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Analysis of Endosulfan Isomers and other Pesticides in Surface Water of the Paraíba do Sul River Basin by Solid Phase Extraction and Comprehensive Two-Dimensional Gas Chromatography Coupled with Time-of-Flight Mass Spectrometry

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In 2008, there was a large endosulfan spill in one of the most important rivers in southeastern Brazil. However, no studies were found to assess the persistence of endosulfan in this environment. The persistence of endosulfan and its metabolites, in addition to other organochlorine pesticides, was evaluated in water samples collected from the Pirapetinga River and Paraíba do Sul River. The solid phase extraction method was modified and validated for 15 organochlorine pesticides and the hyperspeed separation method was applied using comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry. The limit of detection range was 0.38 and 17.96 ng mL^{-1} and limits of quantification were between 1.18 and 54.43 ng mL^{-1}. Endosulfan lactone was detected in the Pirapetinga River (point 4 rainy season, 255 ng mL^{-1} and point 5 dry season, 142 ng mL^{-1}), in addition to hexachlorocyclohexane (point 6 rainy season, 40.69 ng mL^{-1}).

Keywords: endosulfan, Paraíba do Sul River, Pirapetinga River, GC×GC/TOFMS, SPE

Introduction

Emerging contaminants comprise an increasing range of anthropogenic and natural substances.[1] The presence of these micropollutants, such as pharmaceuticals, personal care products (PCPs), steroid hormones, industrial chemicals, pesticides and endocrine disrupting chemicals (EDCs), in the aquatic environment, is a worldwide environmental concern.[1,2]

Organochlorine pesticides (OCPs) are widely used to control pests and diseases, being responsible for the high efficiency of agricultural production.[3] Some compounds have been recognized by the Stockholm Convention as causing adverse effects in humans and the ecosystem, such as endosulfan, hexachlorocyclohexanes (HCHs), aldrin, endrin, chlordane, dieldrin, heptachlor, and dichlorodiphenyltrichloroethane (DDD, DDE, DDT). Many studies have found that OCPs can cause serious endocrine disruption and other adverse health effects of a carcinogenic and non-carcinogenic nature.[4-6]

In November 2008, there was a spill of endosulfan (commercially composed of endosulfan α and β, endosulfan sulfate), used in the production of pesticides and insecticides, in the Pirapetinga River, in Resende, Brazil. The plume of pollution traveled 2 km along the Pirapetinga River and reached the Paraíba do Sul River, resulting in immense fish mortality.[7] This spill damaged the water supply of almost the entire population of the state of Rio de Janeiro (more than 12 million people) and affected thousands of people who live from fishing.[8] Today, this spill is registered as the biggest environmental disaster in the Paraíba do Sul River according to the Associação Pró-Gestão das Águas da Bacia Hidrográfica do Rio Paraíba do Sul (AGEVAP) diagnostic report.[9]

Endosulfan is less persistent than other organochlorine pesticides in the environment, but the half-lives of the toxic components of endosulfan (α-endosulfan, β-endosulfan and endosulfan sulfate) are between nine months and 6 years.[10] These compounds can still transform into new isomers, which are not usually analyzed. Due to its toxicity, an international treaty signed in 2001 by the Stockholm Convention agreed to eliminate or restrict the production

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of endosulfan and other persistent organic pollutants.[11] Considering the volume of endosulfan spilled in this event, it is possible that the site is still impacted by the compound or its degradation products.

The determination of pesticides in environmental matrices has become an important issue due to their potential risk, persistence and tendency to bioaccumulate.[12] Wide ranges of substances, the formation of new isomers in addition to low concentrations in aquatic systems significantly complicate the analytical method development. For trace compounds, analytical methods should include excellent extraction methods and enrichment steps before the gas chromatography (GC) analysis.[1,2,13]

Solid phase extraction (SPE) is widely used to concentrate analytes from water samples onto a relatively small amount of adsorbent and requires only small quantities of organic solvent for elution.[14] This technique has become popular for trace compound enrichment. SPE is used to monitor micropollutants in environmental water samples in conjunction with gas chromatography or liquid chromatography (LC) coupled with mass spectrometry (MS) or tandem mass spectrometry (MS/MS).[2,15-22]

