



Development and multivariate optimization of nanostructured supramolecular liquid-liquid microextraction validated method for highly sensitive determination of methyl parathion in water samples

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ABSTRACT

A simple, rapid and environmentally friendly supramolecular solvent-(SUPRAS)-based liquid phase microextraction method combined with high performance liquid chromatography (HPLC) for the determination of methyl parathion (MP) in water samples was developed. Several factors that affect the coacervation process, such as pH, volume and 1-decanol/THF ratio of supramolecular solvent, vortex time, and inorganic salt concentration were investigated and optimized. Under the optimized conditions, the enhancement factor and preconcentration factor were obtained as 139 and 12.7, respectively and the consumptive index (CI) was 0.79 mL. The limits of detection and quantification were found to be $0.27 \mu\text{g L}^{-1}$ and $0.91 \mu\text{g L}^{-1}$, respectively, while the linear range of analytical curve was ranged from 0.91 up to $500.0 \mu\text{g L}^{-1}$ with correlation coefficient of 0.999. The precision was evaluated in terms of intra-day ($n = 10$) and inter-day ($n = 2$) repeatability and the relative standard deviation percentages (% RSD) for two-level concentration (5.0 and $200.0 \mu\text{g L}^{-1}$) was $<5.3\%$. Imazethapyr, imazapic and imazepyr evaluated as possible interfering molecules did not show interference in the microextraction process, while $200.0 \mu\text{g L}^{-1}$ MP could be extracted in the respective presence of 2-nitrophenol and 4-nitrophenol at the 1:1 and 1:10 (m/m) ratio. The developed method was successfully applied for the determination of MP in artesian well ($20.3 \pm 2.4 \mu\text{g L}^{-1}$) and surface water ($12.2 \pm 3.5 \mu\text{g L}^{-1}$ and $12.7 \pm 2.6 \mu\text{g L}^{-1}$). The accuracy was attested by addition and recovery tests of MP obtaining recovery percentages in the range of 92.0–109.9%, thereby confirming the reliability of the proposed method.

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1. Introduction

The use of Organophosphorus (OPs) pesticides widely spread in agricultural and plant control cause an extensive pollution in the environment. Methyl parathion (MP) is one of the most common insecticides from OPs class and it is classified by United States Environmental Protection Agency (EPA) as a highly toxic pesticide class I [1]. Hence, due to high toxicity, developed countries such as Japan, China, USA and Australia have already banned or had its use restricted. In spite of that, Brazil has been using this pesticide mainly in rice and cotton crops [2,3]. The application at large scale causes the accumulation in soils and leaching to groundwater and surface water, carrying a potential risk for human health [3]. Under the circumstances, the concern of public and regulatory agencies has increasingly for establishing maximum

allowed levels of contaminants in water. According to the parameters of the World Health Organization (WHO), the Brazilian Ministry of Health has established a limit value of $9.0 \mu\text{g L}^{-1}$ for MP in drinking water [4,5].

Routine monitoring of organophosphorous compounds by using gas chromatography (GC) and high performance liquid chromatography (HPLC) are the most important tool for the analysis of pesticides residues in different samples [6,7]. Nevertheless, determination of analytes at low concentrations in complex environmental matrixes usually requires the use of extraction-separation methods for sample cleanup and enrichment. In this context, in order to improve the analytical performance of liquid-liquid extraction procedures, liquid-liquid microextraction based analytical methods environmentally friendly, quick and inexpensive have been goal of researches around the world. Some of these methods include cloud point extraction, (CPE) [8–12], dispersive liquid-liquid microextraction (DLLME) [13], ionic liquid-based dispersive liquid-liquid microextraction (IL-DLLME) [14], single-drop microextraction (SDME) [15], vortex-assisted liquid-liquid microextraction (VA-LLME)

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[16] and dispersive liquid-liquid microextraction based on solidification of floating organic drop (DLLME-SFO) [17].

Supramolecular solvent-based (SUPRAS) method is another and more recent liquid-liquid microextraction approach, which has been widely employed for preconcentration of metal ions and organic compounds [12,18,19]. SUPRAS are water-immiscible micro and nanostructured liquids made up commonly of reverse micelles in a tetrahydrofuran (THF)/water solution spontaneously formatted at a critical aggregation concentration. The feature of the ordered structures in SUPRAS, results in different regions of polarity that offer excellent microenvironment in the extraction of organic compounds. Therefore, forces-driving extraction of nonpolar and polar compounds mainly includes dispersive force and hydrogen bonding. As a result, analytes in a wide polarity range can be simultaneously and efficiently extracted using low extractant volumes in which the coacervation occurs rapidly and at room temperature [20,21]. SUPRAS is considered a liquid-liquid microextraction hybrid method once makes use of amphiphilic compounds as extractant medium and a disperser agent, likewise CPE and DLLME, respectively. Nevertheless, SUPRAS stands up with regard CPE method once water from sample is considered the external stimulus for coacervate formation, while CPE usually makes use of the temperature, thereby requiring long time for heating and, as consequence, decreasing the analytical frequency of method. SUPRAS when compared with DLLME, makes use of non-toxic amphiphilic compounds as extractant solvent, while in the latter one toxic organic solvent is used.

The successful application of SUPRAS as a microextraction method depends upon adequate optimization of the variables that play an important role in the extraction, including the amount of amphiphilic molecule (extractant), THF (disperser agent), water and sample pH, which are dependent on each other.

The one-way optimization is not recommendable for SUPRAS method, since it does not allow to evaluate interactions among variables and is very time-consuming resulting in higher reagent consumption. In this sense, chemometric tools based on multivariate designs have been strongly recommendable because enable the simultaneous study of several control variables and allows the development of mathematical models that permit assessment of the relevance and statistical significance of factors being studied as well as the optimal extraction conditions by applying response surface methodology (RSM) [22].

The aim of the present work was to develop and apply a rapid and environmentally friendly direct supramolecular solvent-based method using the ternary 1-decanol/THF/water mixture for MP determination by HPLC/DAD in water samples in combination with chemometrics tools for optimization. Additionally, according to our knowledge, the feasibility of alkanol-based SUPRAS has not been applied for monitoring of MP in water sample.

