



Simultaneous microextraction of carbendazim, fipronil and picoxystrobin in naturally and artificial occurring water bodies by water-induced supramolecular solvent and determination by HPLC-DAD

Guilherme Luiz Scheel^a, César Ricardo Teixeira Tarley^{a,b,*}

^a Departamento de Química, Universidade Estadual de Londrina, Rod. Celso Garcia Cid, PR 445 Km 380, Campus Universitário, Londrina, PR, CEP, 86051-990, Brazil

^b Instituto Nacional de Ciência e Tecnologia (INCT) de Bioanalítica, Universidade Estadual de Campinas (UNICAMP), Instituto de Química, Departamento de Química Analítica, Cidade Universitária Zeferino Vaz s/n, Campinas, SP, CEP, 13083-970, Brazil

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ABSTRACT

Carbendazim, fipronil and picoxystrobin are pesticides widely utilized worldwide to enhance yield, improve quality and maximize economic returns of several cultures. However, due to potentially adverse effects to health and to ecosystems, their detection and monitoring in waters became a major concern. In this report, a new supramolecular solvent-based microextraction method, constituted of reverse micelles of 1-decanol arranged into a tetrahydrofuran/water medium, was developed to preconcentrate and monitor those pesticides in several natural and artificial waters by determination with High-Performance Liquid Chromatography – Diode Array Detector (HPLC-DAD). A 2^{6-1} fractional factorial design with central point and Derringer-Suich desirability function were utilized to optimize the microextraction conditions. High preconcentration factors (21.43 to carbendazim, 71.10 to fipronil and 71.36 to picoxystrobin) and extraction factors (21.45 to carbendazim, 84.47% to fipronil and 83.00% to picoxystrobin) were obtained. The limits of detection (LOD), quantification (LOQ), the precision (RSD-relative standard deviation) and the accuracy (RE-relative error) of the developed method ranged between 0.23 and 0.45 $\mu\text{g L}^{-1}$, 0.78–1.50 $\mu\text{g L}^{-1}$, 1.65–6.53% and 0.11–6.00%, respectively. Recovery values obtained by applying the proposed method in spiked atmospheric water, groundwater, surface water and artificial water samples at $\mu\text{g L}^{-1}$ levels varied in the range of 93.5–110.0%. The quantification of fipronil in a natural sample water, in values higher than established by some international guidelines, reassures the importance of investigating and monitoring pesticides in natural and artificial waters.

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1. Introduction

Applied by over decades on several cultures to enhance yield, improve quality and maximize economic returns, pesticides have drawn considerable attention by being often detected in naturally or artificial occurring water bodies, may affecting ecosystems and causing several health problems to animals and humans [1–4]. Less than 1% of the total amount of pesticides applied for pest control reach the target [4]. A large quantity is lost and, once into aquatic environment, can be absorbed by organisms, not only eliciting acute detectable effects, but inducing other damages like genetic disorders and physiological alterations, which reduce life span in the long run [4–7]. Carbendazim, fipronil and picoxystrobin are examples of pesticides widely employed worldwide and, due to physical-chemical characteristics such as

persistence (low degradation rate) and mobility, traces were already detected in natural and artificial waters [8–10].

As a result, different international legislations such as the European Union (EU), United States Environmental Protection Agency (USEPA) and others established maximum allowed concentrations for these pesticides [11–14]. European Union establishes the maximum value in drinking water at a concentration of 0.1 $\mu\text{g L}^{-1}$ for any individual pesticide or 0.5 $\mu\text{g L}^{-1}$ for total pesticide levels [11]. Modeled estimates made by United States Environmental Protection Agency (USEPA) to carbendazim and picoxystrobin amounts permitted in drinking water, considering chronic effects, are 860.0 $\mu\text{g L}^{-1}$ and 5.53 $\mu\text{g L}^{-1}$, respectively [12,13]. Australian guidelines for drinking water establish values for fipronil and carbendazim of 0.70 $\mu\text{g L}^{-1}$ and 90.0 $\mu\text{g L}^{-1}$, respectively [14]. Considering those strict regulation and the importance of monitoring the presence of pesticide residues at low concentrations, reliable methods with high detectability, selectivity and analytical frequency are required.

Several techniques have been exploited to determine pesticides; however, chromatographic methods have been traditionally utilized

* Corresponding author. Departamento de Química, Universidade Estadual de Londrina, Rod. Celso Garcia Cid, PR 445 Km 380, Campus Universitário, Londrina, PR, CEP, 86051-990, Brazil. Tel.: +55 041 3371 4366.

E-mail address: tarley@uel.br (C.R. Teixeira Tarley).

due to their sensitivity, reliability and efficiency [15–17]. Presently, high-performance liquid chromatography (HPLC) or gas chromatography (GC) coupled with mass spectrometry (MS) and/or tandem MS (MS/MS) seems to be the most acceptable techniques for pesticide determination. To analytes containing high to medium volatility and thermally stability, GC-MS or GC-MS/MS are the chosen techniques due the combination of high efficiency with the structural specificity of MS. However, polar, nonvolatile or thermally unstable analytes are more difficult to identify by these techniques in natural samples [18,19]. HPLC coupled with diode array detector (DAD) is also frequently utilized, by being more affordable and capable of identify several pesticides by their spectra. Comparing the analytical performances, the conventional HPLC coupled with DAD is inferior to MS or tandem MS [20]. Therefore, samples pretreat procedures are indispensable to determine pesticides at trace levels with conventional HPLC-DAD [20,21].

Miniaturized sample pretreatment procedures are an important step in pesticide analysis by presenting several advantages beyond extraction and preconcentration, such as a decrease in the use of toxic solvents and decrease/elimination of possible interfering compounds [22–24]. Among them, pretreatment with supramolecular solvent (SUPRAS) microextractants have attractive intrinsic properties for extraction processes. SUPRAS is a recent terminology to refer to nanostructured liquids produced in colloidal solutions of amphiphilic compounds (above the critical aggregation concentration) by spontaneous, sequential phenomena of self-assembly and coacervation. Those nanostructures present regions containing different polarity, offering several types of interactions to the analytes and mixed mechanisms for their solubilization [25–27].

The morphology of SUPRAS depends on the solvent nature, the solution conditions and the relative size of the head group and hydrocarbon chain of the amphiphile [28–30]. In water-induced SUPRAS composed by carboxylic acid or alkanols (nonionic amphiphile compounds) inverted hexagonal micelles are spontaneously formed into tetrahydrofuran (THF)/water medium. To the analyte microextraction, forces driving extraction are hydrogen bonding and hydrophobic, the former being an extremely effective solubilization mechanism for polar compounds [30]. The compatibility with separation and detection techniques, suitability to sample treatments adaptable to the extraction of one/ various

analytes in very different types of samples, simplicity, quickness and low cost makes SUPRAS a powerful alternative of microextractants [28–30].

In this report, the development of a method utilizing supramolecular solvent to microextract, preconcentrate and improve the HPLC-DAD sensitivity into the simultaneous determination and inspection of carbendazim, fipronil and picoxystrobin from several naturally or artificial occurring water bodies samples, is proposed. To produce the reverse micelle-based SUPRASs aggregates of alkanols, the solvent 1-decanol was utilized in THF/water medium. Multivariate optimizations were performed to select the optimal conditions of SUPRAS microextraction. To evaluate the influence of dissolved organic carbon, undoubtedly presented in those waters, interference studies were realized. Analytical features were evaluated, and the analytical performance was verified by analysis of several natural waters (atmospheric waters, surface waters and groundwaters) and artificial waters (man-made lakes) from distinct locations in Brazil.