Environmental analysis is on the rise with the introduction of comprehensive two-dimensional gas chromatography (GC×GC) providing a significant increase in separating power and peak capacity, as well as an increase in the overall speed of analysis.[23] Organochlorine pesticides were studied in sediment and biota[24,25] using this technique, including 160 pesticides in surface water, stem flow, and throughfall from an impacted agriculturally wetland area.[16] An other study investigated the distribution of pesticides in precipitation,[26] and the characterization of biologically active micropollutants in hospital wastewater.[27] GC×GC combined with time-of-flight mass spectrometry (TOFMS) showed reliable detection power and accurate quantification of pesticide residues even at very low concentration levels.

The objective of this study was to develop an analytical method using SPE and hyperspeed GC×GC/TOFMS separation with a consumable-free cryogenic modulator for the analysis of pesticides, and to apply the method to water samples from the region of the Paraíba do Sul River basin affected by the 2008 endosulfan accident. Therefore, the method was directed to the quantification of endosulfan and metabolites. Other OCPs were also included in the target analysis, considering the available analytical standards. Non-targeted analysis was also performed for other pesticides.

Experimental

Chemicals

The products used were reference standards purchased from Sigma-Aldrich (tetrachloro-*m*-xylene, α-HCH, β-HCH, δ-HCH, γ-HCH, heptachlor, aldrin, heptachlor-epoxide, *trans*-chlordane, α-endosulfan, chlordane, dieldrin, 4,4'DDE, endrin, β-endosulfan, 4,4'DDD, endrin aldehyde, 4,4' DDT, endosulfan sulfate, endrin ketone, methoxychlor, decachlorobiphenyl) with a concentration of 200 μg mL^{-1} in hexane and toluene 1:1. The other standards (endosulfan ether, endosulfan lactone) with 99.9% purity were purchased in bulk from Sigma-Aldrich, São Paulo, Brazil. Hexane, acetone, dichloromethane, acetonitrile, toluene, methanol, dimethyldichlorosilane suitable for GC (Bellefonte, PA, purity ≥ 99.9%) were obtained from Sigma-Aldrich, São Paulo, Brazil.

Standard solutions

The analytical curves of the method were constructed at concentration levels of 3.0 μg mL^{-1} to 1.0 ng mL^{-1}. A stock solution of 1000 μg mL^{-1} was prepared with the bulk standards of endosulfan ether and endosulfan lactone and diluted in hexane and acetone 1:1. A stock solution was prepared by combining the 200 μg mL^{-1} standard mix solution. The final concentration of the 24 analytes in these stock solutions was 10 μg mL^{-1} in dichloromethane. The stock solution of this mixture was used for further validation and recovery experiments.

Instrumentation

The GC×GC/TOFMS analysis was performed on an Agilent 7890B gas chromatography system (Agilent Technologies, Santa Clara, CA, USA) coupled to a Leco Pegasus 4D (LECO, St. Joseph, MI, USA) TOFMS mass spectrometer with a two-stage cryogenic modulator without consumables (SP Scientific, Warminster, PA, USA). A Schulz model CSV10 air compressor (Shultz, Joinville, SC, Brazil) and a Dominion SP1 UPS (CM Comandos Lineares, São Paulo, SP, Brazil) were used. Separation was achieved using a Restek Rtx-5 column (5% diphenyl/95% dimethyl polysiloxane phase) with a 10 m × 0.18 mm × 0.20 μm film thickness coupled to a Rxi-17Sil column (midpolarity silarylene phase-similar to 50% phenyl/50% dimethyl polysiloxane) with dimensions 1.0 m × 0.15 mm × 0.15 μm film thickness. A 0.50 m × 0.25 mm uncoated capillary was used in the transfer line to reduce the maintenance time.

