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Determination of Pesticides in the Lower Sao Francisco River in Brazil

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Abstract

A significant proportion of the pesticides that are widely used in agriculture are highly toxic pollutants, despite their low concentrations. They have high capacity for polluting water, soil and air, especially during their application. The difficulty and cost of analyses to identify them and the inefficiency of conventional water treatment for human consumption, combined with the lack of legislation on this subject, has favored their accumulation in the environment. The present study was conducted in the lower part of the São Francisco River, in Brazil, between the Xingó hydroelectric power plant (municipality of Piranhas, Alagoas State [AL]) and the mouth of the river (municipality of Piaçabuçu, Alagoas State [AL]). This stretch of the river is approximately 240 km long. Water was sampled in November 2021, at transects downstream from the municipalities of Piranhas AL, Pão de Açúcar AL, Traipu AL, São Brás AL, Propriá (Sergipe State) and Penedo AL. The technique used for analytical monitoring was gas chromatography coupled to mass spectrometry (GC-MS). The presence of 14 pesticides was detected, among the 31 that were evaluated. Among the compounds identified, three are classified as extremely toxic, six are classified as highly toxic and five are classified as moderately toxic. The presence of three compounds was identified in the municipality of Pão de Açúcar and two of these were highly toxic. In Traipu, there were four compounds, among which one was extremely toxic and two were highly toxic. In São Brás, there were four compounds, among which three were the same as found in Traipu. Propriá and Penedo presented the highest diversity of pesticide contaminants, respectively nine and ten pollutants.

Keywords: Chromatography; Electric Vehicle; Emerging pollutants

Introduction

With advances in agriculture, sustainable means for combating pests that threaten food supply have increasingly been sought [1]. Pesticides are widely used against these food crop pests but their distribution can reach the wider environment in aqueous solution, especially during rainfall. They percolate down through the soil and eventually reach the groundwater [2,3]. Because of the persistence of pesticides in the environment, great mobility, high bioaccumulation and toxicity, they have become a source of pollution at the global level [4,5].

Despite the importance of pesticides for protecting and ensuring good-quality crops, they are of concern regarding human health [6,7]. Their use and the handling practices involved give rise to high levels of exposure and adverse health effects. Exposure of humans to pesticides results in immunosuppression, hormonal interruption, reduced intelligence, reproductive distortion and cancer. The impacts of this exposure can be divided into acute problems, such as the onset of Parkinson's disease, and chronic problems such as vision reduction, for example [8,9].

As a measure to protect public health, guidance levels for pesticides in drinking water have been implemented by national governments. There are several guidance values, and a few of them are issued by the World Health Organization (WHO) and the United Nations Food and Agriculture Organization (FAO), which establish acceptable levels of pesticide residues.

Currently, in Brazil, there are almost 5,000 pesticides that have been released for use. These contain more than 550 active ingredients that have been authorized by the Ministry of Agriculture for use in formulations on the market, as agricultural pesticides on crops and for plant protection products. Registration of pesticides is regulated through Decree No. 4,074/2002; this is a responsibility shared between the Ministry of Agriculture, Livestock and Supply (MAPA), Ministry of the Environment (MMA) and Ministry of Health.

Because of the risks that these pollutants bring to health and the environment, it is necessary to constantly monitor the presence of pesticides in water, with regard to the toxicity level of each compound. Moreover, to understand the effects of contaminants, it is essential to quantify and monitor concentrations at the emission source, in environmental compartments and in living organisms [10]. In Brazil, the National Water Quality Assessment Program (PNQA, 2022) aims to contribute to sustainable management of water resources and guide the development of policies for the recovery of environmental quality in inland water bodies.

Selection of these compounds for regulation is not easy to evaluate, regarding both identification and quantification. Mass spectrometry (MS), an analytical identification technique for compounds of interest, has been gaining a prominent position for use in organic environmental analyses [11]. An approach consisting of use of gas chromatography with mass spectrometry (GC-MS) combined with solid-phase microextraction (SPME) techniques is mentioned in regulated methods (ISO 27108:2013 and ASTM D 6520:2000). Such an approach is essential in order to undertake sensitive positive structural identification of pesticides and other pollutants in the environment [12].