2. Material and methods

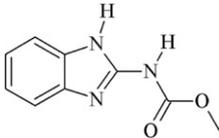
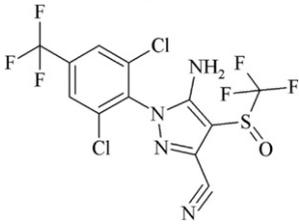
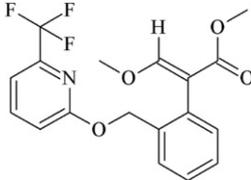
2.1. Reagents and standards

All reagents utilized were of analytical or HPLC grade and all working solutions were prepared in ultrapure water (18.2 MΩ cm) from an ELGA® PURELAB Maxima (High Wycombe, Bucks, UK) purification system. Acetonitrile (ACN, ≥ 99.9%), THF (≥99.9%) and 1-decanol (≥98.0%) were purchased from Sigma-Aldrich® (St. Louis, MO, USA) while methanol (99.9%) from Panreac® (Barcelona, Spain), all HPLC grade. The pesticide standards for carbendazim, fipronil and picoxystrobin were purchased from Sigma-Aldrich® (St. Louis, MO, USA). Individual pesticide solutions containing 100 mg L⁻¹ were prepared in methanol and stored in amber glass vials into the refrigerator. Under these conditions, they remained stable for at least three months. The working solutions containing the pesticides were prepared daily from the stock solutions by dilution with ultrapure water. Technical grade humic acid (HA) was also acquired from Sigma-Aldrich® (St. Louis, MO, USA) and a stock solution of 500 mg L⁻¹ was prepared in potassium hydroxide (KOH) 0.1 mol L⁻¹. Analytical grade sodium chloride (NaCl) was acquired by Química Moderna® (Barueri, SP, Brazil).

2.2. Apparatus

The pH values were measured with a Metrohm® laboratory digital pH meter pH 827 (Herisau, Switzerland). A SCILOGEX® MX-S vortex oscillator (Rocky Hill, CT, USA) was used to assist the supramolecular solvent-based microextraction procedure and a

Table 1
Physical and chemical properties of carbendazim, fipronil and picoxystrobin.

Pesticides	Chemical Structure ^{a,b}	Log K _{ow} ^{a,b}	Solubility in water (mg L ⁻¹) ^{a,b}	pK _a ^{a-c}
Carbendazim		1.48	29.00 (pH 4.00) 8.00 (pH 7.00) 7.00 (pH 8.00)	4.20 9.60
Fipronil		4.00	1.90–2.40	No dissociation
Picoxystrobin		3.60	3.10	No dissociation

K_{ow} = n-octanol/water partition coefficient.

^a T. Roberts, D. Huston, *Metabolic Pathways of Agrochemicals. Part II: Insecticides and Fungicides*. 1. ed. The Royal Society of Chemistry: Cambridge, 1999.

^b J. Do et al. *J. Fd Hyg. Safety*, 27, 2012.

^c Y. El Maataoui et al., *Turk. J. Chem.*, 41, 2017.

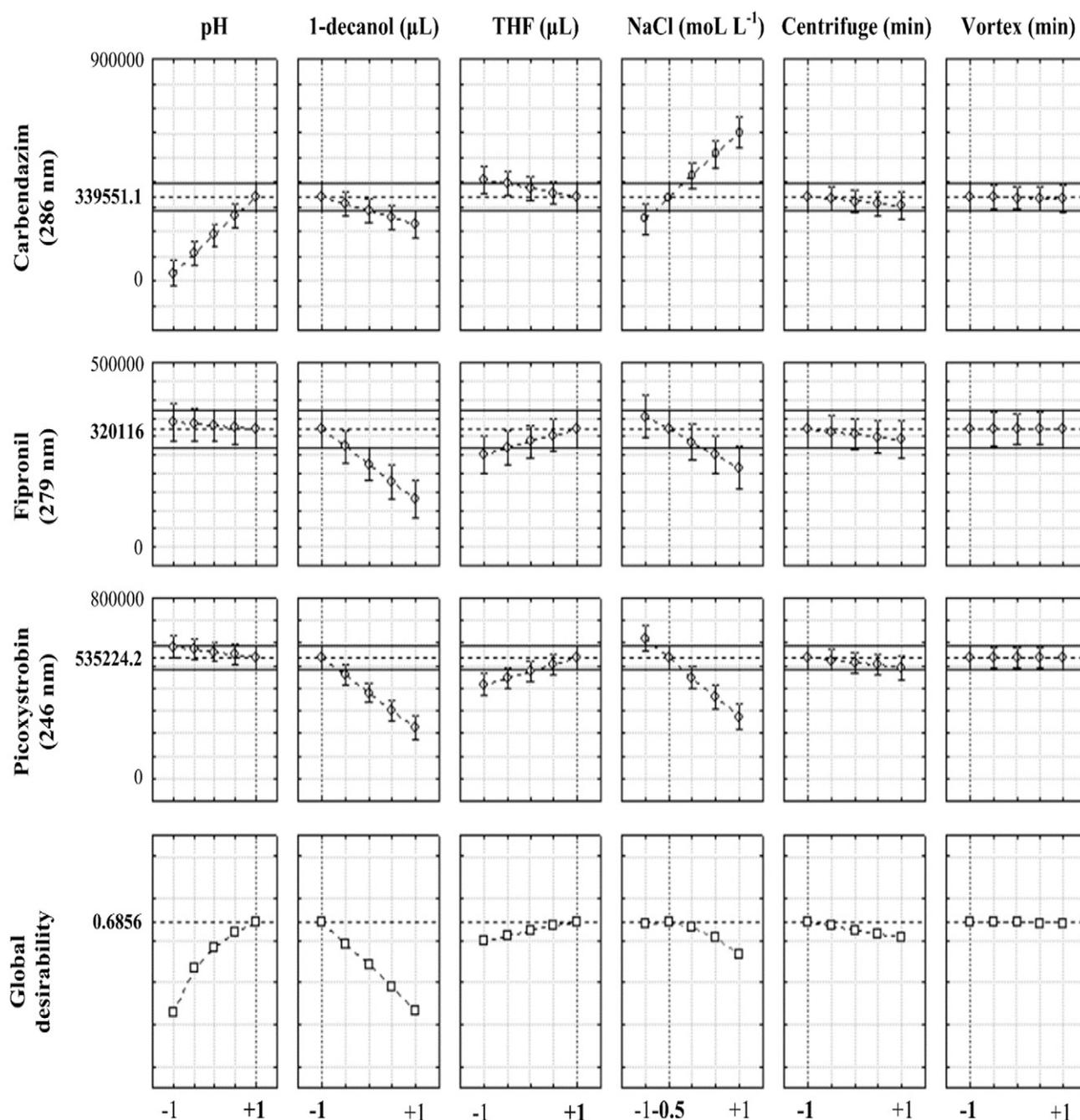


Fig. 1. Desirability function profiles and global desirability to pesticides responses obtained by the 2^{6-1} fractional factorial design with central point.

QUIMIS® 0222T2 centrifuge (Diadema, SP, Brazil) to the phase separation process. The analyzes were performed on a Shimadzu® Prominence LC-20AD/T LPGE KIT high-performance liquid chromatograph (Tokyo, Japan) with manual injection volumes of 20 μL .