A sample of 1 µL was injected in splitless mode using ultrahigh-purity helium as the carrier gas at a constant flow rate of 1 mL min^{-1}. The inlet and transfer line temperatures were set at 250 and 300 °C, respectively, and the ion source was set at 230 °C. The modulator temperature offset was 15 °C and the modulation period was 3 s. The modulator chiller was set at −80 °C. The mass range was set at *m/z* 45-550 u.m.a and a spectral data acquisition rate of 100 spectra s^{-1} was used with the detector voltage optimized at 300 volts above the tuning voltage. The column was set at 75 °C for 0.5 min, ramped at 20 °C min^{-1} to 280 °C (1 min hold time), and total run of 11.75 min.[28]

Data analysis

RStudio version 1.2.5033[29] was used to perform descriptive statistics. The data acquisition and processing were performed with Leco® ChromaTOF software version 4.51.6.0 (Saint Joseph, MI, USA).

Sample preparation and metabolite extraction

All samples used for the validation method and optimization studies were extracted by the modified SPE method from the literature.[30] The extraction was performed in the same week of sampling and placed in a refrigerator at 4 °C until processed. Briefly, samples were acidified with hydrochloric acid until reaching pH 2 (PH meter model JK-PHM-005, JKI, Minhang District, Shanghai, China). One liter portion was introduced by suction into the C_{18} cartridge previously conditioned with 10 mL of methanol and 10 mL of water. Target analytes were eluted from the column by passing 10 mL of dichloromethane at a maximum flowrate of approximately 10 mL min^{-1} applying a low vacuum. The extracts were evaporated to dryness under a gentle stream of nitrogen and the final extract was suspended in 2 mL of dichloromethane before injection into the GC×GC/TOFMS system.

Water samples

Samples were collected from the Pirapetinga River and the Paraíba do Sul River, in Resende, State of Rio de Janeiro, Brazil (Figure 1) between October 2021 and February 2022.

Sampling points were located in the region where a pesticide factory spilled over 8,000 L of endosulfan in the Pirapetinga River in 2008. Samples were collected in a 1 L glass bottle. The glassware used for the collection was cleaned with water and detergent, followed by distilled water to remove any impurities. After dryness, acetone was used for cleaning and, after evaporation, hexane was used to remove possible non-polar contaminants. After dryness, the glassware was heated in an oven at 280 °C for 2 h. The silanization of glass surfaces was performed with 5% dimethyldichlorosilane (DMDCS) solubilized in toluene (Sigma-Aldrich, São Paulo, Brazil), to avoid the interaction of analytes with the glass walls, increasing the efficiency of recoveries. The method was based on Čajka *et al.*[31] The locations of sampling points are shown in Table 1.

Results and Discussion

Solid phase extraction method

It was necessary to optimize the reference SPE method[30] to include endosulfan lactone and endosulfan ether as target analytes. Those organic compounds presented weak polarity, so an SPE sorbent with similar polarity facilitates enrichment.[21] An SPE sorbent used to enrich OCPs in water samples was carbon 18 reversed-phase silica.[30,32] The ideal elution solvent should be strong enough to elute all target

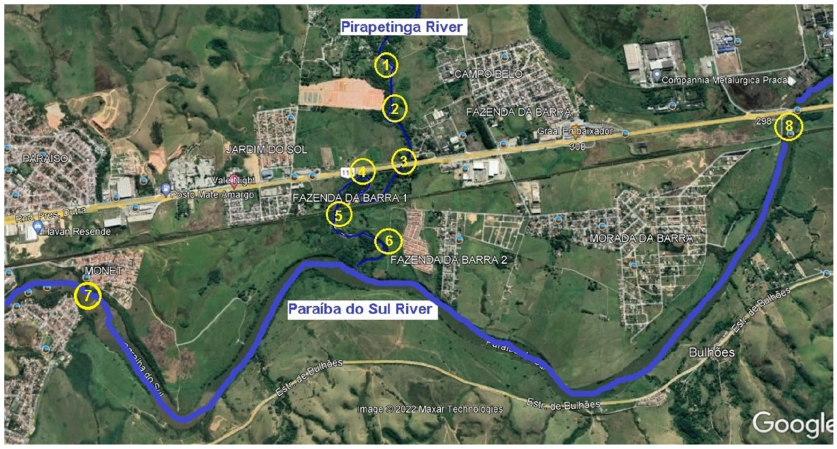

Figure 1. Map of the studied region and the affected rivers.