SPME can be done in two ways: headspace mode (HS-SPME)

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or through immersion of fibers in liquid samples (direct SPME). When complex arrays are processed, HS-SPME is preferred because interference can clog the extractor that covers the fiber; analytes need to be volatile enough to pass easily into the headspace [13]. In some studies, a limitation of SPME has also been described, relating to the nature of the hydrophobic analytes that are attached to the wall of the sample containers, thereby reducing the accuracy of determinations. In this context, it is believed that on-site SPME sampling is the approach to be used in the future for resolving this problem [14].

According to FAOSTAT (2022), Brazil is considered to be the country with the highest availability of renewable water resources in the world. The São Francisco River, the main river in eastern South America, is classed in Brazil as a water body of great economic, social and ecological importance. With a length of 1,811 miles, it is the fourth largest river system on the continent and the largest river entirely in Brazil. It is an important source of hydroelectric energy, irrigation, water supply, fishing, aquaculture and navigation in the east and northeast of Brazil [15].

However, intensive anthropic use has resulted in impacts on the river. Thus, a need to adopt public policies and means for revitalization of this asset has arisen [16].

The present study was carried out on the lower São Francisco River, along the stretch of the river between the downstream side of the Xingó hydroelectric power plant, in the municipality of Piranhas, Alagoas (AL), and the mouth of the river, in the municipalities of Piaçabuçu, AL, and Brejo Grande, Sergipe (SE). For this, a single extraction procedure was established, using SPME combined with use of GC-MS, in the selected ion monitoring mode (SIM) and scanning mode (SCAN), with the aim of screening for 31 pesticides in surface waters. The methodology was applied at different sampling stations as part of a wide-ranging water quality monitoring survey, which included sampling downstream from six municipalities in the basin in order to assess the risk caused by pesticides in the São Francisco River.

Materials and methods

This study was conducted in the region of the lower São Francisco River, corresponding to the area between the municipality of Piranhas and the mouth of the river between the states of Alagoas and Sergipe. This stretch of the river is approximately 240 km long. Samples were collected in November 2021, at strategic points in the river (Table 1, Figure 1).

Initially, interviews were conducted among producers and local farmers in the lower São Francisco River region during 2020, regarding their main crops and use of agrochemicals and fertilizers. Through this, it was possible to select the main products used in the study area. The pesticide standards, totaling 31 chemical compounds, were acquired from Supelco (USA) in 1 mL ampoules. Table 2 presents some data on the monitored compounds, including: CAS (registered name for the chemical compound in the Chemical American Society database), chemical formula and molecular mass.

Table 1: Water sample collection points downstream from each municipality.

Cities	Date of collection	Geolocation of sample collection	
		Latitude	Longitude
Piranhas	11/1/2021	9°38'8.82"S	37°46'36.27"O
Pão de Açúcar	11/2/2021	9°44'52.18"S	37°27'30.02"O
Traipu	11/3/2021	9°58'20.72"S	37° 0'31.10"O
São Brás	11/4/2021	10° 7'35.06"S	36°54'56.03"O
Própria	11/5/2021	10°12'17.79"S	36°50'21.44"O
Penedo	11/7/2021	10°16'21.64"S	36°35'34.89"O

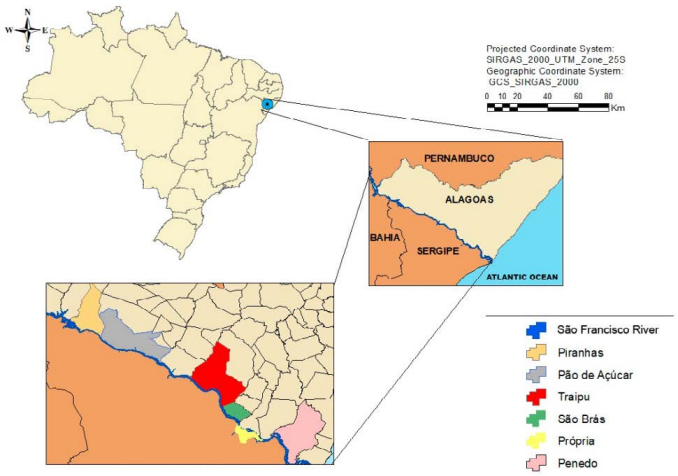

Figure 1: Geographical location of collection points.