2.3. HPLC analysis

For the chromatographic analysis a Kinetex core-shell C_{18} was used (250 mm \times 4.6 mm and 5 μm particle size) from Phenomenex® (Torrance, California, USA) at flow rate of 1.0 mL min^{-1} from a binary linear gradient consisting of acetonitrile and water (ACN: H_2O , v/v), wavelengths at 286 nm to carbendazim, 279 nm to fipronil and 246 nm to picoxystrobin. The gradient consisted of: ACN: H_2O (27:73, v/v), 0.00–6.00 min; ACN: H_2O (61: 39, v/v), 6.00–6.01 min; ACN: H_2O (61: 39, v/v), 6.01–20.00 min. To stabilize the column for subsequent analysis, the initial gradient was percolated by 7 min. The pesticides retention times were 7.86, 17.27 and 17.76 min for carbendazim, fipronil and picoxystrobin, respectively.

2.4. Supramolecular solvent-based microextraction procedure

In glass tubes containing 10.0 mL of pesticide solution in the concentration of 200 $\mu\text{g L}^{-1}$ and approximately 1.5 mol L^{-1} NaCl ($\approx 8.75\%$, w/v), 50 μL of 1-decanol and 500 μL of THF were added. Subsequently, the mixture was stirred by a vortex oscillator by 0.5 min (which is sufficient to spontaneously form the supramolecular solvent into solution) and subjected to centrifugation at 2000 rpm by 5 min to complete the separation of supramolecular solvent. With a Hamilton® 50 μL fixed needle syringe model 1705 N (Reno, NV, USA) the supramolecular solvent was withdrawn, transferred to microtubes and stored in refrigerator. Prior to the HPLC-DAD analysis, the samples were defrosted and diluted in methanol (1:1 v/v) for homogenization.

2.5. Multivariate optimization procedures

The SUPRAS microextraction and pre-concentration of carbendazim, fipronil and picoxystrobin was optimized by a 2^{6-1} fractional factorial design with central point

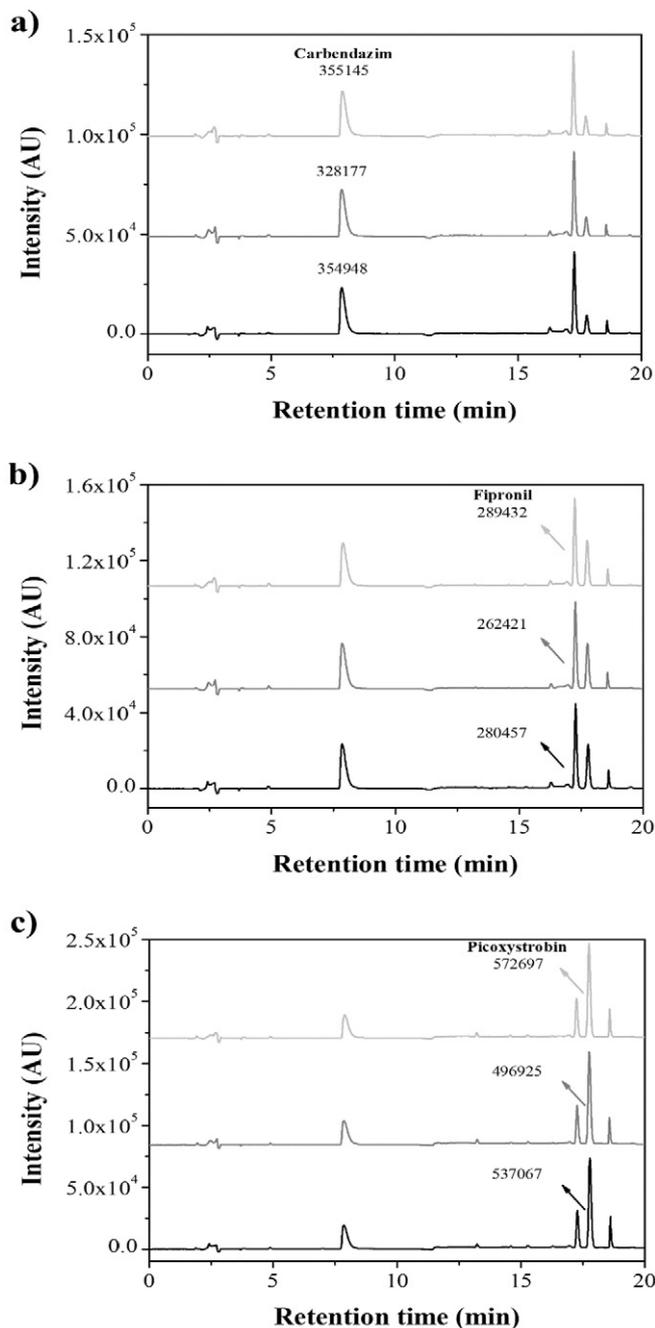


Fig. 2. Graphical representations of HPLC-DAD chromatograms to the validation triplicates (each represented by one color) of $200 \mu\text{g L}^{-1}$ pesticides solution submitted by SUPRAS microextraction under the optimized conditions and wavelengths of a) 286 nm, b) 279 nm and c) 246 nm. The respective analyzed pesticide into the selected wavelength and the obtained chromatographic areas are signaled into the representation.

considering as variables the pH, the added volume of 1-decanol, the added volume of THF, the concentration of NaCl in the solution, centrifuge time and the vortex stirring time. The lower, central and higher levels were: 3.00, 5.00 and 7.00 to the pH value; 50 μL , 125 μL and 200 μL to the volume of 1-decanol; 100 μL , 300 μL and 500 μL for the THF volume; 0.86 mol L^{-1} , 2.14 mol L^{-1} and 3.42 mol L^{-1} to NaCl concentration; 5.00 min, 12.50 min and 20.00 min to the centrifuge time; 0.50 min, 0.75 min and 1.00 min to vortex stirring time. The experiments were performed randomly and in triplicate. After the application of the 2^{6-1} fractional factorial design in the responses, the Derringer-Suich desirability function was utilized to obtain one best condition to all pesticides.

2.6. Analytical parameters procedure

Under optimized conditions and a preconcentration volume of 10.0 mL, the analytical performance of the method was evaluated by linear regressions, preconcentration factor

Table 2

Inter/intraday precision, accuracy and confidence intervals of the preconcentration of carbendazim, fipronil and picoxystrobin by SUPRAS microextraction.

Parameters	Pesticides					
	Carbendazim		Fipronil		Picoxystrobin	
Nominal concentration ($\mu\text{g L}^{-1}$)	2.00	900.00	2.00	300.00	2.00	300.00
Interday ($n^a = 10$)						
Analyzed concentration ($\mu\text{g L}^{-1}$)	2.07	894.68	2.02	308.02	1.96	308.81
Precision (RSD, %) ^b	5.63	1.65	3.25	4.22	3.09	4.00
Accuracy (RE, %) ^c	3.50	0.59	1.00	2.67	2.00	2.94
Confidence interval (t_9 , 95%)	0.08	10.60	0.05	9.29	0.04	8.84
Interday ($n^d = 3$)						
Analyzed concentration ($\mu\text{g L}^{-1}$)	2.12	901.87	2.05	303.55	2.12	299.67
Precision (RSD, %)	2.91	6.23	4.62	3.95	6.53	2.80
Accuracy (RE, %)	6.00	0.21	2.50	1.18	6.00	0.11
Confidence interval (t_2 , 95%)	0.19	18.96	0.29	12.01	0.34	20.81

^a n: number of determinations.

^b RSD (relative standard deviation) (%).

^c RE (relative error) (%).

^d n: number of days.