2. Experimental methods

2.1. Chemical reagents

All reagents were analytical or HPLC grade. Methanol (99.9%), THF ($\geq 99.9\%$), 1-decanol ($\geq 98.0\%$) and sodium chloride ($\geq 99.5\%$) were purchased from Sigma-Aldrich® (St. Louis, MO, USA). 2-nitrophenol ($\geq 99\%$) and 4-nitrophenol ($\geq 99\%$) from Acros® Organic (Ottawa, ON, Canada), imazethapyr, imazapic and imazepyr were acquired from Sigma-Aldrich (São Paulo, SP, Brazil). Stock solutions of MP (100 mg L^{-1}) were prepared in methanol and stored in amber flasks in freezer (-20°C). Working solutions were prepared freshly and diluted with ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$) collected from a purification system ELGA® PURELAB (Woodridge, IL, USA).

2.2. Instruments

Chromatographic analyzes were performed on a HPLC (Shimadzu, Kyoto, Japan) system composed of a LC-20AT pump, CTO-20A column

oven and a degasser system DGU20A. Chromatographic separation was carried out using a C18 CLC-ODS analytical column ($5.0 \mu\text{m}$, $250 \text{ mm} \times 4.6 \text{ mm}$) containing a guard column Phenomenex ($5.0 \mu\text{m}$, $4.0 \text{ mm} \times 3.0 \text{ mm}$) with mobile phase composed of methanol and water (MeOH:H₂O, 75:25 v/v), flow rate of 1.0 mL min^{-1} , injection volume of $20.0 \mu\text{L}$ and oven temperature of 30°C . The peaks' purity was determined on a diode-array detector (DAD) monitored at λ_{max} 273 nm. Under these conditions the MP retention time was 5.6 min. Vortex agitator SCILOGEX® MX-S (Rocky Hill, CT, USA) and a centrifuge QUIMIS®0222T2 (Diadema, SP, Brazil) were used to blend fluids quickly to assist the supramolecular solvent-based microextraction and phase separation process, respectively. The supramolecular rich phase formed was removed by using a HPLC syringe Hamilton® $50.0 \mu\text{L}$ model 1705 N (Reno, NV, USA). Solutions and pH sample was measured with a Metrohm 827 pH mobile digital pH meter (Herisau, Switzerland).

2.3. Supramolecular solvent-based microextraction procedure

The supramolecular solvent-based microextraction procedure is illustrated in Fig. 1. 10.0 mL of sample adjusted at pH 6.0 were placed in a 20.0 mL screw cap glass tube, then, $280 \mu\text{L}$ of THF/1-decanol mixture [2.8:1 (v/v)] containing 5.0% NaCl (w/v) was added into tube. Afterwards, the mixture was vigorously shaken using a vortex agitator for 4 min to favor the extraction and spontaneous supramolecular formation into the bulk solution. The phase separation of the supramolecular solvent was accelerated by centrifugation at 3500 rpm for 10 min. Finally, the volume of enrichment phase, which was located at the top of conical tube was removed by using a HPLC syringe. In order to reduce the viscosity of the rich supramolecular phase containing MP, THF and 1-decanol, the mixture was diluted with methanol at 1:1 (v/v) ratio and injected into the chromatographic system.

2.4. Multivariate optimization of SUPRA procedure by using factorial design

In order to select the significant factors that play an important role on supramolecular solvent-based microextraction, the optimization was performed in two steps. Firstly, a preliminary evaluation by using a two-level 2^{5-1} fractional factorial design was performed to investigate the experimental region of interest and the statistical design was made containing central point ($n = 3$) to determine the experimental error and evaluate the curvature of the first-order model. In order to estimate an appropriate relationship between the analytical response (area peak) and the conditions that control the supramolecular step process, the following independent factors were evaluated: pH of sample (4.5 to 7.5), % NaCl (1.0 to 9.0% w/v), vortex time (120 to 360 s), THF/1-decanol ratio (2:1 to 1:2 v/v) and volume (100 to $400 \mu\text{L}$). The influence of the factors on the analytical response (area peak) was analyzed through a Pareto Chart, which demonstrates graphically the significance or not of the factors and their interactions. The standardized effect was calculated by the ratio between the effect and the error standard obtained during the experiments and the optimum values of the levels were classified according to standardized effects at a confidence interval of 95% [22,23].

Afterwards, in order to provide better information than the first-order design, the steepest ascent method was applied as a previous way to give more accurate information of optimum neighborhood rapidly and efficiently to determine center points of each parameter for further optimization step. The path of the steepest ascent started from the central point and a series of exploratory runs were carried out to eliminate some variables. The point where the path of the steepest ascent reached its plateau would be near the optimum point and was used for further optimization study [24,25].

Based on the experimental domain indicated by first-order model and steepest ascent, a second-order design was applied for two variables by using Doehlert matrix and RSM to establish the optimum condition of the method [23]. Lagrange's criterion was used to check the