Table 1. Location of the water sampling points (1-8) in Resende, Brazil

Collect point	River	Location
Point 1	Pirapetinga	22°26'50.63" S 44°24'18.08" W
Point 2	Pirapetinga	22°27'6.56" S 44°24'14.34" W
Point 3	Pirapetinga	22°27'23.65" S 44°24'12.50" W
Point 4	Pirapetinga	22°27'25.71" S 44°24'24.15" W
Point 5	Pirapetinga	22°27'35.09" S 44°24'32.62" W
Point 6	Pirapetinga	22°27'46.84" S 44°24'17.57" W
Point 7	Paraíba do Sul	22°27'56.15" S 44°26'9.66" W
Point 8	Paraíba do Sul	22°27'13.37" S 44°22'13.81" W

compounds, and the elution strength of the organic solvent depends on the type of sorbent used. Dichloromethane was selected as the elution solvent.

The separation of analytes was achieved using GC×GC/TOFMS method previously reported.[23,25] According to the average theoretical peak time (ATPT) calculations, this method can be classified as hyperspeed separation.[28,33] The increased resolution and the use of columns with different polarities allow the detection of target and non-target compounds at trace-level concentrations, simultaneously. Figure 2 shows a water sample spiked with a total of 24 analytes, including 5 isomers of endosulfan.

Recovery results for all analytes studied at concentrations of 0.1, 0.2, and 0.3 μg L^{-1} are presented in Figure 3. Recoveries were calculated by comparing peak areas obtained from spiked samples to peak areas derived from an injected standard solution. The results were shown in all three levels tested and used for accuracy evaluation. Precision was evaluated considering peak area relative standard deviation (RSD).

To obtain the dispersion of the results, 3 different concentrations with 3 replicates each were evaluated in the linear range of the method.[34,35] Depending on the analytical and sample complexity, acceptable recoveries can be from 50 to 120%, with a precision of up to 15%.[34,36] Figure 3

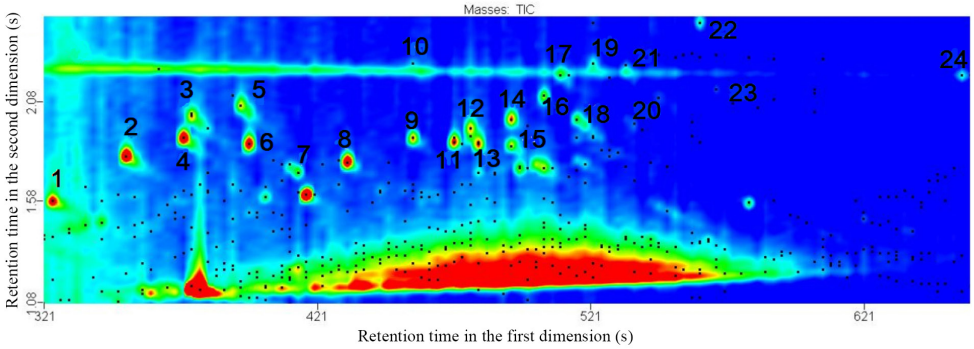

Figure 2. Chromatograms of river samples fortified with analytical standards. 1: tetrachloro-*m*-xyleno, 2: alpha HCH, 3: delta HCH, 4: beta HCH, 5: gamma HCH, 6: endosulfan ether, 7: heptachlor, 8: aldrin, 9: heptachlor epoxide, 10: endosulfan lactone, 11: *trans*-chlordane, 12: alpha endosulfan, 13: chlordano, 14: dieldrin, 15: 4,4' DDE, 16: endrin, 17: beta endosulfan, 18: 4,4' DDD, 19: endrin aldehyde, 20: 4,4' DDT, 21: endosulfan sulfate, 22: endrin ketone, 23: methoxychlor, 24: decachlorobiphenyl.