Table 2: Compounds monitored in the lower San Francisco River.

Compounds	CAS No.	Chemical Formula	Molecular Mass ($g.mol^{-1}$)
Ethylenediaminetetraacetic acid (EDTA)	60-00-4	$C_{10}H_{16}N_2O_8$	292.2
Alpha-BHC	319-84-6	$C_6H_6Cl_6$	290.8
Beta-BHC	319-85-7	$C_6H_6Cl_6$	290.8
Lindane	58-89-9	$C_6H_6Cl_6$	290.8
Delta-BHC	319-86-8	$C_6H_6Cl_6$	290.8
Heptacloro	76-44-8	$C_{10}H_5Cl_7$	373.3
Aldrin	309-00-2	$C_{12}H_8Cl_6$	364.9
HeptachlorepoxideIsomer B	1024-57-3	$C_{10}H_5C_{l7}O$	389.4
γ-Chlordane	5103-74-2	$C_{10}H_6Cl_8$	409.7
α-Chlordane	5103-71-9	$C_{10}H_6Cl_8$	409.7
Endosulfan I (alpha)	959-98-8	$C_9H_6Cl_6O_3S$	406.9
DDE	72-55-9	C14 H8 Cl4	318
Dieldrin	60-57-1	$C_{12}H_8Cl_6O$	380.9
Endrin	72-20-8	$C_{12}H_8Cl_6O$	380.9
Endosulfan II (Beta Isomer)	33213-65-9	$C_9H_6Cl_6O_3S$	406.9
DDD	72-54-8	$(ClC_6H_4)_2CHCHCl_2$	320
Endrinaldehyde	7421-93-4	$C_{12}H_8Cl_6O$	380.9
Endosulfan sulfate	1031-07-8	$C_9H_6Cl_6O_4S$	422.9
DDT	50-29-3	$(ClC_6H_4)_2CHCCl_3$	354.4
Endrin Cetona	53494-70-5	$C_{12}H_8Cl_6O$	380.9
Methoxychlor	72-43-5	$C_{16}H_{15}Cl_3O_2$	345.6
Diquat	85-00-7	$C_{12}H_{12}N_2Br_2$	344
Metribuzin	21087-64-9	$C_8H_{14}N_4OS$	214.2
Glifosato	1071-83-6	$C_3H_8NO_5P$	169
Ametryn	834-12-8	$C_9H_{17}N_5S$	227.3
Atrazine	1912-24-9	$C_8H_{14}ClN_5$	215.6
Prometon	1610-18-0	$C_{10}H_{19}N_5O$	225.2
Prometryn	7287-19-6	$C_{10}H_{19}N_5S$	241.3
Propazine	139-40-2	$C_9H_{16}N_5Cl$	229.7
Simazine	122-34-9	$C_7H_{12}ClN_5$	201.6
Terbutryn	886-50-0	$C_{10}H_{19}N_5S$	241.3

The compounds were identified using mass spectrum data from the NIST 14 library (NIST/EPA/NIH Mass Spectra Library, version 2.2, USA), linear retention indexes, and data from the literature and pattern

injection. Linear retention indexes (LRI) were calculated in accordance with the Van den Dool equation in Kratz (1963), using n-alkane (C7 to C30) standards with purity above 99.5% (Sigma-Aldrich).

SPME procedure using headspace mode combined with GC-MS (HS-SPME/GC-MS)

To extract contaminants of interest, which had boiling points less than or equal to 270°C, solid-phase microextraction in headspace mode at 70°C was applied. 15 mL vials equipped with a 'mininert' valve (Supelco, Bellefonte, PA, USA) were accurately filled up with about 5 mL of the water samples collected.

A divinylbenzene/carboxin/polydimethylsiloxane (DVB/CAR/PDMS) fiber of film thickness 50/30 µm (Supelco, Bellefonte, PA, USA) was used, housed in a manual support (Supelco, Bellefonte, PA, USA).