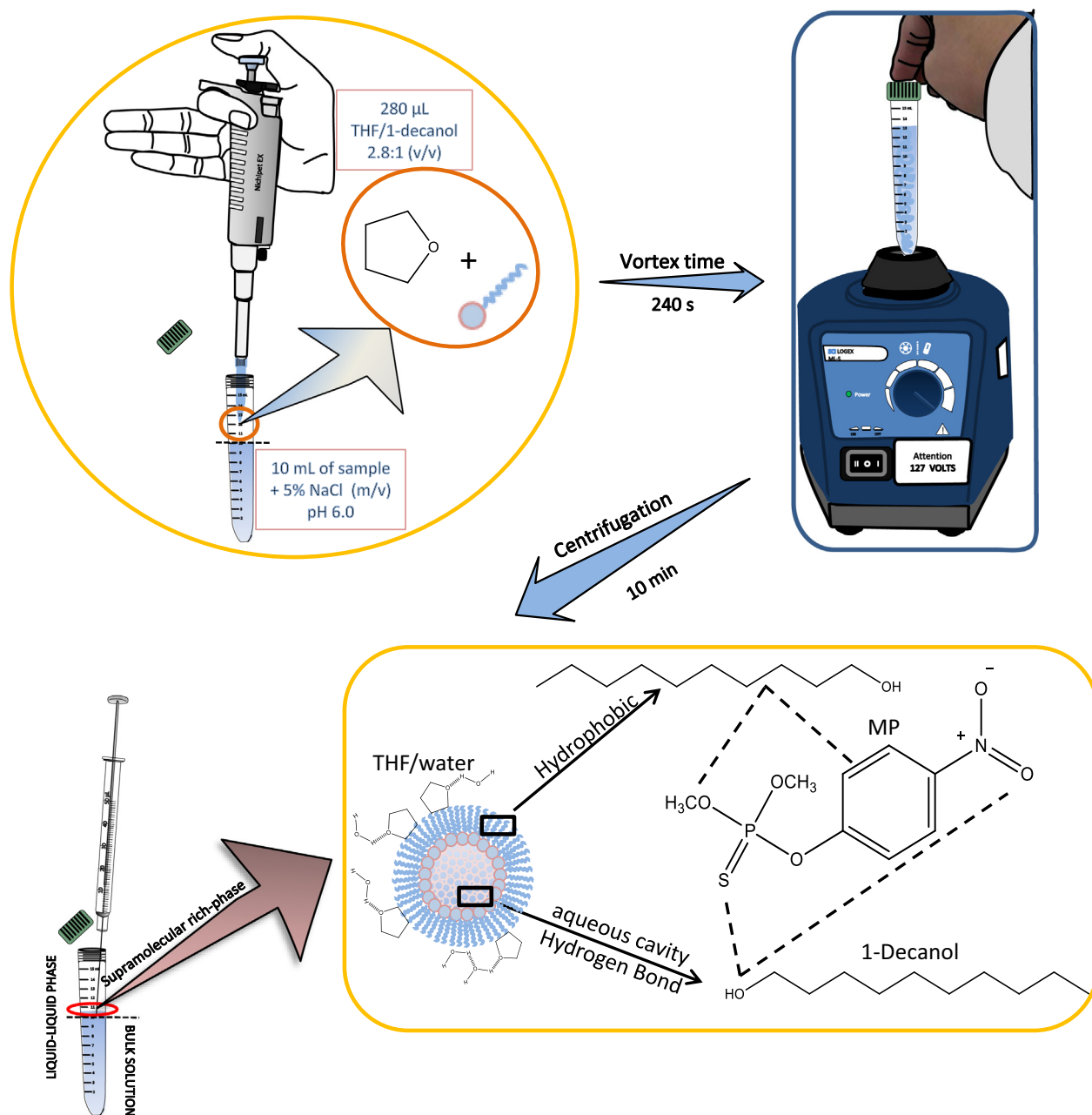


Fig. 1. Schematic process of self-assembly and coacervation in the supramolecular microextraction of MP.

existence of a critical point in the second-order model according to calculated Hessian determinant [26] of the response function obtained according to Eqs. (1) and (2):

$$H = \begin{vmatrix} \partial^2 y / \partial A^2 & \partial^2 y / \partial A \partial B \\ \partial^2 y / \partial B \partial A & \partial^2 y / \partial B^2 \end{vmatrix} \quad (1)$$

The Hessian determinant reduces to

$$H(A, B) = \left(\frac{\partial^2 y}{\partial A^2} \right) \times \left(\frac{\partial^2 y}{\partial B^2} \right) - \left(\frac{\partial^2 y}{\partial A \partial B} \right) \times \left(\frac{\partial^2 y}{\partial B \partial A} \right) \quad (2)$$

in which A and B are the regression coefficient of the second-order model obtained for two variables. The critical point (a_0, b_0) is obtained

if $H(a_0, b_0) > 0$ and $\delta^2 y / \delta A^2(a_0, b_0) < 0$, thus a maximum curvature is observed at response surface. On the other hand, a minimum response is present if $H(a_0, b_0) > 0$ and $\delta^2 y / \delta A^2(a_0, b_0) > 0$ or a point saddle exists at surface in case of $H(a_0, b_0) < 0$ [26]. If the response surface has a maximum, the critical values is calculated by partial derivative solving the equation systems $\delta y / \delta A = 0$ and $\delta y / \delta B = 0$ obtained for a second-order model from response surface according to Eq. (3):

$$y(\text{response}) = a + \alpha A + \beta B + \gamma(A)^2 + \delta(B)^2 + \varepsilon(A \times B) \quad (3)$$

in which y is the experimental response to be optimized, a is the constant term, α and β are coefficients of the first-order factorial design, γ and δ are coefficients of the quadratic terms and ε is the coefficient of interaction between the two factors. The factorial designs (first and second-order) were evaluated using the analytical signal (peak area) and the assays performed randomly to avoid possible systematic errors. The volume of sample was fixed at 10.0 mL and the experiments were

carried out by using MP solution at a $200 \mu\text{g L}^{-1}$ concentration. Statistical data were processed in a StatSoft Statistica 7.0 software package.

2.5. Analytical performance of proposed method

Under optimized conditions the analytical performance of method was determined according to International Union of Pure and Applied Chemistry (IUPAC) [27]. The correlation coefficient (r) of analytical curve, which is a measure of the linear degree association between MP concentration and signal was obtained and to confirm the relationship of two variables (linearity), the experimental F_{cal} value was calculated by using the ratio of residual variance to squared pure error and compared to tabulated critical F_{tab} . The experimental F_{cal} ratio is given by:

$$F_{cal} = \left(\frac{S_{y/x}}{S_y} \right)^2 \quad (4)$$

in which the residual standard deviation $S_{y/x}$ can be calculated according to Eq. (5) while S_y , the pure error which is a measure of the instrumental noise can be estimated and given by Eq. (6):

$$S_{y/x} = \sqrt{\frac{\sum_{i=1}^L (y_i - \hat{y}_i)^2}{I-2}} \quad (5)$$

$$S_y = \sqrt{\frac{\sum_{i=1}^L \sum_{q=1}^Q y_{iq} - y_i^2}{I-Q}} \quad (6)$$

The terms y_i and \hat{y}_i described in the equation are the experimental and estimated response values for sample i , y_{iq} and y_i are the curve analytical response for replicate q and mean response, respectively, at level i , L and Q are the total number of curve analytical samples, concentration levels and replicates at each level, respectively. By using null hypothesis test H_0 and alternative H_a , the regression model can be test whether is linear or non-linear. Assuming that $F_{cal} > F_{tab}$ value at level α , $F(\alpha, I-2, I-L)$, rejected the null hypothesis, i.e., there is evidence of lack of fit for the linear model [28,29].

