considerable time. For the salt addition, the best results were without salt added to the sample. In this way, a time of 145 min was established for the extraction without the need to add NaCl to the sample.

Fig. 7 Response surface obtained for the optimization of the extraction time versus NaCl (%) through the Doehlert design using 15 mL of UP water, pH 6.00, $100 \mu\text{g L}^{-1}$ of each analyte, 250 μL of desorption solvent MeOH:AcEt (60:40, v/v) and 35 min of desorption time

3.2.5 Optimization of the cleaning step

The cleaning step of the bars was optimized to study the possible reuse in other extractions without carryover effect. The number of cycles that would be necessary for cleaning using the conditions established in the liquid desorption step was evaluated with the use of 250 μL of MeOH:AcEt (60:40, v/v) in an ultrasonic bath for 35 min. The result of the number of cleaning cycles is shown in Figure 2-S of the Supplementary Material.

It was observed that after the second cleaning cycle the analyte areas were considerably reduced. In this condition, the analytical frequency was not affected and the carryover effect was reduced. Therefore, 2 cleaning cycles of 35 min each using 250 μL of MeOH:AcEt (60:40, v/v) in an ultrasonic bath were fixed for this step.

After the optimizations, the condition comprised 145 min of extraction time, without NaCl addition, use of 250 μL of MeOH:AcEt (60:40, v/v) as desorption solvent, 35 min of desorption time in an ultrasonic bath, and 2 cleaning cycles of 35 min using 250 μL of MeOH:AcEt (60:40, v/v) in an ultrasonic bath.

3.3 Analytical figures of merit and sample analysis

Calibration curves were constructed using a sample collected at point 1 of the Camboriú River Basin. The optimized condition for BA μ E using WAX as extraction phase was applied. The results are presented in Table 2.

According to Table 2, the method presents a good linear correlation, since the R values are higher than or equal to 0.9803. The LODs ranged from 1.67 to 2.50 $\mu\text{g L}^{-1}$ and LOQs ranged from 5.0 to 7.5 $\mu\text{g L}^{-1}$. The values obtained for both limits are lower than the maximum permitted values (VMP) established by "Ordinance 2914/2011/MS" [7] for water designated for human consumption, demonstrating the applicability of the method for river water samples. Also, the samples were subjected to a salinity test in a refractometer, and the results were approximately zero, indicating that the samples were in accordance with the conditions optimized in UP water. In this way, the accuracy of the proposed method was evaluated through the relative recovery and the precision through intra-day ($n=3$) and inter-day ($n=9$) assays. The results obtained are presented in Table 3, at three concentration levels common to all analytes according to the analytical curves. The tests were carried out in a sample collected from point 1 of the Camboriú River Basin.

As can be seen in Table 3, the results of the relative recoveries ranged from 80 to 108% at the concentration

Table 3 Relative recoveries, intra-day and inter-day precisions for the proposed method

Analyte	Fortification level ($\mu\text{g L}^{-1}$)	Relative recovery (%) ($n=3$)	Precision (RSD, %)	
			Intra-day ($n=3$)	Inter-day ($n=9$)
CFN	7.5	80	3	12
	50	94	4	3
	125	81	1	11
CRB	7.5	82	11	12
	50	119	2	9
	125	116	8	7
MPT	7.5	90	3	6
	50	113	9	6
	125	99	5	5
TBZ	7.5	87	8	7
	50	119	7	14
	125	112	1	11
BZP	7.5	81	14	16
	50	119	10	13
	125	117	5	8
TFL	7.5	107	1	19
	50	118	1	7
	125	98	1	1
PDM	7.5	108	5	4
	50	111	6	6
	125	121	10	10

of 7.5 $\mu\text{g L}^{-1}$, 94–119% at the concentration of 50 $\mu\text{g L}^{-1}$ and 81–121% at the concentration of 125 $\mu\text{g L}^{-1}$. Precision intra-day ranged from 0.1 to 14%, and precision inter-day ranged from 1 to 19%. These results are considered acceptable according to the Association of Official Agricultural Chemists [4]. Thus, the proposed method was accurate and precise and, therefore, appropriate to be applied for the determination of these analytes in river water samples.