A gas chromatograph was used together with an ion-trap mass spectrometer (Shimadzu, GC-MS/QP2010 Plus, Kyoto, Japan). The conditions used were the following: injector temperature, 260°C; injection mode, without division; capillary column, DB-5, 60 m long, 0.25 mm internal diameter, film thickness 0.25 µm (Agilent J&W); oven temperature, 45°C maintained for 5 min, then increased to 80°C at a rate of 10°C min^{-1} and to 240°C at 2°C min^{-1}; helium gas at a constant pressure of 100 kPa; transfer line temperature, 250°C; and acquisition range, 40-500 m/z.

Validation of the HS-SPME/GC-MS method

Preparation of standard solutions

Standard stock solutions were prepared at an approximate concentration of 1 $mg.L^{-1}$ in dichloromethane or acetone, according to the solubility of the analyte. From these solutions, a working solution was prepared at a concentration of 10 $\mu g.L^{-1}$ with all standards. For the analysis by means of HS-SPME/GC-MS in SIM mode, analytical curves were constructed at concentrations between 0.005 and 10 $\mu g.L^{-1}$. The curve values were determined and adjusted using the maximum value allowed according to CONAMA Resolution No. 357 [17], shown in the Table 3.

Calibration curve and detection and quantification limits

Linearity was determined in terms of the evolution of the regression curves of volume versus standard concentration and was expressed as the linear coefficient (R^2). The limits of detection (LD) and quantification (LQ) were determined based on the standard deviation of the intersection of the analytical curve(s) and the slope of the line(s). These are presented in Equations 1 and 2, respectively.

$$LD = 3,3\frac{s}{S}$$

$$LQ = 10\frac{s}{S}$$

Table 3: Limit values from the Brazilian legislation.

Analytical Parameters	Limit Values
	(µg L^{-1})
DDT	0.002
Aldrin	0.05
HeptachlorepoxideIsomer B	0.01
Lindane	0.02
y-Chlordane	0.04
Toluene	2

All the analyses were performed in triplicate, using the SIM mode and using the major and secondary ions. The analyses on the samples did not present peak interferents, which thus conferred selectivity to the method developed.

Results and Discussion

With the calibration curve, the linearity range investigated for six analytes (n = 6) can be seen, along with the linear correlation coefficients, LD, LQ and maximum values, as established by the Ministry of Health through Ordinance no. 518 of 2004. The presence of six compounds (Table 4), with R^2 ranging from 0.981 to 0.996, was confirmed. The detection limits for the method remained in the range of 0.005 to 1.0 $\mu g.L^{-1}$, and the quantification limits were between 0.001 and 0.003 $\mu g.L^{-1}$, i.e. in accordance with the values established by the legislation. The pesticides identified did not have values above (LQ), and therefore were below the permitted concentration, as defined by CONAMA Resolution No. 357 [17].

All the analytical monitoring was performed using gas chromatography coupled to mass spectrometry. The chromatographic profile in SIM mode is shown in Figure 2.

Table 5 shows the compounds identified through the SIM mode in the six municipalities studied along the lower São Francisco River. Table 6 shows the compounds identified in SCAN mode in the six municipalities along the lower São Francisco River.

Using the HS-SPME/GC-MS method, in SIM mode, for the municipality of Piranhas, none of the contaminants studied were detected. However, in SCAN mode, through the calculation referring to the LRI, four compounds with great toxicological potential could be identified: carbendazim, fluoroacetamide, naphthalene and toluene. The fungicide carbendazim is widely used on fruit and vegetable crops in Brazil. The chromatographic profile is shown in Figure 3.

Table 7 presents the classification applied, along with the toxicological class as defined through the Collegiate Board Resolution, RDC 294 (2019), correlated with the occurrence downstream of the municipalities.

Among the 14 compounds identified, three are classified as

Table 4: Analytical parameters obtained through SPME/GC/MS in SIM mode.