The limit of detection (LOD) and quantification (LOQ) were calculated based on the analyte concentration which gives a signal at least three and ten times larger than the standard deviation of the blank signal, respectively, according to follow Eqs. (7) and (8):

$$LOD = \frac{3 \times S.D.}{S} \quad (7)$$

$$LOQ = \frac{10 \times S.D.}{S} \quad (8)$$

in which S. D. is the standard deviation of blank signal ($n = 10$) and S the slope of analytical curve. The preconcentration factor (PF) was determined as the slope ratio (SR) of the analytical curves with and without microextraction. The enrichment factor (EF) and consumptive index (CI), defined as the ratio of the volume of supramolecular rich phase with respect to the initial sample volume and the ratio between sample volumes (mL) and PF, respectively, were obtained according to follow equations [30,31]:

$$EF = \frac{V_{sample}}{V_{supramolecular}} \quad (9)$$

$$CI = \frac{V_{sample}}{PF} \quad (10)$$

in which V_{sample} and $V_{supramolecular}$ are the volume of sample before and after supramolecular microextraction process, respectively. The precision in terms of intra-day ($n = 10$) and inter-day ($n = 2$)

repeatability for two-level concentration (5.0 and $200.0 \mu\text{g L}^{-1}$) was determined and assessed as %RSD, and the accuracy of analytical procedure was evaluated by using the addition and recovery tests in spiked samples [27].

2.6. Application in real water samples

Surface water samples were collected in amber glass flasks from Arapongas city and different locals of rice cultivation in the municipality of Querência do Norte, located at north and extreme northwest region of Paraná (Brazil), respectively. Furthermore, samples from artesian well were also taken from Assis (São Paulo) and Arapongas. Samples collected were adjusted to pH 2.0 by the addition of concentrated sulfuric acid and stocked at refrigerator (4°C) [32]. The samples were filtered under vacuum using $0.45 \mu\text{m}$ Nylon® membrane filters (GVS Filter Technology, Morecambe, UK) in order to remove suspended particles and pH adjusted to 6.0 before supramolecular microextraction. For assessing the accuracy of method, the samples were also spiked with known amount of MP and subjected to the proposed method.

3. Results and discussion

3.1. 2^{5-1} Fractional factorial design

The coded, real experimental domain of the factors and the analytical signals (peak area) obtained in each experiment are shown in Table 1.

The influence of the factors in the analytical signal can be observed at Pareto Chart (Fig. 2).

From the analysis of the Pareto chart, the negative estimated effect (-13.34) of THF/1-decanol ratio indicates better efficiency of microextraction when using the 2:1 (v/v) ratio. Such outcome indicates that when low concentration of amphiphilic molecule is used, the

Table 1

Factors, levels and the experimental matrix of the 2^{5-1} fractional factorial design with central point ($n = 3$) for optimization procedure of MP supramolecular microextraction and determination by HPLC-DAD.

Factors	Levels		
	Low (-1)	0	High (+1)
pH of sample	4.5	6.0	7.5
% NaCl (w/v)	1.0	5.0	9.0
THF/1-decanol ratio	2:1	1:1	1:2
Volume THF/1-decanol (μL)	100	250	400
Vortex time (s)	120	240	360

Experiment	pH	% NaCl	THF/1-decanol	Volume	Vortex time	Signal (peak area/1000) ^a
8	1	1	1	-1	-1	99.8
3	-1	1	-1	-1	-1	61.4
5	-1	-1	1	-1	-1	134.7
2	1	-1	-1	-1	-1	707.7
14	1	-1	1	1	-1	500.0
CP ^b	0	0	0	0	0	850.1
4	1	1	-1	-1	1	918.9
CP	0	0	0	0	0	847.2
7	-1	1	1	-1	1	87.9
10	1	-1	-1	1	1	321.9
13	-1	-1	1	1	1	504.7
9	-1	-1	-1	1	-1	274.4
CP	0	0	0	0	0	809.9
12	1	1	-1	1	-1	269.8
16	1	1	1	1	1	491.4
11	-1	1	-1	1	1	256.4
1	-1	-1	-1	-1	1	847.2
15	-1	1	1	1	-1	522.9
6	1	-1	1	-1	1	119.6

^a MP concentration: $200.0 \mu\text{g L}^{-1}$.

^b CP: Central point.

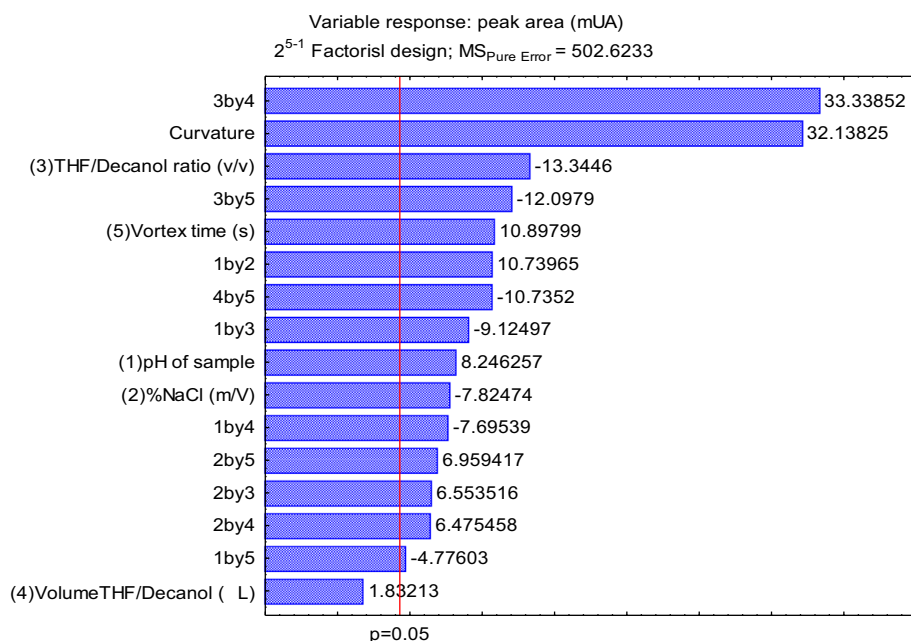


Fig. 2. Pareto Chart from the 2^{5-1} fractional factorial design.