(PF), extraction percentage (EP), limits of quantification (LOQ) and detection (LOD), inter-intraday precision, accuracy and confidence intervals. All figures of merit were determined in accordance with international regulations [31,32] and/or according to literature [33–35]. The linear regressions were constructed by submitting sample solutions containing pesticides concentrations in the range of 25–1000 $\mu\text{g L}^{-1}$ to carbendazim and 25–400 $\mu\text{g L}^{-1}$ to fipronil and picoxystrobin to SUPRAS microextraction, in triplicate, and were evaluated by analysis of variance (ANOVA) after the addition of the respective LOQ. The PF was calculated by the ratio of slopes of the linear regressions with and without preconcentration step. The EP of pesticides was calculated by the difference between the chromatographic area values of an initial solution and the supernatant after preconcentration divided by the initial solution value, in triplicate. The LOD and LOQ were determined as $3\text{SD}/m$ and $10\text{SD}/m$, respectively, where SD is the standard deviation of ten blank measurements, and m is the slope of the calibration curve with SUPRAS preconcentration. Interday ($n = 10$) and intraday ($n = 3$) precision, accuracy and confidence intervals were calculated with two standard solutions containing 2.0 and 900.0 $\mu\text{g L}^{-1}$ to carbendazim and 2.0 and 300.0 $\mu\text{g L}^{-1}$ to fipronil and picoxystrobin. The relative standard deviations (RSD, %) were calculated to determine the precisions. Accuracy was determined by calculating the relative error percentage (RE, %).

2.7. Interference evaluation in pesticides determination

To investigate possible interferences in carbendazim, fipronil and picoxystrobin preconcentrations, solution containing different concentrations of pesticides and humic acid were subjected to supramolecular solvent microextraction procedure under optimized conditions, in triplicate. Into solutions containing 2.0, 20.0 and 200.0 $\mu\text{g L}^{-1}$ of each pesticide, volumes of HA were added to obtain concentrations of 5.0 mg L^{-1} or 12.5 mg L^{-1} . Moreover, to evaluate the temporal interference of HA over the pesticides preconcentrations, solutions containing 200 $\mu\text{g L}^{-1}$ of carbendazim, fipronil and picoxystrobin were submitted to a Novatecnica® NT155 electric orbital shaker by several days. The interference effect was estimated by carbendazim, fipronil and picoxystrobin recoveries percentages defined as the ratio between the obtained analytical concentration and the nominal concentration.

2.8. Sample collection, preparation and preservation

The natural water (atmospheric waters, surface waters and groundwaters) and artificial water (man-made lakes) samples were collected from distinct locations within four Brazilian Federative Units (Paraná, São Paulo, Rio de Janeiro and Minas Gerais). Rainfall water was collected in Londrina city, on 26 December 2018. Hailfall water was collected in Bom Jesus do Sul city, on 14 July 2018, and defrosted. Artesian well waters were collected in Londrina and Quatá cities. Stream water was collected in Londrina. Lake waters were collected in Londrina, Quatá, Apucarana and Belo Horizonte cities. Coastal seawaters were collected in Guaratuba and Rio de Janeiro cities. All samples were collected in amber glass containers and adjusted to pH 2.00 by the addition of concentrated sulfuric acid. Then, they were filtered through 0.45 μm Nylon® filters (GVS Filter Technology, Morecambe, UK) in order to remove suspended particles and stored in refrigerator under light protection until analysis.

Prior the analysis, salinity measurements were performed to the coastal seawater samples. Salinity was determined by the evaporation of seawater to dryness. The ratio between the residue and the evaporated water is the salinity [36]. Then, aliquots of 20.0 mL were added into shallow cylindrical glasses (previously weighted) and heated at 70 °C in a SLabor® SP-100/100 drying oven (Presidente Prudente, SP, Brazil) until dryness. Subsequently, the shallow cylindrical glasses containing the salts remaining as the residue were weight and by difference the total salts mass were obtained. To Guaratuba seawater the obtained evaporation salinity was $3.46 \pm 0.05\%$ (w/v) and to Rio de Janeiro

Table 3

Comparison between literature methods and the proposed method to carbendazim, fipronil or/and picoxystrobin determination.

Analytes	Preconcentration method	Linear range ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	Sample type	Detection technique	Reference
Carbendazim	–	200.0–15000.0	225.00	67.00	Water matrices	IC-hv-FD	[111]
Carbendazim	DLLME	5.0–600.0	4.00	1.20	Water and soil matrices	UV-Vis	[112]
Fipronil	SPME	5.0–200.0	4.70	1.40	Water matrices	HPLC-DAD	[113]
Fipronil	SPE (C_{18} commercial cartridges)	50.0–500.0	30.00	10.00	Water matrices	HPLC-DAD	[34]
Picoxystrobin	SBSE	30.0–5000.0	35.00	10.00	Fruits matrices	HPLC-DAD	[114]
Picoxystrobin	–	11.3–6979.2	11.30	8.40	Water and urine matrices	Anodic redissolution voltammetry	[115]
Carbendazim	SPE (SDVB cartridges)	–	0.99	0.75	Water matrices	HPLC-DAD	[116]
Fipronil	IL-DLLME	2.0–100.0	–	0.53	Water matrices	HPLC-DAD	[117]
Carbendazim	SUPRAS	1.50–1000.0	1.50	0.45	Water matrices	HPLC-DAD	This work
Fipronil	–	1.14–400.0	1.14	0.34	–	–	–
Picoxystrobin	–	0.78–400.0	0.78	0.23	–	–	–

IC-hv-FD: ion chromatography with fluorescence detector and post-column photochemical reactor; DLLME: dispersive liquid-liquid microextraction; UV-Vis: ultraviolet-visible spectrophotometry; SPME: solid phase microextraction; HPLC-DAD: high performance liquid chromatography with diode array detector; SPE: solid phase extraction; SBSE: stir bar sorptive extraction; SDVB: styrene-divinylbenzene copolymer; IL-DLLME: ionic liquid dispersive liquid-liquid microextraction; SUPRAS: supramolecular solvent.

seawater $3.60 \pm 0.02\%$ (w/v). Afterwards, to perform the SUPRAS microextraction, NaCl was added to reach the salt optimized concentration.

2.9. Computational programs

All chromatographic area values were processed utilizing the software LabSolutions® LC solution version 1.25 (Shimadzu, Tokyo, Japan). To perform and evaluate the 2^{6-1} fractional factorial design, the Derringer-Suich desirability function and its representation, the experimental data were processed with Statsoft® Statistica 7.0 software (Statsoft, Tulsa, USA). Graphical representation and ANOVA in the linear regressions were made by the software Origin® Pro 8 SR0 v8.0724(B724) (Origin Lab Corporation, MA, USA).

3. Results and discussions

3.1. Supramolecular solvent microextraction of pesticides

3.1.1. Amphiphile interactions and pesticides properties

In the microextraction by SUPRAS, understanding interactions between solvent and analytes are important to comprehend and evaluate the method. The amphiphile 1-decanol is a n-alkanol which does not dissociate ($\text{pK}_a \approx 15$), retaining the same structure throughout the pH range [37]. By having the amphiphilic nature (hydrophobic hydrocarbon tails and a polar alcohol group), 1-decanol inverted hexagonal micelles provide excellent extraction properties for a wide variety of organic compounds (such as pesticides), by interaction forces, e.g. hydrogen bonding, dipole-dipole, dipole-induced dipole and dispersive [29,30]. Nevertheless, carbendazim fipronil and picoxystrobin possess intrinsic characteristics which may influence their microextraction, as exemplified in Table 1 and further discussed.