Analytical Parameters	Linear Range	R^2	*LD*	*LQ*
	(µg L^{-1})		(µg L^{-1})	(µg L^{-1})
DDT	0.005 – 0.05	0.996	0.0009	0.001
Aldrin	0.005 – 0.05	0.981	0.0008	0.002
Beta-BHC	0.05 – 0.5	0.993	0.0008	0.001
HeptachlorepoxideIsomer B	0.005 – 0.05	0.99	0.0007	0.001
Lindane	0.05 – 0.5	0.996	0.0009	0.002
y-Chlordane	0.05 – 0.5	0.989	0.0008	0.003

Table 5: Compounds identified using HS-SPME/GC-MS, SIM mode.

Analytical Parameters	Piranhas	Pão de Açúcar	Traipu	São Brás	Própria	Penedo
DDT					*cd.*	*cd.*
Aldrin					*cd.*	*cd.*
Beta-BHC					*cd.*	*cd.*
HeptachlorepoxideIsomer B			*cd.*	*cd.*		
Lindane		*cd.*	*cd.*	*cd.*	*cd.*	*cd.*
y-Chlordane					*cd.*	*cd.*

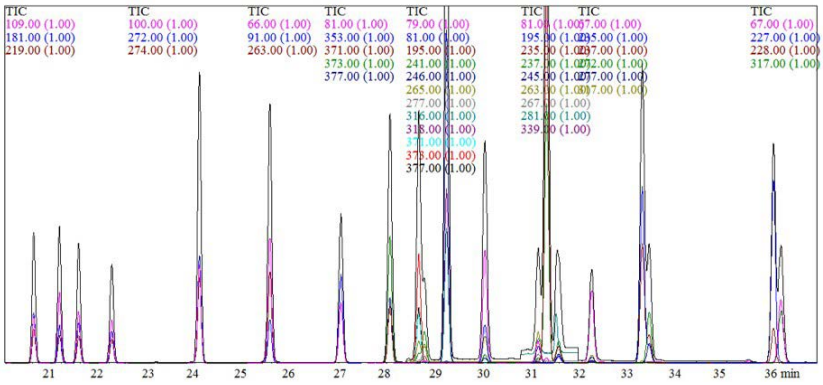

Figure 2: Chromatographic profile in SIM Mode of monitored compounds.

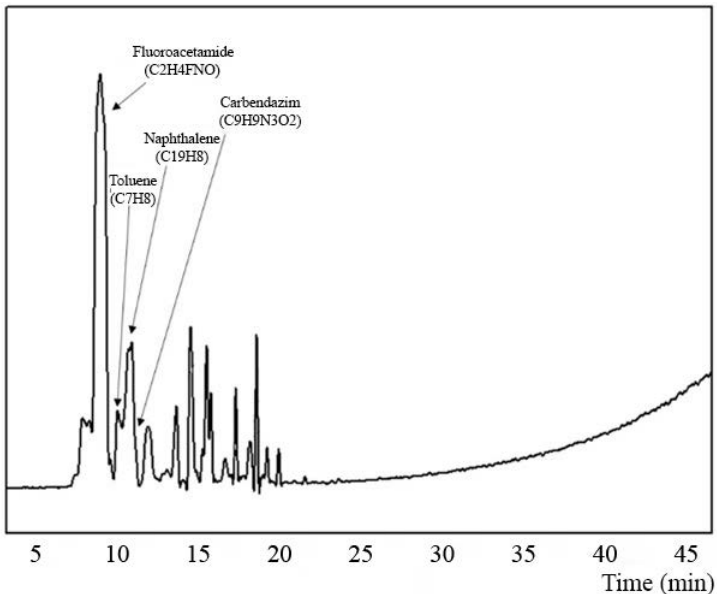

Figure 3: Chromatographic profile of the sample from the municipality of Piranhas.

Table 6: Compounds identified using HS-SPME/GC-MS, SCAN mode.

Analytical Parameters	Piranhas	Pão de Açúcar	Traipu	São Brás	Própria	Penedo
1,4-Diclorobenzene					*cd.*	*cd.*
2-Etil Hexanol						*cd.*
2,6,10,15-Tetramethylheptadecane			*cd.*			
3-Trifluoroacetoxypentadecane				*cd.*		
Carbendazim	*cd.*					
Fluoroacetamide	*cd.*	*cd.*	*cd.*	*cd.*	*cd.*	*cd.*
Naphthalene	*cd.*					
Oxima-, methoxy-phenyl-					*cd.*	*cd.*
Toluene	*cd.*	*cd.*			*cd.*	*cd.*

extremely toxic (I), six are classified as highly toxic (II) and five are classified as moderately toxic (III).