proportion of water in the ternary mixture amphiphilic molecule/THF/water becomes high, thus making the partial desolvation of micelles more efficient. In similar way, it is known that THF-water fraction plays a double role, as disperser solvent and agent of the 1-decanol self-assembly [33,34]. Thus, when high concentration of THF is used, a more efficient dispersion of 1-decanol self-assembly is observed, thereby increasing the extraction efficiency of analyte [35,36]. Considering the effect of volume of THF/1-decanol mixture evaluated alone, no statistical influence on the microextraction was noticed ($p_{\text{value}} < 0.05$).

On the other hand, one should note that the interaction of THF/1-decanol ratio and the volume of this mixture was the most significant estimated effect with positive value of 33.33, showing that these factors must be simultaneously optimized. It seems that higher mixture volume than 100.0 μL provides a more efficient supramolecular microextraction due to its strong interaction effect caused by THF/1-decanol ratio. Such result stands up the great importance in using multivariate designs to optimize the SUPRAS method, once the ternary mixture constituted of amphiphilic molecule/THF/water is the more important parameter to be optimized.

The influence of salting out effect in liquid-liquid microextraction procedures is very well known. Within experimental domain (1.0–9.0%, w/v) and considering the negative estimated effect (–7.82), it seems that when high salt concentration (9.0%, w/v) is used most likely the original charge distribution of amphiphilic molecules might be disrupted, thereby hindering the coacervate formation. Moreover, the diffusion rate of the MP from the aqueous phase towards organic phase (coacervate) might also be decreased [37]. It must be point out that the decrease of extraction efficiency when high salt content is used is also more pronounced for molecules with high $\text{Log } K_{\text{ow}}$ value, such as MP 2.94–3.04 [38–40]. Salt concentration lower than 1% was not investigated in the fractional factorial design to avoid microemulsion formation [41].

Regarding to vortex time parameter, the results suggest that the low level (120 s) was not enough to transfer analyte towards the solvent extractor (1-decanol).

According to Pareto chart, the MP extraction is increased with increasing pH of samples (4.5 to 7.5). In order to understand the effect of pH on coacervation phenomenon it is important to point out that 1-decanol does not dissociate ($\text{p}K_{\text{a}} 15$) [42,43] throughout the pH range

investigated and provides a mixed-mode mechanism to assemble an efficient microextraction, while MP is in its molecular and deprotonated form ($\text{p}K_{\text{a}} = 7.15$) observed at pH 7.5 [44,45]. Therefore, hydrogen bonding through polar head of amphiphilic hydrocarbon, as well as dispersion forces with MP molecule might explain the better extraction at a higher pH value.

In order to attest the linearity of model, we can use the null hypothesis, $H_0: \beta = 0$, when there is no linear relationship, according to Eq. (11):

$$F_{\text{cal}} = \frac{MQ_R}{MQ_r} < F_{\text{tab}} \quad (11)$$

As $F_{\text{cal}} (203.1) > F_{\text{tab}} (19.4)$ for 16 and 2 degrees of freedom at the 95% confidence level; discard the possibility of $\beta = 0$, i.e., there is a linear relationship between the variables. This was consistent, considering the number of regression coefficient in the first-order model ($p = 17$), the maximum percentage of variation explained was $r_{\text{adj}} 0.997$.

3.2. Steepest ascent: moving the variables to maximum region of response surface

After established the influence of variables on the supramolecular-based microextraction according to achieved results from the 2^{5-1} fractional factorial design, a set of experiments was carried out for moving the variables to maximum region of response surface, whose experiments were started from the central point. Table S1 shows the levels of variables evaluated and the obtained analytical responses.

The path of the steepest ascent showed a maximum response in the central point, which is agreement with 2^{5-1} fractional factorial design, whose better responses were also obtained close to central point. From the obtained results, the vortex time, salt concentration and pH were fixed as the best conditions as 240 s, 5.0% and 6.0, respectively. However, taking into account the strong interaction of THF/1-decanol ratio and the volume of this mixture, a Doehlert design was carried out for final optimization of these variables as shown in Table 2.

Table 2
Doehlert Matrix design for two-variables (THF/1-decanol ratio and volume).

Experiment	Decoded variables		Peak area/1000
	THF/1-decanol ratio	Volume (μL)	
1	3:1	300	843.4
2	3:1	300	873.0
3	3:1	300	835.7
4	5:1	300	389.8
5	4:1	400	466.8
6	1:1	300	513.5
7	2:1	200	539.6
8	4:1	200	327.9
9	2:1	400	574.7

From the Doehlert design, a quadratic equation model (Eq. (12)) was obtained, whose statistical significance was evaluated by analysis of variance (ANOVA).

$$y(\text{peak area}) = -2144.96_{(\pm 681.53)} + 412.32_{(\pm 173.63)}(\text{THF/Decanol ratio}) - 87.98_{(\pm 19.32)}(\text{THF/Decanol ratio})^2 + 15.67_{(\pm 3.73)}(\text{Volume}) - 0.03_{(\pm 0.01)}(\text{Volume})^2 + 0.26_{(\pm 0.42)}(\text{THF/Decanol ratio} \times \text{Volume}) \quad (12)$$

A brief review of squares sum of model and residues (decomposed into lack of fit and pure error) from quadratic model are described in Table S2.

According to ANOVA, the $F_{cal} (16.5) < F_{tab} (18.2)$ indicates absence of lack of fit at 95% confidence level. Moreover, the correlation between the observed experimental results and the predicted values, demonstrated that the model is well fitted, considering the determination coefficient of 0.979.