Carbendazim or methyl-2-benzimidazolcarbamate is a systemic fungicide of the benzimidazole carbamate class used to protect and eradicate a variety of pathogens affecting a range of crops. It is a weak acid and undergoes into protonation-deprotonation reactions in aqueous solution, forming cationic, neutral or anionic species according to the pH value. With pH below the first equilibrium constant ($\text{pK}_{a1} = 4.20$), carbendazim molecules exist mainly as cations while at a pH value above the second equilibrium constant ($\text{pK}_{a2} = 9.60$) the predominant form is anionic. Between the two constants ($\text{pK}_{a1} < \text{pH} < \text{pK}_{a2}$) the molecularly neutral form is dominant [38]. Carbendazim is moderately hydrophobic ($\log K_{ow} = 1.48$) and is significantly more soluble when the pH of the medium is acidified due to protonation of the benzimidazole ring [39]. Therefore, carbendazim exhibit a pronounced hydrophilic character, interacting greatly with water and, consequently, prejudicing the interactions between the pesticide and the supramolecular solvent under certain conditions.

The pesticide fipronil, or 5-amino-1-[2,6-dichloro-4-(trifluoromethyl) phenyl]-4-[(trifluoromethyl) sulfinyl]-1H-pyrazole-3-carbonitrile, is an insecticide of class phenylpyrazoles commonly used in the control of agricultural insects as well as non-agricultural practices [40,41]. The molecule is poorly soluble in water and presents a high hydrophobic characteristic ($\log K_{ow} = 4.00$), but it also presents functional groups capable of perform hydrogen bonds, allowing hydrophilic interactions. Throughout the pH range, fipronil is presented in molecular form [39–41]. Those fipronil features quite favor mixed interactions with the supramolecular solvent composed by nonionic amphiphiles.

Picoxystrobin, or methyl (E)-3-methoxy-2-[2-(6-trifluoromethyl-2-pyridyloxymethyl) phenyl] acrylate, belongs to a relatively new class of synthetic fungicides known as strobilurins, inspired by a of natural β -methoxy-acrylic acid fungicide derivatives which have recently been introduced in agriculture because of their stability and efficacy against a wide range of pathogenic plant fungi [42,43]. The molecule has a significant hydrophobic characteristic ($\log K_{ow} = 3.60$) [44], corroborating with its low solubility in water, however, it also has functional groups capable of hydrogen bonding. Like fipronil, picoxystrobin does not show dissociation in the pH range and is favored to interact with the supramolecular solvent.

3.1.2. Multivariate optimization

The optimal conditions to carbendazim, fipronil and picoxystrobin preconcentration by SUPRAS microextraction were determined utilizing a 2^{6-1} fractional factorial design with central point and the Derringer-Suich desirability function. To the fractional factorial design, the variables values, coded levels and pesticides responses to each assay are contained in Table S1 (into supplementary data). The chromatographic area values were utilized to construct the model equations and the statistical significance was evaluated by ANOVA. Two-way interactions model showed a better fit between the variables and chromatographic area values obtained to each pesticide and, by the given resolution being VI, the binary interactions between the variables were not neglected, as showed in Equations (1)–(3).

$$\begin{aligned} \text{Carbendazim} = & 215011.3 (\pm 2902.1) + 327089.6 \times \text{pH} (\pm 6070.1) - 39892.4\text{f}1 \\ & - \text{decanol} (\mu\text{L}) (\pm 6070.1) - 18295.9 \times \text{THF} (\mu\text{L}) (\pm 6070.1) + 171500.5 \\ & \times \text{NaCl} (\text{molL}^{-1}) (\pm 6070.1) - 22007.9 \times \text{centrifuge} (\text{min}) (\pm 6070.1) - 6412.0 \\ & \times \text{vortex} (\text{min}) (\pm 6070.1) - 47932.9 \times \text{pH} \times 1 - \text{decanol} (\mu\text{L}) (\pm 6070.1) \\ & - 45618.6 \times \text{pH} \times \text{THF} (\mu\text{L}) (\pm 6070.1) + 115333.8 \times \text{pH} \times \text{NaCl} (\text{molL}^{-1}) (\pm 6070.1) \\ & - 27541.1 \times \text{pH} \times \text{centrifuge} (\text{min}) (\pm 6070.1) - 28351.6 \times 1 \\ & - \text{decanol} (\mu\text{L}) \times \text{THF} (\mu\text{L}) (\pm 6070.1) 54707.5 \times 1 - \text{decanol} (\mu\text{L}) \times \text{NaCl} (\text{molL}^{-1}) (\pm 6070.1) \end{aligned} \quad (1)$$

$$\begin{aligned} \text{Fipronil} = & 190311.0 (\pm 2698.4) - 34631.0 \times \text{pH} (\pm 5644.2) - 150099.0 \times 1 \\ & - \text{decanol} (\mu\text{L}) (\pm 5644.2) + 24938.0 \times \text{THF} (\mu\text{L}) (\pm 5644.2) - 69601.0 \\ & \times \text{NaCl} (\text{molL}^{-1}) (\pm 5644.2) - 12324.0 \times \text{centrifuge} (\text{min}) (\pm 5644.2) + 6449.0 \\ & \times \text{vortex} (\text{min}) (\pm 5644.2) - 34250.0 \times \text{pH} \times \text{NaCl} (\text{molL}^{-1}) (\pm 5644.2) - 39850.0 \\ & \times 1 - \text{decanol} (\mu\text{L}) \times \text{THF} (\mu\text{L}) (\pm 5644.2) \end{aligned} \quad (2)$$

$$\begin{aligned} \text{Picoxystrobin} = & 309522.0 (\pm 2744.9) - 77815.0 \times \text{pH} (\pm 5741.3) - 243499.0 \times 1 \\ & - \text{decanol} (\mu\text{L}) (\pm 5741.3) + 44696.0 \times \text{THF} (\mu\text{L}) (\pm 5741.3) - 184951.0 \\ & \times \text{NaCl} (\text{molL}^{-1}) (\pm 5741.3) - 17492.0 \times \text{centrifuge} (\text{min}) (\pm 5741.3) + 13142.0 \\ & \times \text{vortex} (\text{min}) (\pm 5741.3) - 68181.0 \times \text{pH} \times \text{NaCl} (\text{molL}^{-1}) (\pm 5741.3) - 66378.0 \\ & \times 1 - \text{decanol} (\mu\text{L}) \times \text{THF} (\mu\text{L}) (\pm 5741.3) + 66343.0 \times 1 - \text{decanol} (\mu\text{L}) \\ & \times \text{NaCl} (\text{molL}^{-1}) (\pm 5741.3) \end{aligned} \quad (3)$$

The model equations presented adjusted correlation coefficients values of 0.953, 0.963 and 0.961 to carbendazim, fipronil and picoxystrobin, respectively. According to ANOVA, the model equations presented adequate adjustments due to the calculated F-values of lack of fit (the ratio value between the mean square of the lack of fit and pure error) to carbendazim (14.30), fipronil (2.54) and picoxystrobin (9.69) being lower than the tabulated value ($F_{1,2} = 19.40$) at a confidence level of 95%. To all three pesticides, vortex stirring time and centrifuge time were not significant, including their binary interactions with other variables (not showed in the equations). Regarding the other variables, all presented significance, as well as some binary interactions (the non-significant were not included in the equations), however, differences between the tendencies were evidenced.