In Table 4 a comparison is shown between the proposed method and others described in the literature that

Table 2 Analytical figures of merit of the proposed method and VMP for the analytes under study in drinking water

Analyte	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	Linear range ($\mu\text{g L}^{-1}$)	R	Linear Equation	VMP ($\mu\text{g L}^{-1}$)
CFN	1.51	5.0	5–125	0.9972	$y=67.07x+271.7$	–
CRB	1.51	5.0	5–125	0.9957	$y=580.4x+403.61$	7.0
MPT	1.51	5.0	5–125	0.9983	$y=502.54x+1854.5$	9.0
TBZ	1.51	5.0	5–250	0.9940	$y=764.16x+6651$	180.0
BZP	2.27	7.5	7.5–125	0.9803	$y=1122x+2015.3$	–
TFL	1.51	5.0	5–125	0.9998	$y=549.93x-234.27$	20.0
PDM	2.27	7.5	7.5–125	0.9946	$y=786.47x+412.99$	20.0

Table 4 Comparison of the proposed method with the literature data for the determination of the analytes under study in aqueous samples

Analytes	Extraction technique	Instrum.	Sample volume (mL)	Solvent volume (mL)	References
CFN	SPE	LC-ESO-ToF	>100	>10	[2]
CFN	SBSE	LC-MS/MS	50	>5	[19]
CFN, CRB, TBZ, TFL	SPE	LC-ToF-MS	200	–	[33]
CRB, TBZ	RDSE	UHPLC-MS	50	>3	[14]
PDM	SPE	Electro-analytical Methods	10	10	[17]
TFL	SPE	UPLC-MS/MS	500–1000	>3	[24]
CFN, CRB, BZP, MPT, TBZ, TFL, PDM	BAμE	HPLC-DAD	15	0.003	Proposed Method

determined the same analytes in aqueous samples. In this comparison, the extraction technique, sample volume and solvent volume were considered. As can be observed, the BAμE is a low-cost and easy-to-prepare technique, and it can be reused for several cycles, which is advantageous when compared with the SPE, which generally uses one cartridge for each extraction. Also, the BAμE uses a smaller volume of sample and organic solvents than the other techniques compared, which generates a smaller quantity of residues. These characteristics evidence the environmentally friendly aspects of the method developed.

After the analytical figures of merit were determined, 24 water samples were collected in the Camboriú River Basin, SC, Brazil and analyzed. Table 2-S of the Supplementary Material shows the conditions during the collection. As can be seen, the samples were collected after intense rains that increase turbidity, volume and velocity of the water. This river is affected by rice growing in some of its points. For the development of the methodology, point 1 was selected, as there is no interference from this type of agriculture and no interfere in the analyte chromatographic peaks. For the remaining 7 points, 21 replicates were made, and no peaks of the analytes are present. Two possible conclusions can be made, the first that local farmers do not use these compounds in their cultivation or the analytes are present at lower limits than those established by this method, requiring an evaluation with more sensitive instruments, such as those demonstrated in Table 4.

3.4 Evaluation of the stability and reproducibility of the bars

To assess bar stability and reproducibility, the extractions were performed according to the optimized condition. The bar stability was performed using three bars that passed through different numbers of extraction: bar 1 (used 5 times); bar 2 (used 10 times); and bar 3 (used 20 times).

The bar reproducibility was evaluated using three bars that passed through the same number of extractions. All experiments were performed in triplicate. The results for bar stability and bar reproducibility are presented in Figure 3-S and 4-S of Supplementary Material, respectively.

According to Figure 3-S, the chromatographic areas do not present the significant difference between the bars used different times, maintaining the stability and efficiency of extraction up to 20 cycles, even losing extractive phase as previously described in Sect. 3.1. As regards the bar reproducibility, it can be observed in Figure 4-S that the bars present similar results for the extraction, indicating that the bars are reproducible, so the extractions can be performed simultaneously.

4 Conclusion

In this study, an environmentally-friendly method based on the BAμE technique using WAX as extraction phase was developed and fully optimized for the determination of 5 pesticides and 2 emerging contaminants in river water. The bars are easy to produce, present a low cost and can be used without loss of extraction efficiency for up to 20 cycles of extraction. Also, the method used a low mass of extraction sorbent (around 4 mg), low sample and solvent volumes (15 mL and 300 μL, respectively), emphasizing the environmental aspects of the proposed method. The analytical figures of merit were evaluated demonstrating the applicability of the developed method with LODs and LOQs that were satisfactory and below the VMP established by Ordinance 2.914/2011/MS for drinking water. The accuracy and the intra and inter-day precisions were in accordance with the validation guidelines of the AOAC. Besides, the methodology was applied in 24 samples collected in the Camboriú River, and the analytes were not detected. The method can present high-throughput

aspects, and it is possible to carry out up to 6 experiments simultaneously using a Voltage Regulator Variac system, and for perspective, other systems can be coupled, further improving the analytical frequency, as well as possible automation. Therefore, the presented study proved to be a good alternative for the determination and monitoring of pesticides and emerging contaminants in river water samples.

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Data availability The authors confirm that the data supporting the findings of this study are available within the article.

Compliance with ethical standards

Conflict of interest No potential conflict of interest was reported by the authors.

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