In order to confirm presence of critical points in the response surface, the Lagrange's criterion based on Hessian determinant was applied to second-order model. According to partials derivate (Eqs. (1) and (2)) obtained for model (Eq. (12)), the Hessian $H(a_0, b_0) = 11.9 > 0$ and $(\partial^2 y / \partial^2 \text{THF/Decanol}) = -199.5 < 0$, thereby demonstrating a maximum on the response surface.

After established the validation of quadratic model, the response surface illustrates in Fig. 3 was obtained.

The critical points of the surface were calculated by solving the equations system obtained from the partial derivation of the function (Eq. (12)) in relation to each factor (variable): $(\partial y / \partial \text{THF/Decanol ratio})$ and $(\partial y / \partial \text{Volume})$. The maximum points appear within the experimental domain and the corresponding values are 2.8:1 (v/v) and 280 μL for THF/1-decanol ratio and volume, respectively. Probably, the relationship between the coacervate volume and the THF indicates that progressively more THF was incorporated to the coacervate above 2.8:1 ratio, and caused the gradual incorporation of both THF and water into the SUPRAS rich phase, consequently the reverse micelles became more and more diluted [34,46].

3.3. Analytical performance of the method

Under optimized condition the analytical curve for supramolecular microextraction of MP was linear in the range of 0.91–500.0 $\mu\text{g L}^{-1}$ according to equation $y(\text{peak area}) = 4476.1[\text{MP}, \mu\text{g L}^{-1}] + 8134.0$ with a correlation coefficient of 0.999. Furthermore, the linearity of model was

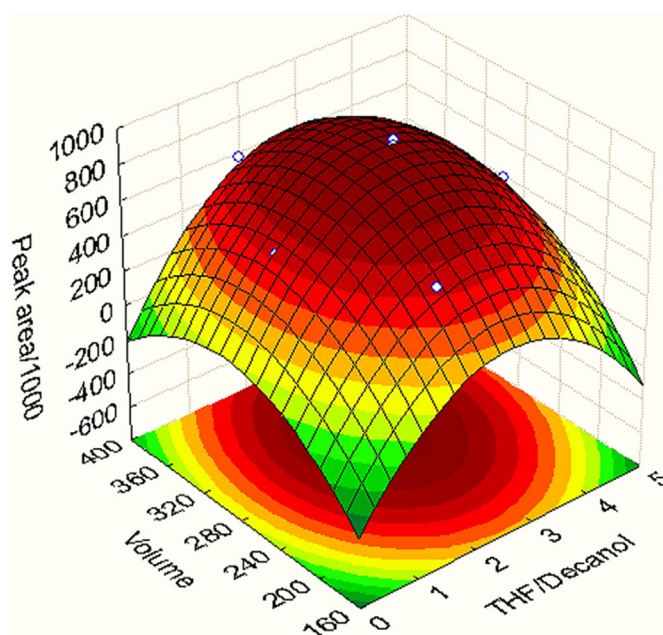


Fig. 3. Response surface for THF/Decanol ratio and volume factors. Conditions: pH 6.0, NaCl 5.0% (m/v) and 240 s of Vortex time.

attested according to Eqs. (4)–(6). Assuming that $F_{cal} (0.95) < F_{critical} (2.40)$ value at level α , $F(0.05, 19, 14)$, accepts the null hypothesis, i.e., there is no evidence of lack of fit for the linear model [28,29]. The assessment of the linearity and test F obtained for the analytical curve ($n = 3$) is summarized in Table S3. The limits of detection (LOD) and quantification (LOQ), calculated according to the IUPAC (Eqs. (7) and (8)), were found to be 0.27 $\mu\text{g L}^{-1}$ and 0.91 $\mu\text{g L}^{-1}$ [27].

The analytical curve built in the linear range of 50.0–300.0 $\mu\text{g L}^{-1}$ for the MP without preconcentration step furnished the linear equation $y(\text{peak area}) = 352.7[\text{MP}, \mu\text{g L}^{-1}] + 8718.9$. From the slope ratio (SR) between the linear models, a preconcentration factor (PF) of 12.7 times was obtained. In addition, based on the ratio of initial sample and supra-molecular rich phase volume (around 72.0 μL) the enrichment factor (EF) (Eq. (9)) obtained for the method was equal to 139 times.

The obtained consumptive index (CI), which is considered an interesting parameter to compare procedures using different volumes, was too much low (0.79 mL) [31]. The precision intra-day ($n = 10$) and inter-day ($n = 2$) of the method was evaluated in terms of repeatability by determining MP concentrations of 5.0 and 200.0 $\mu\text{g L}^{-1}$. The %RSD was ranged from 4.61 to 5.29% for intra-day and 2.23 to 3.60% inter-day. The analytical performance of the method was compared with previously published methods for MP determination (Table 3).

The supramolecular method has as highlight the low sample consumption, wide linear range and satisfactory enrichment factor. The main advantage of the method by comparison to other methods was the adequate limit of detection for MP determination (below the maximum value allowed by Brazilian Ministry of Health, 9.0 $\mu\text{g L}^{-1}$) [5] even without using expensive cost organic solvent and equipment, such as the ionic liquid and mass spectrometry, respectively. Furthermore, despite being highly sensitive, the mass spectrometry is considered a complex technique and requires relatively high skill level for operators. In addition, even though the lower solvent volume, most of the extraction procedure based on SDME and SFO drop compared to SUPRAS are time consuming (30 min under agitation) and present some drawbacks such as microdrop instability and solvent loss during extraction, reducing the repeatability of the method [18,49]. These results showed the proposed method has enough sensitivity and great potential to be widely used for the determination of pesticides, such as MP.

Table 3

Comparison of supramolecular microextraction developed with others microextraction procedures using different separation techniques and detectors.