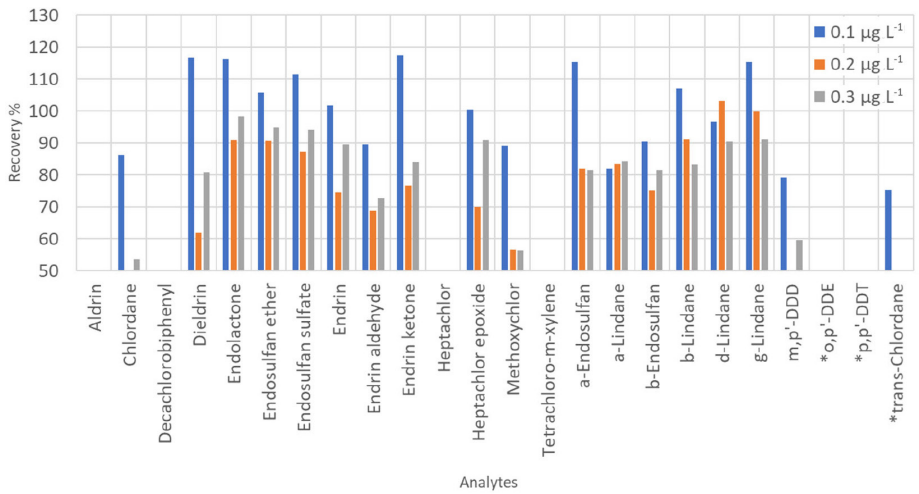

Figure 3. Recovery values of the SPE method in three concentration levels.

presents recoveries results above 50% ranging from 56.3 (methoxychlor) to 117.4% (endrin ketone). The RSD range obtained by the extraction method was from 4.2 to 19%. Aldrin, chlordane, decachlorobiphenyl, tetrachloro-*m*-xylene, dichlorodiphenyltrichloro-ethane (m,p'DDD, o,p'DDE, p,p'DDT), heptachlor and *trans*-chlordano presented recoveries below 50% and were not considered in the quantification study.

Higher recoveries were observed for the lower concentration for almost all analytes. Tsipi and Hiskia[37] obtained similar results for organochlorine pesticide and triazines in drinking water of Athens. In concentrations of 0.01 μg L^{-1}, they observed greater recoveries in relation to the concentration of 0.02 and 0.1 μg L^{-1}. For some isomers of the endrin family, the recoveries were also diverse. Considering that the analyte-ligand interactions for the C_{18} reversed phase are hydrophobic interactions of a weak nature, the large sample volume (1 L) may be responsible for removing the analyte from the stationary phase before solvent elution, resulting in a reduction in analyte recovery.

For the analysis of endosulfan (α, β and sulfate), the accuracy was obtained through recovery values in the range of 75 to 116%. The precision obtained in the replicates ranged from 4.2 to 14.8%. For the new isomers included in this study (endosulfan lactone and ether), recoveries ranged from 90.8 to 116.3% and 90.7 to 105.8% with RSD ranging from 4.2 to 14.8% and 5.9 to 12%, respectively.

Other OCP (α-HCH, β-HCH, δ-HCH, γ-HCH, heptachlor-epoxide, endrin, endrin ketone) obtained recoveries ranging from 72.6 to 119.7% and RSD ranging from 0.9 to 17.1%.

Methoxychlor obtained a recovery of 56.3 and 56.6% (200 and 300 ng mL^{-1}) with an RSD of 10.7 and 14.0%, dieldrin obtained a recovery of 62% (200 ng mL^{-1}) with an RSD of 12.9% and endrin aldehyde 68.7% of recovery (200 ng mL^{-1}) with an RSD of 13.9%. These results were similar to those obtained by Vassilakis *et al.*,[30] Pellicer-Castell *et al.*,[38] and Karadeniz and Yenisoy-Karakas.[39]

Analytical performance of SPE- GC×GC/TOFMS method

In the present method using GC×GC/TOFMS, it was possible to perform target and non-target analysis simultaneously, due to the TOFMS non-scanning principle. The analysis method used, according to Mazza *et al.*,[28] obtained limit of detection results ranging from 0.39 to 17.96 ng L^{-1}, with residual square values (R^2) greater than 0.99 and RSD values lower than 5% (n = 3). The method provided linear ranges from 1.2 to 1000 ng mL^{-1}.