In the municipality of Pão de Açúcar, the presence of three compounds was identified: lindane, fluoroacetamide and toluene; two of these were highly toxic. In Traipu, four compounds were found: heptachlor epoxide isomer B, lindane, 2,6,10,15-tetramethyl heptadecane and fluoroacetamide; one of these was extremely toxic and two were highly toxic. In São Brás, four compounds were found: heptachlor epoxide isomer B, lindane, 3-trifluoroacetoxy pentadecane and fluoroacetamide; three of these were identical to those found in Traipu. Propriá and Penedo presented the highest diversity of pesticide contaminants: DDT, aldrin, beta-BHC, lindane, y-chlordane, 1,4-dichlorobenzene, fluoroacetamide, oxime methoxy phenyl and toluene. In addition to these, the pollutant 2-ethyl hexanol was also detected in Penedo. Therefore, in Propriá and Penedo, nine and ten pollutants out of the 31 studied were identified, respectively.

It was observed that the compound fluoroacetamide, which is an acute and highly toxic rat poison, was present in all samples collected in the six municipalities. This is a matter of great concern.

This survey aimed to identify the pesticides present in water

Table 7: Occurrence and classification of the pesticides and chemicals identified.

Analytical Parameters	Application	Toxicological Class	Occurrence
1,4-Diclorobenzene	Insecticide	III	Propriá / Penedo
2-Etil Hexanol	Organochlorine Pesticide	III	Penedo
2,6,10,15-Tetramethylheptadecane	Hydrocarbon	II	Traipu
Aldrin	Insecticide	III	Propriá / Penedo
Beta-BHC	Fungicide / Insecticide	II	Propriá / Penedo
Carbendazim	Fungicide	1	Piranhas
DDT	Insecticide	II	Propriá / Penedo
Fluoroacetamide	Insecticide	II	All
HeptachlorepoxideIsomer B	Organochlorine Pesticide	I	Traipu / São Brás
Lindane	Insecticide	II	Except Piranhas
Naphthalene	Insecticide / PAH	I	Piranhas
Oxima-, methoxy-phenyl-	Fungicide	III	Propriá / Penedo
Toluene	BTEX	III	Except Traipu e São Brás
y-Chlordane	Fungicide / Insecticide	II	Propriá / Penedo

in municipalities along the lower São Francisco River. The results demonstrated the extent to which this water body is contaminated by agrochemicals. A study by Ferreira et al. (2022) portrayed how pesticide contamination in water not only directly impacts the quality of drinking water in local areas, but also gives rise to indirect damage through transfer between species such as in the food chain and in the soil [18].

Studies have proven that combined or separate exposure to agrotoxins carries risks to human health due to the action of agents such as carcinogens, neurotoxins, toxins and endocrine disruptors [19]. In addition, pesticides may give rise to transient or permanent changes to the immune and hematological systems [20, 21]. Kim et al. (2017) also found in their experiments that exposure to agrochemicals is associated with the incidence of some diseases in the population, such as asthma, Parkinson's disease and cancer [22].

It is of great importance to detect and identify the pesticides present in rivers and other water bodies so that ways to reduce the adverse effects that these contaminants have on human health and the environment can be found.

Conclusion

The HS-SPME/GC-MS method developed in this study proved to be fundamental for determining the existence of pesticides in the lower San Francisco River, with extreme sensitivity and selectivity. It met the requirements in the range of $\mu g.L^{-1}$, even in the presence of organic matter, and at different concentrations. The SIM and SCAN modes applied in pesticide determinations showed good results, even in the presence of organic matter. The detection and quantification limits found were low, but sufficient to detect these substances, at a level lower than that established by the Brazilian legislation.

This study has proven to be very important from the point of view of alerting the population and officials responsible for public policy and the environment, and for raising their awareness. In addition, the occurrence of new "unregulated" contaminants requires more constant monitoring. Therefore, this study will provide support for implementation of new policies and specific regulations, which are fundamental for achieving and maintaining the healthy balance of the environment.

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