In order to conciliate the best working conditions among the obtained model equations, seeking to maximize the analytical responses, the Derringer-Suich desirability function was utilized. This function transforms the measured properties of each criterion into a dimensionless scale called desirability (d). The scale of the individual desirability function varies between $d = 0$, for a completely undesirable response, and $d = 1$, for a fully desired response, in which values above the selected would not matter. To transform the individual criteria into values of desirability, two types of transformation are possible: a unilateral and a bilateral transformation. In order to maximize the response (target value as the most desirable response), the one-sided transformation was applied according to Equation (4), where Y_i is the test response, r is the weight, L and H are the most undesirable and desirable responses of all the tests, respectively [45–48]. The weights were equal to 1 for all pesticides.

$$d_i = 0, \text{ if } Y_i \leq L \quad d_i = \left(\frac{Y_i - L}{H - L} \right)^r, \text{ if } L \leq Y_i \leq H \quad d_i = \text{QUOTE } 1, \text{ if } Y_i \geq H \quad (4)$$

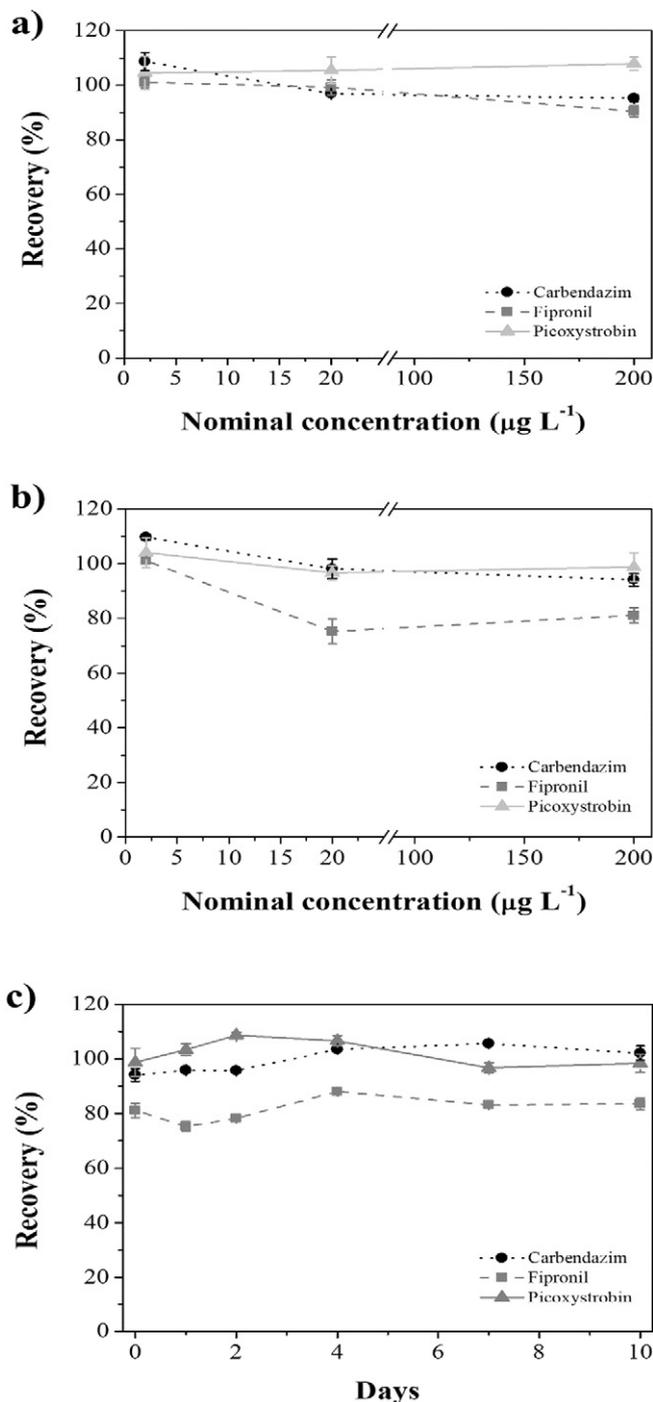


Fig. 3. Analytical recovery percentages for pre-concentration of carbendazim, fipronil and picroxystrobin in presence of humic acid at concentrations of a) 5.0 mg L⁻¹, b) 12.5 mg L⁻¹ and c) 12.5 mg L⁻¹ with time variation. (n = 3).

By having the individual desirabilities, it is possible to obtain the global desirability (D_g). The global desirability function is defined as the weighted geometric average of the individual desirabilities, Equation (5), where m is the number of responses studied in the optimization process [46–48].

$$D_g = (d_1 \times d_2 \times \dots \times d_m)^{1/m} \quad (5)$$

Obtaining these values, it is possible to obtain the best working condition for both pesticides simultaneously, the expectations of the chromatographic area values and their confidence intervals, according to Fig. 1. At pH variation, carbendazim showed a significant increase at the highest level (pH = 7.00). This is justified by the interaction improvement of carbendazim with the inverted micellar aggregates due to this pesticide being in neutral molecular form, favoring hydrogen bonds and resulting in a greater extracted amount

[49]. To fipronil and picroxystrobin, increasing the pH caused only a slight decrease in the response. Therefore, the pH value as 7.00 was indicated by D_g as the selected value. To the 1-decanol volume, all pesticides exhibited higher chromatographic area intensities in the inferior level (50 μ L). This pattern shows that higher volumes occasioned dilutions in the pesticide concentrations, decreasing the analytical responses. Then, the selected volume of 1-decanol by D_g was 50 μ L.

The increase in THF volume showed a response increase to fipronil and picroxystrobin, whereas for carbendazim it presented a decrease. In SUPRAS made up by carboxylic acids or alkanols, the increase of the organic solvent leads to an increase in the vacuole sizes of the micellar aggregates, justifying the response increase to fipronil and picroxystrobin by those pesticides being more voluminous. However, more addition of THF also results into a decrease of the amphiphile concentration in SUPRAS, may jeopardizing the extraction and preconcentration of some analytes, such as carbendazim [30,37]. To the D_g , the increase in chromatographic area intensity of the two pesticides tends to influence the selection of the highest volume of THF (500 μ L).

An increase in the ionic strength of the sample solutions can enhance the mass transfer of analytes into the organic phase. This is the “salting out” effect, in which hydration spheres around salt ions reduces the amount of water availability, shifting the partition equilibrium of neutral organic solutes [50,51]. As observed, carbendazim responses increase with the increasing of NaCl concentration, whereas to fipronil and picroxystrobin the responses decrease. By being the most hydrophilic analyzed pesticide, carbendazim requires higher amounts of salt to achieve the maximum “salting out” effect. On other hand, higher salt concentrations may decrease the diffusion kinetics of analytes into the organic phase, as observed to fipronil and picroxystrobin [51]. In D_g value, fipronil and picroxystrobin influence the selection of salt concentration values closer to the lower level while carbendazim tends to the higher level. Therefore, an intermediate NaCl concentration value of approximately 1.50 mol L⁻¹ (or 8.75% m/v) was appointed.

Vortex stirring time and centrifuge time showed small variations between the levels. Coincidentally, the lower levels (0.5 min to vortex stirring time and 5 min to centrifuge time) were selected by D_g . The confidence intervals to the chromatographic area values in the selected D_g value of 0.6856 were: 285055.9 \leq carbendazim \leq 394046.3, 269445.0 \leq fipronil \leq 370787.0 and 483681.7 \leq picroxystrobin \leq 586766.7. To validate the optimum conditions obtained by the Derringer-Suich desirability function, chromatographic analysis in those conditions were performed in triplicate, according to Fig. 2. All the obtained chromatographic area values to carbendazim, fipronil and picroxystrobin are contained in the confidence intervals.