It is important to emphasize that the limits of detection (LODs) and limits of quantification (LOQs) were similar to those obtained with electron capture detector (ECD) methods.[30,32,38,40] GC-ECD is considered the analytical technique with lower limits of detection for organichlorine compounds. Table 2 summarizes the comparison of the figures of merit of the obtained method with the literature.

The advantage of the application of the GC×GC/TOFMS method is the reduction of analysis time and simultaneous non-target analysis. This reduction improves drastically the sample throughput with a significant carrier gas saving. The carrier gas economy can be as high as three times in comparison with other methods from the literature,[41] or even more.[42]

The application of the consumable-free modulator is also an important point since it did not add a significant cost *per* analysis compared with conventional GC since it uses a conventional air compressor for the hot and cold jets.

Surface water samples

Sixteen surface water samples were collected between 2020 and 2021 and extracted according to the SPE-validated method. This method was successfully applied for the target analysis of the 15 OCPs and also for a non-target analysis of other pollutants.

Target analysis of the 15 OCPs determined isomers of endosulfan lactone and β-HCH. These compounds

Table 2. Analytical performance and comparison of extraction conditions of the adopted procedure

Reference	Sorbent	Analytical technique	Run time / min	LOD / (ng mL^{-1})	LOQ / (ng mL^{-1})	Recovery / %	RSD / %
This work	C_{18}	SPE-GC×GC/TOFMS	11.75	0.4-17.9	1.2-54.4	81.9-117.4	4.2-19.0
Vassilakis *et al.*[30]	C_{18}	SPE-GC-ECD	64	1.0-60.0	–	51.5-96.3	3.8-10.2
Pellicer-Castell *et al.*[38]	Au/Ti-UVM7	SPE-GC-ECD	36	0.3-20.0	1.0-61.0	62.0-118.0	4.0-22.0
Pérez-Trujillo *et al.*[40]	C_{18}/ C_{18} Hydra Chromabond	SPE-GC-ECD	32	2.4-12.0	–	70.5-92.4	1.0- 9.3
Nascimento *et al.*[41]	C_{18}/Florisil/ Chromasorb	D-μSPE-GC/MS	33	0.5-22.4	1.7-74.5	50.4-100.0	1.9-19.6
Lyytikäinen *et al.*[42]	C_{18}	SPE-GC-ECD	35.5	0.8-7.4	–	75.0-212.0	6.0-26.0

LOD: limit of detection; LOQ: limit of quantification; RSD: relative standard deviation; SPE-GC×GC/TOFMS: solid-phase extraction followed by comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry; SPE-GC-ECD: solid-phase extraction followed by gas chromatographyelectron-capture detection; D-μSPE-GC/MS: dispersive micro-solid phase extraction followed by gas chromatography mass spectrometry.

are listed as banned substances in Brazil. The endosulfan lactone analyte was detected (Figure 4) at a concentration of 142 ng mL^{-1} in the stretch of the Pirapetinga River in the dry season (point 5).

However, in January 2022 (rainy season), endosulfan was also found at point 4 with the highest concentration, 255 ng mL^{-1}. Concentrations of organochlorine pesticides, including β-HCH and endosulfan lactone in surface waters are not mentioned in the National Environment Council of Brazil, CONAMA 357/2005, but there are limits for γ-HCH and endosulfan alpha, beta and endosulfan sulfate.[43] However, it is possible that these chemicals compounds are carcinogenic, persistent, bioaccumulative, and endocrine disrupting.[11]

More polar and toxic compounds such as endosulfan diol, endosulfan ether, and endosulfan lactone are formed through biological oxidation and enzymatic oxidative processes of endosulfan alpha and beta.[44,45] With the formation of the lactone, the bioaccumulation potential and toxicity increase.[46] Another analyte found in the same period at point 6 is β-HCH with approximately 40.7 ng mL^{-1} (Figure 5).

Commercial endosulfan is a brown crystalline substance consisting of two isomers (alpha and beta) in a ratio of approximately 70:30 as stipulated in Geneva by the World Health Organization.[47] When considering residue levels, the sum of the alpha and beta isomers plus the endosulfan sulfate metabolite, which is similar in toxicity to the parent compound, must be considered. The absence of commercial isomers at the analyzed site indicates that the metabolites detected are not from recent contamination since the original compounds are degraded and not detected above de LOD.