Method	Analytical technique	Sample	Sample (mL)	Extractant	Disperser	Solvent (μL)	Linear range ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	EF ^a	Reference
CP	LC	Waste water and groundwater	10.0	Pole ^b	–	300	50.0–3000	1.86	–	20.0	[47]
DLLME	GC/ECD	Drinking water	5.0	Toluene	ACN	600	0.25–20.0	0.083	0.25	57.3	[10]
SDME	GC-FID	River water	10.0	Toluene	–	1.0	9.0–60.0	1.0	3.0	221	[12]
CP	LC-DE	River water	15.0	Triton X-114	–	150	0.97–58.0	0.21	–	38	[48]
SDME	GC-MS	Tap and river water	10.0	THF	–	1.0	0.15–40.0	0.05	0.15	–	[49]
VLDS-SD-DLLME	HPLC-DAD	Tap, surface and agricultural water	10.0	1-dodecanol	ACN	1100	1.0–500	0.5	1.5	78	[50]
TC-LI-DLLME	HPLC-UV	Rain, ground, reservoir and river water	10.0	[C ₆ MIM][PF ₆] ^c	–	10.0	1.0–100	0.17	–	50	[51]
DLLME-REPSM	MEKC	Tap and surface water	10.0	CH ₂ Cl ₂	ACN	2300	20–1000	5.0	–	477	[52]
IL-DLLME	HPLC-UV	Tap, well, rain and river water	5.0	[C ₈ MIM][PF ₆] ^d	MeOH	1.035	10.5–1045	0.5	–	80	[11]
VA-LLME	HPLC-UV	Waste and river water	15.0	1-Bromobutane	–	80.0	1.0–500	0.38	–	228	[13]
VA-LLME-SFO	LC-MS/MS	River water	5.0	1-Decanol	–	50.0	0.2–200	0.06	0.19	48	[14]
DLLME-SFO	LC-MS/MS	River water	5.0	1-Decanol	MeOH	540	0.5–500	0.14	0.45	43	[14]
SUPRAS	HPLC-DAD	Surface and artesian water	10.0	1-Decanol	THF	280	0.91–500	0.27	0.91	139	This work

Cloudy Point (CP); Dispersive Liquid–Liquid Microextraction (DLLME); Single-Drop Microextraction (SDME); Vortex-Assisted Low Density Solvent based on Solvent Demulsified Dispersive Liquid–Liquid Microextraction (VLDS–SD–DLLME); Temperature-Controlled Ionic Liquid Dispersive Liquid-phase Microextraction (TC-LI-DLLME); Dispersive Liquid–Liquid Microextraction combined with Reversed Electrode Polarity Stacking Mode (DLLME–REPSM); Ionic Liquid-based Dispersive Liquid–Liquid Microextraction (IL-DLLME); Vortex-Assisted Liquid–Liquid Microextraction (VALLME); Vortex Assisted Liquid–Liquid Microextraction based on Solidification of Floating Organic drop (VALLME-SFO); Dispersive Liquid–Liquid Microextraction based on Solidification of Floating Organic drop (DLLME-SFO); Gas Chromatograph coupled with Electron Capture Detector (GC/ECD); Gas Chromatography with Flame Ionization Detection (GC-FID); Liquid Chromatography with Dual Electrochemical detection (LC-DE); Gas Chromatography–Mass Spectrometry (GC-MS); Micellar Electrokinetic Chromatography (MEKC); Liquid Chromatography tandem Mass Spectrometry (LC-MS/MS).

^a Enrichment Factor (EF).

^b Polyoxyethylene 10 lauryl ether (POLE).

^c 1-Hexyl-3-methylimidazolium hexafluorophosphate [C₆MIM][PF₆].

^d 1-Octyl-3-methylimidazolium hexafluorophosphate [C₈MIM][PF₆].

3.4. Influence of other pesticides on MP microextraction

In order to evaluate the effect of possible interferents on the supramolecular microextraction process, imazethapyr, imazapic and imazepyr herbicides from the imidazolines class were evaluated. These herbicides are often used to control weeds in the rice cultivation and applied in association with organophosphorus compounds in the agriculture crop. Moreover, 2-nitrophenol and 4-nitrophenol are metabolite compounds of various nitro-organophosphorus pesticides as well as methyl parathion and, as consequence, have been considered as emerging pollutants in water sample. Thus, these nitrophenols were also evaluated as interferents.

From the results, none of the evaluated herbicides were extracted by the supramolecular phase. Such outcome might be attributed to high solubility in water of these herbicides. Herbicides with higher aqueous solubility and lower log K_{ow} values such as imazethapyr (log K_{ow} 1.49, pK_a 2.1–3.9), imazapic (log K_{ow} 0.16–0.39, pK_a 3.9) and imazepyr (log K_{ow} 0.22, pK_a 1.9–3.6) tend to be more mobile in the aqueous phase than MP, suggesting poor transfer of the herbicides to organic phase [53,54]. On the other hand, 2-nitrophenol and 4-nitrophenol were easily extracted during the supramolecular rich phase formation and then evaluated at different ratios (w/w) (Table S4). It was observed that no interference was obtained for 2-nitrophenol at 1:1 (w/w) ratio, while MP could be extracted in the presence of 4-nitrophenol up to 1:10 (w/w) ratio with recovery range varying from 93.4 to 100.1% (Fig. S1). On the basis of partition coefficient, the capacity of nitrophenols microextraction could be attributed to higher log K_{ow} , 1.79 and 1.91 for 2-nitrophenol and 4-nitrophenol, respectively, compared to herbicides from the imidazolines class. Furthermore, as the pK_a of 2-nitrophenols (6.8) and 4-nitrophenol (7.2) are higher than pH used in the microextraction (pH 6.0), these molecules are at neutral form and could be strongly extracted by nonionic decanol through hydrogen bonds [55].

3.5. Analysis of real water samples

The feasibility of practical application of proposed method was evaluated from analysis of different water samples (surface water and artesian well).

The accuracy of the suggested method was verified by means of addition and recovery tests (Table 4).

The organophosphorus was not detected in artesian well from Arapongas. On the other hand, MP was quantified in artesian well from Assis and surface water from Querência do Norte and Arapongas city with concentrations of $20.3 \pm 2.4 \mu\text{g L}^{-1}$, $12.2 \pm 3.5 \mu\text{g L}^{-1}$ and $12.7 \pm 2.6 \mu\text{g L}^{-1}$, respectively, thereby indicating a concentration above the level recommended for human consumption and suggesting a contamination of the water from cultivation crop region by organophosphorus. The recoveries value obtained from fortified samples with MP at $10.0 \mu\text{g L}^{-1}$ ranged from 92.0% to 109.9%. Thus, a good agreement was obtained between the added and recovered amounts of MP indicating the feasibility of method for interference-free determination of MP in water samples. Fig. 4 shows the chromatograms obtained from spiked and non-spiked samples.