3.2. Analytical parameters

After the insertion of the LOQ, the linear regressions of carbendazim, fipronil and picroxystrobin with SUPRAS microextraction under optimized conditions (Fig. S1) were statistically evaluated by one-way ANOVA, as showed in Table S2. At a 95% confidence level, the ratio between the mean squares of the model by the residue (F-values) gave values considerable higher than the tabulated ($F_{1,12} = 4.74$ and $F_{1,6} = 5.99$), indicating an adequate fit of the experimental data into the model. Reinforcing the adequate data adjustment, the adjusted correlation coefficients (R_{adj}) values were equal to 0.999. Moreover, the p-values of the linear regressions presented values lower than 0.05, reaffirming the coefficients significances.

To calculate PF values, linear regressions of the pesticides without preconcentration by SUPRAS microextraction were performed in concentration range between 50 and 500 μ g L⁻¹ (Fig. S1), in triplicate. Those linear regressions equations and the respective adjusted correlations coefficients are depicted in the supplementary material. The PF values were calculated by the ratio between the slopes of linear regressions with and without preconcentration by SUPRAS microextraction. To carbendazim, fipronil and picroxystrobin the obtained PF values were 21.43, 71.10 and 71.36, respectively. To EP, carbendazim, fipronil and picroxystrobin presented percentages values of 21.45%, 84.47% and 83.00%, respectively. The obtained values to LOD and LOQ were: 0.45 μ g L⁻¹ and 1.50 μ g L⁻¹ to carbendazim, 0.34 μ g L⁻¹ and 1.14 μ g L⁻¹ to fipronil and 0.23 μ g L⁻¹ and 0.78 μ g L⁻¹ to picroxystrobin. Inter/intraday precisions, accuracies and confidence intervals were calculated for pesticides, as shown in Table 2. The results presented RSD and RE lower than 7.00%, attesting little variation between the measurements and good agreement with the nominal concentration. Moreover, the obtained values were contained within the confidence intervals at a 95% confidence level.

An analytical features comparison between the proposed preconcentration method with other publications reported literature to preconcentrate or/and determine carbendazim, fipronil or picroxystrobin, mainly by HPLC-DAD, is showed in Table 3. The comparison suggests advantages of the proposed method utilizing SUPRAS microextraction, including lower or similar LOD and LOQ, short extraction time and simplicity compared with methods in which utilize adsorbent materials, since no synthesis is required. Moreover, the proposed method presents broad linear range and low values of sample and solvent volumes.

3.3. Interference evaluation

Naturally occurring organic carbon in natural and artificial waters may cause significant interferences by possible interactions with the pesticides [52,53] and/or with SUPRAS constituents. Corresponding to a major fraction of the dissolved organic carbon, humic substances are nonvolatile compounds typically composed of several functional groups (carboxylic acids, phenolic hydroxyl, carbonyl and hydroxyl groups) and are divided into fulvic and humic acids [54]. Humic acids (HAs) may provide multiple interactions

Table 4
Addition/recoveries values to distinct natural and artificial water samples. (n = 3).

Sample location	Concentration added ($\mu\text{g L}^{-1}$)			Concentration found \pm s ($\mu\text{g L}^{-1}$)			Recovery \pm s (%)		
	Carbendazim	Fipronil	Picoxystrobin	Carbendazim	Fipronil	Picoxystrobin	Carbendazim	Fipronil	Picoxystrobin
<i>Atmospheric water</i>									
Rainfall water ^a	0.00	0.00	0.00	ND	ND	ND			
	5.00	5.00	5.00	4.96 \pm 0.15	5.12 \pm 0.16	5.19 \pm 0.11	99.3 \pm 2.9	102.3 \pm 3.2	103.7 \pm 2.2
	10.00	10.00	10.00	10.59 \pm 0.31	10.68 \pm 0.22	10.58 \pm 0.30	105.9 \pm 3.1	106.8 \pm 2.2	105.8 \pm 3.0
Hailfall water ^b	0.00	0.00	0.00	ND	ND	ND			
	5.00	5.00	5.00	4.99 \pm 0.26	5.50 \pm 0.20	5.14 \pm 0.29	99.7 \pm 5.2	110.0 \pm 4.0	102.8 \pm 5.7
	10.00	10.00	10.00	9.60 \pm 0.51	9.91 \pm 0.01	10.46 \pm 0.01	96.1 \pm 5.1	99.1 \pm 0.8	104.6 \pm 1.0
<i>Surface water</i>									
Guaratuba	0.00	0.00	0.00	ND	4.51 \pm 0.30	ND			
	5.00	5.00	5.00	5.49 \pm 0.05	9.76 \pm 0.08	5.34 \pm 0.11	109.8 \pm 1.0	102.7 \pm 1.6	106.8 \pm 2.2
	10.00	10.00	10.00	10.89 \pm 0.16	14.40 \pm 0.19	10.67 \pm 0.33	108.9 \pm 0.1	99.3 \pm 0.1	106.8 \pm 0.2
Rio de Janeiro	0.00	0.00	0.00	ND	ND	ND			
	5.00	5.00	5.00	5.01 \pm 0.22	5.49 \pm 0.04	5.12 \pm 0.01	100.1 \pm 4.3	109.8 \pm 0.9	102.4 \pm 0.1
	10.00	10.00	10.00	10.83 \pm 0.20	10.46 \pm 0.38	10.41 \pm 0.16	108.3 \pm 2.0	104.6 \pm 3.8	104.1 \pm 1.6
Londrina	0.00	0.00	0.00	ND	ND	ND			
	5.00	5.00	5.00	4.90 \pm 0.06	4.75 \pm 0.20	5.00 \pm 0.18	98.08 \pm 1.1	95.0 \pm 4.0	100.0 \pm 3.7
	10.00	10.00	10.00	10.21 \pm 0.28	10.46 \pm 0.13	10.57 \pm 0.07	102.1 \pm 2.8	104.6 \pm 1.3	105.7 \pm 0.7
<i>Groundwater</i>									
Quatá	0.00	0.00	0.00	ND	ND	ND			
	5.00	5.00	5.00	4.97 \pm 0.07	5.22 \pm 0.27	5.22 \pm 0.21	99.4 \pm 1.3	104.4 \pm 5.4	104.5 \pm 4.2
	10.00	10.00	10.00	10.71 \pm 0.20	10.59 \pm 0.15	10.65 \pm 0.19	107.1 \pm 2.0	105.9 \pm 1.5	106.5 \pm 1.9
Londrina	0.00	0.00	0.00	ND	ND	ND			
	5.00	5.00	5.00	5.00 \pm 0.12	5.05 \pm 0.12	5.52 \pm 0.13	100.0 \pm 2.4	101.1 \pm 2.4	110.3 \pm 2.6
	10.00	10.00	10.00	10.82 \pm 0.15	10.47 \pm 0.57	10.61 \pm 0.15	108.3 \pm 1.6	104.7 \pm 5.6	106.1 \pm 1.5
<i>Artificial water</i>									
Belo Horizonte	0.00	0.00	0.00	ND	ND	ND			
	5.00	5.00	5.00	4.98 \pm 0.25	5.03 \pm 0.14	5.28 \pm 0.11	99.6 \pm 5.0	100.6 \pm 2.8	105.5 \pm 2.2
	10.00	10.00	10.00	10.38 \pm 0.08	10.29 \pm 0.22	10.70 \pm 0.26	103.8 \pm 0.0	102.9 \pm 0.1	106.9 \pm 0.1
Apucarana	0.00	0.00	0.00	ND	ND	ND			
	5.00	5.00	5.00	5.19 \pm 0.16	4.68 \pm 0.06	5.13 \pm 0.11	103.8 \pm 3.1	93.5 \pm 1.2	102.6 \pm 2.2
	10.00	10.00	10.00	10.34 \pm 0.18	10.58 \pm 0.52	10.84 \pm 0.06	103.4 \pm 1.8	105.8 \pm 5.2	108.4 \pm 0.6
Quatá	0.00	0.00	0.00	ND	ND	ND			
	5.00	5.00	5.00	5.13 \pm 0.24	5.13 \pm 0.04	5.19 \pm 0.20	102.7 \pm 4.7	102.6 \pm 0.8	103.9 \pm 4.8
	10.00	10.00	10.00	9.56 \pm 0.42	10.12 \pm 0.14	10.95 \pm 0.20	95.7 \pm 4.2	101.2 \pm 1.4	109.5 \pm 2.0
Londrina	0.00	0.00	0.00	ND	ND	ND			
	5.00	5.00	5.00	5.04 \pm 0.12	5.06 \pm 0.18	5.07 \pm 0.07	100.9 \pm 2.5	101.2 \pm 3.6	101.5 \pm 1.5
	10.00	10.00	10.00	9.81 \pm 0.18	10.41 \pm 0.09	10.97 \pm 0.19	98.2 \pm 1.9	104.1 \pm 0.9	109.7 \pm 1.9