The lactone metabolite indicates a hydrolysis process undergone by commercial isomers followed by a redox

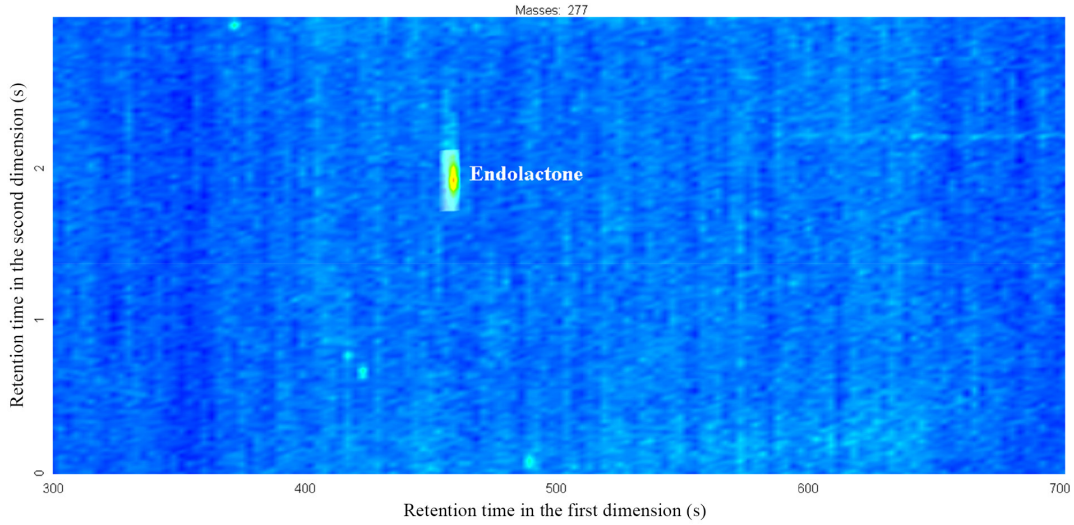

Figure 4. Endosulfan lactone analyte found in the Pirapetinga water sample from point 5.

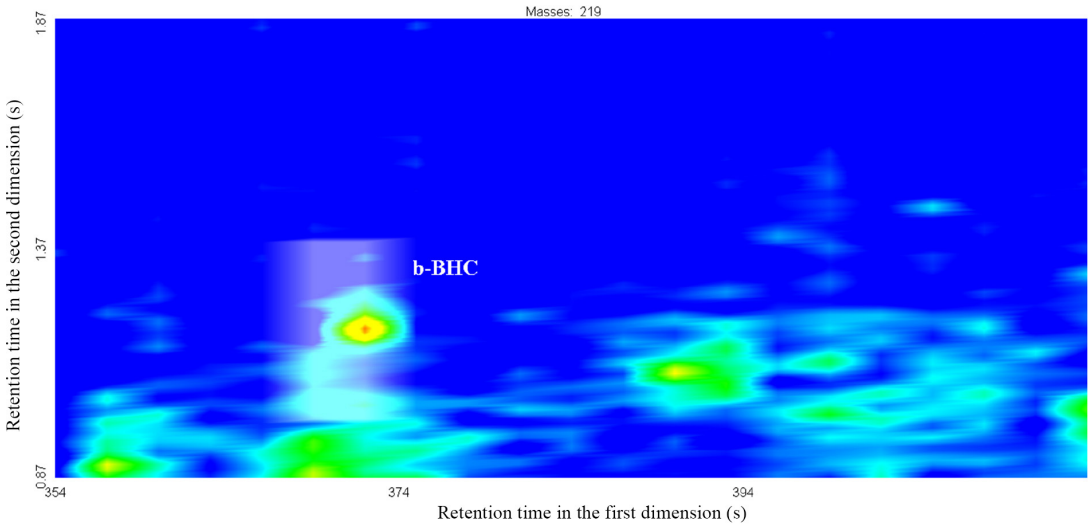

Figure 5. β-HCH analyte found in the Pirapetinga water sample from point 6.

process that lasts for long periods.[48] The possible presence of these compounds brings many risks to public health since the existing concentrations in treated water are not known and whether the water treatment process can remove them. All water treatment plants in the region applied only the conventional treatment. The clarification step is carried out with flocculators, decanters, and filters; disinfection is achieved using chlorinators and, finally the polishing, which consists of pH adjustment, correction of residual chlorine and fluoridation is done.