4. Conclusion

A rapid, simple and environmentally friendly method using supramolecular extraction procedure based on reverse micelles of 1-decanol in THF/water was presented for the first time to extract and

Table 4

Application of the supramolecular proposed method for the analysis of MP in water samples (n = 3).

Sample	MP ($\mu\text{g L}^{-1}$)		Recovery (%)
	Concentration added ($\mu\text{g L}^{-1}$) \pm SD ^a	Concentration found ($\mu\text{g L}^{-1}$) \pm SD	
Surface water (Arapongas)	–	12.7 ± 2.6	–
Surface water (Querência do Norte)	10.0	21.9 ± 0.6	92.0
Artesian well (Arapongas)	–	12.2 ± 3.5	–
Artesian well (Assis)	10.0	22.6 ± 1.3	104
Artesian well (Arapongas)	–	ND	–
Artesian well (Assis)	10.0	9.2 ± 1.8	92.0
Artesian well (Assis)	–	20.3 ± 2.4	–
Artesian well (Assis)	10.0	31.3 ± 0.9	109.9

ND: not detected (below of limit of detection).

^a Standard deviation.

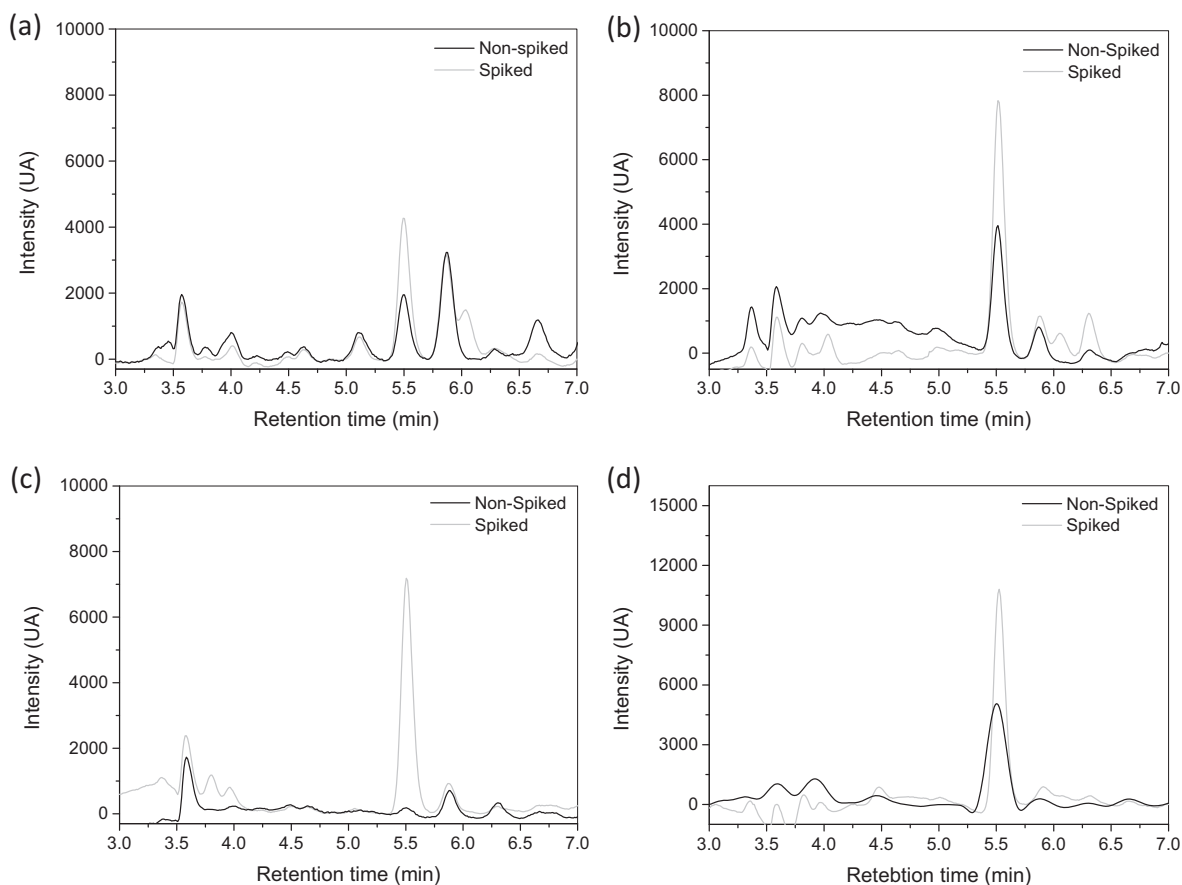


Fig. 4. Chromatograms obtained from non-spiked and spiked samples ($10.0 \mu\text{g L}^{-1}$) of (a) Arapongas (Surface water), (b) Querência do Norte (surface water), (c) Arapongas (Artesian well) and (d) Assis (Artesian well).

concentrate MP from environmental aqueous samples. A low volume of 1-decanol organic solvent was used, which is less toxic than the conventional solvents widely used in conventional LLE. The proposed method was successfully applied to MP determination in surface water and artesian well. Considering the advantages identified, the method has potential to be used as an alternative green extraction method in the field of residue analysis, such as organophosphorus (OPs) common pesticides from natural water. The presence of MP pesticides in natural waters from different regions of Brazil shows clearly the importance of investigate the use of OPs from several crop cultivations.

CRediT authorship contribution statement

Leandro L.G. de Oliveira: Validation, Formal analysis, Investigation, Data curation, Writing - original draft. **Marianne V.F. Kudo:** Validation, Formal analysis, Investigation, Data curation, Writing - original draft. **Caroline T. Lopes:** Writing - review & editing, Visualization. **César R.T. Tarley:** Conceptualization, Resources, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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