s: standard deviation; ND: not detected (below the limit of detection).

with several compounds by chelation, charge-transfer interactions, dipole-dipole interaction, ion exchange reactions, π bonding, van der Waals bonding and/or hydrogen bonding due to its peculiar structure [52–54]. Therefore, two HA concentrations were evaluated as possible interferents into solutions containing different concentrations of the analyzed pesticides and temporal interference was evaluated into one solution, as showed Fig. 3.

To HA concentration of 5.0 mg L⁻¹, carbendazim, fipronil and picoxystrobin at all evaluated concentrations exhibited recoveries values between 90 and 110%, indicating satisfactorily tolerance of the SUPRAS microextraction method. To HA concentration of 12.5 mg L⁻¹, the pesticides at lowest concentrations also showed satisfactorily recoveries however, at concentration of 200.0 $\mu\text{g L}^{-1}$, fipronil presented interference. The two HA concentrations visually reduced SUPRAS content. To investigate if the HA into the higher evaluate concentration interfere by interacting with fipronil or with SUPRAS constituents, a solution containing 200 $\mu\text{g L}^{-1}$ of pesticides was keep under days with orbital agitation to mimetize a water flow, Fig. 3c.

As noted, the recovery values to fipronil continued randomly below the acceptable interval, while to carbendazim and picoxystrobin they remained satisfactory. Those results corroborate with the visual speciation, indicating lesser formation of water-induced reverse micelles due to interactions between HA and SUPRAS constituents and, consequently, forcing the analyzed pesticides to compete with themselves to occupy the micellar vacuous. Even with the presence of interference by HA in the microextraction of the higher evaluated pesticides concentration, it is worth mentioning that the highest concentration value of HA is contained in the dissolved organic carbon range for swamps, marshes and bogs. Other natural and artificial waters contain lower concentrations of dissolved organic carbon and, consequently, lower concentrations of HA [54]. In addition, the presence of HA in the chromatograms were not evidenced, demonstrating the SUPRAS properties as restricted access solvent.

3.4. Natural and artificial waters analysis

In order to evaluate the proposed method feasibility to detect and quantify carbendazim, fipronil and picoxystrobin, non-spiked and spiked samples from two artesian wells (located in Londrina and Quatá cities), three man-made lakes (located in Londrina, Apucarana and Belo Horizonte cities), one balneario (located in Quatá city), two coastal seawaters (located in Guaratuba and Rio de Janeiro cities), one stream (located

in Londrina city) and two distinct atmospheric waters (collected in Londrina and Bom Jesus do Sul cities) were submitted to SUPRAS microextraction and listed in Table 4. The recoveries obtained from samples fortified with carbendazim, fipronil and picoxystrobin at two concentrations (5.0 and 10.0 $\mu\text{g L}^{-1}$) are also listed in Table 4. Recovery values ranged from 93.5 to 110.0% were obtained, indicating the absence of matrix effect, no interference and the method feasibility to determinate simultaneously those pesticides at low levels from several water types.

Among all analyzed waters, only Guaratuba seawater presented a pesticide: fipronil at concentration of 4.51 \pm 0.30 $\mu\text{g L}^{-1}$. To illustrate the fipronil presence into Guaratuba seawater, chromatograms and DAD spectra from spiked and non-spiked samples were depicted in Fig. 4. The presence of fipronil in this water may be justified by the pesticide wide utilization in non-agricultural practices, e.g. wood preservation, topical pet care products, liquid termiticides, gel baits, granular turf products and others [55,56]. The found value is rather concerning due to be higher than the maximum allowed concentration value of fipronil to some international legislation.

4. Conclusion

The microextraction and preconcentration of carbendazim, fipronil and picoxystrobin utilizing water-induced SUPRAS composed of reverse micelles of 1-decanol arranged in THF/water medium, with determination by HPLC-DAD, proved to be suitable to determinate trace concentrations of these pesticides in natural and artificial water samples. Allying multivariate optimization procedures (fractional factorial design and Derrig-Suich desirability function), it was possible to obtain optimized conditions even with the analytes exhibiting distinct molecular behaviors. Through the validation parameters, the method proved efficiency and reliability to determinate the analyzed pesticides in atmospheric water, surface water, groundwater and artificial water samples. By not require high amounts of organic solvent (550.0 μL per

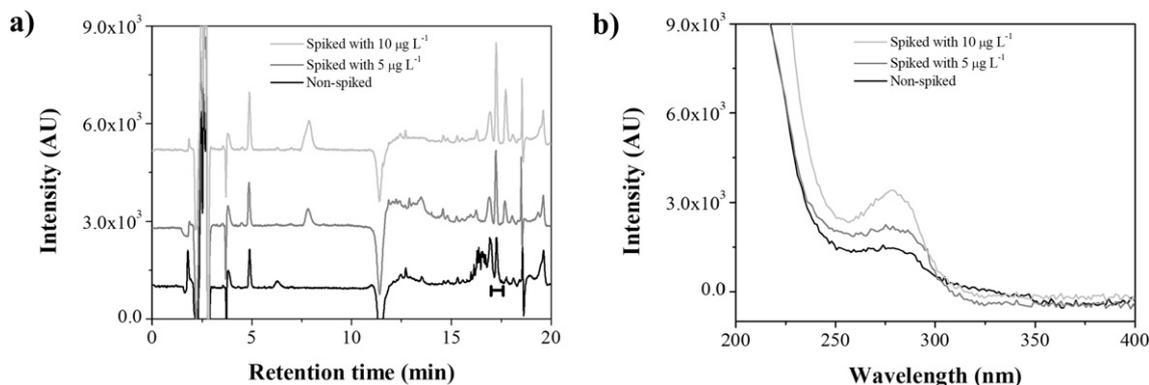


Fig. 4. Guaratuba's costal seawater a) chromatogram (with fipronil underlined) and b) DAD spectra of non-spiked and spiked samples at 279 nm.

sample), by permit direct analysis (since the extraction solvent does not need to be evaporated) and by the feasibility of freezing several samples for further analysis, the method proved to be quite simple, rapid and environmentally friendly. Moreover, the quantification of fipronil in a natural water sample, in values higher than established by some international guidelines, reassures the importance of investigating and monitoring pesticides in natural and artificial waters.

Conflicts of interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2019.111897>.

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