According to Westerhoff *et al.*,[49] conventional treatment methods remove less than 25% of the concentration of most endocrine disruptors, and the presence of a chlorination step, very common for water disinfection in Brazil, can promote a reduction of 20 to 90% at concentration levels or potentiate the formation of more toxic by-products.

Non-target analysis

The same analysis was directed to the tentative identification of non-targeted pesticides. The analytes were tentatively identified based on spectral similarity with the NIST mass spectra library in the water samples by the same GC×GC/TOFMS method. It is worth mentioning that the confirmation of the identity of these compounds could be performed with authentic analytical standards in a future study. Table 3 summarized the non-target pesticides tentatively identified in the samples from points 1 to 8 in both seasons.

Among the tentatively identified pesticides, chlorfenapyr, an insecticide/acaricide from the group of uncouplers of oxidative phosphorylation via proton gradient disruption[50] was found in the waters of the Pirapetinga River, in addition to propamocarb (carbamate), systemic fungicide, and dinocape, triazol fungicide, allowed by the Brazilian Health Regulatory Agency (ANVISA) for agricultural use. However, binapacryl, a fungicide from the dinitrophenol family that belongs to the list of ingredients banned by ANVISA,[51] was tentatively identified, as well as bensulide, an organophosphate herbicide. These results indicated that the application of target analysis of these specific pesticides can also be important in this region to better evaluate the environmental impact and persistence of unregulated pesticides.

Conclusions

The method optimized in this work for the determination of 15 organochlorine pesticides through SPE and fast-GC×GC/TOFMS was performed and successfully employed in river water samples of the Pirapetinga and the Paraíba do Sul rivers. The LOD was in the range of 0.39 to 17.96 ng mL^{-1} with a significant reduction of analysis time in comparison with analytical methods reported in the literature.

Compounds like endosulfan lactone and endosulfan ether, extended to incorporate the standard mix, obtained acceptable parameters according to figures of merit. Endosulfan lactone showed recovery of 116.26% (RSD 4.2%) with LOD and LOQ of 17.96 and 54.43 ng mL^{-1}, respectively. The endosulfan ether showed 105.81% recovery (RSD 11.5%) with LOD and LOQ of 0.87 and 2.64 ng mL^{-1}, respectively.

Endosulfan lactone was detected in two sampling points in the concentrations of 142 to 255 ng mL^{-1}. β-HCH was detected with concentration of 42 ng mL^{-1} in water samples from the Pirapetinga River. The results may indicate a high risk of contamination of 12 million people by pesticides. The water was and still is used for drinking, leisure, bathing, and fishing even after the accident 13 years ago. Persistent residues of organochlorine pesticides are known for their toxicity to both humans and aquatic life.

Although the study was carried out in a short sampling period, it can be anticipated that the obtained results are substantial subsidies for the creation of a monitoring plan of organochlorine pesticide residues along the Paraíba do Sul Basin and a study of risks to human health. In addition, it affirms the importance of controlling products destined for Brazilian agriculture.

Table 3. Pesticides tentatively identified in the water samples

Pesticide	Point	^1t_R / s	^2t_R / s	Similarity	Reverse	Area / %	S/N
Chlorfenapyr	P2	336	2.94	955	999	0.00358	19.27
Dinocape	P4	465	0.05	706	819	0.00342	26.28
Propamocarb	P6	372	0.09	692	726	0.00496	18.96
Bynapacril	P3	405	2.74	660	744	0.00106	10.34
Bensulide	P3	396	0.98	583	818	0.00706	13.47

^1t_R: the first-dimension retention time, ^2t_R: the second-dimension retention time, S/N: signal/noise.

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