

REVISTA AIDIS

de Ingeniería y Ciencias Ambientales:
Investigación, desarrollo y práctica.

THEORETICAL ESTIMATE AND MULTIRESIDUE ANALYZE USING SPME-GC- IT/MS/MS FOR MANAGEMENT OF PESTICIDES IN WATER OF THE RURAL ZONE OF CEARÁ, BRAZIL

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ESTIMATIVA TEÓRICA E ANÁLISE MULTIRRESÍDUO
USANDO SPME-GC-IT/MS/MS PARA GERENCIAMENTO DE
AGROTÓXICOS EM ÁGUA DA ZONA RURAL DO CEARÁ,
BRASIL

Recibido el 30 de mayo de 2016; Aceptado el 13 de octubre de 2016

Abstract

The paper aimed to evaluate the pesticide contamination in groundwater and surface waters in Iguatu, important city of High Jaguaribe basin, in the rural zone of Ceará, Brazil. United States Environmental Protection Agency (USEPA) model, Groundwater Ubiquity Score (GUS) index (groundwater) and GOSS method (surface water) were applied to analyze the theoretical risk of contamination of water. A survey of the main active ingredients used in local crops was performed through and data collection with producers of the region. Significant percentage of substances was considered high toxicity (I and II). About 40% of the pesticides investigated showed high potential of contamination in groundwater, according EPA and GUS index. Evaluation by GOSS method showed high risk of contamination in surface waters to clethodim, lambda-cyhalothrin, paraquat, atrazine and picloram. Screening of residues using solid phase microextraction (SPME) and gas chromatography mass spectrometry (GC-IT/MS/MS) was satisfactory. It was not detected presence of pesticides in surface water and groundwater samples of rural zone of Ceará, Brazil. The toxic residues management is important to ensure the quality of water resources and the environment.

Key Words: multiresidue, SPME, chromatography, groundwater, surface water.

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Resumo

O trabalho teve como objetivo avaliar a contaminação por agrotóxicos em águas subterrâneas e superficiais em Iguatu, importante cidade da bacia do Alto Jaguaribe, na zona rural do Ceará, Brasil. Índices da Agência de Proteção Ambiental dos Estados Unidos- EPA e GUS (águas subterrâneas) e método de GOSS (água de superficial) foram aplicados para analisar o risco teórico de contaminação da água. Levantamento dos principais ingredientes ativos utilizados em culturas locais foi realizado através da coleta de dados com os produtores da região. Percentagem significativa de substâncias foi considerada elevada toxicidade (I e II). Cerca de 40% dos agrotóxicos investigados apresentaram alto potencial de contaminação nas águas subterrâneas, de acordo com índices da EPA e GUS. Avaliação pelo método de GOSS mostrou elevado risco de contaminação das águas superficiais para cletodim, lambda-cialotrina, paraquat, atrazina e picloram. *Screening* dos resíduos utilizando microextração em fase sólida (SPME) e cromatografia gasosa acoplada à espectrometria de massa (GC-IT /MS/MS) foi satisfatória. Não foi detectada presença de agrotóxicos nas águas superficiais e subterrâneas da zona rural do Ceará, Brasil. A gestão de resíduos tóxicos é importante para garantir a qualidade dos recursos hídricos e do meio ambiente.

Palavras-chave: multirresíduo, SPME, cromatografia, água subterrânea, água superficial

Introduction

The water supply is currently one of the main problems of the modern world. The level of environmental contamination by organic pollutants has grown in recent years (Amin *et al.*, 2013). Brazil has been considered the world's largest consumer of pesticides (Abrasco 2012; Milhome *et al.*, 2015).

In 2013, about 6.8 kg a.i./ha were consumed in Brazil (IBGE, 2013). National System of Toxic-Pharmacological Information (SINITOX, 2012) estimated 99,035 cases of human poisoning by pesticides in Brazil. Pesticides exposure can cause respiratory problems such as bronchitis, asthma, gastrointestinal and muscular problems, weakness to affect the central nervous system (Ye *et al.*, 2013). Thus, the control and monitoring of residue levels has been relevant (Köck-Schulmeyer *et al.* 2014; Jardim and Caldas 2012).

In rural zone of Ceará-Brazil, the basin of the High Jaguaribe has an extensive irrigated area, producing a variety of crops such as cotton, banana, bean, corn and rice. This variety of crops is susceptible to pests and the use of chemical products is intense. The dispersion of pesticides in the environment generates risk of degradation of the water and soil (Soares and Porto 2007; Cabrera *et al.*, 2008; Reemtisma *et al.*, 2013).

Potential contamination in groundwater and surface water may be evaluated by different models (Caracciolo *et al.*, 2005; Kumar *et al.*, 2015; Neh *et al.*, 2015; Brito *et al.*, 2012, Fennol *et al.*, 2014). Through the physical and chemical properties, such as the half-life in soil ($DT_{50\text{soil}}$) and the adsorption coefficient on soil organic matter (K_{oc}) is possible to predict the potential for contamination of groundwater by the United States Environmental Protection Agency (USEPA)

(Cohen *et al.*, 1995), model and Groundwater Ubiquity Score- GUS index (Gustafson, 1989). Surface water can be analyzed by GOSS method (Goss, 1992), which considers the soil half-life of the compound ($DT50_{soil}$), its water solubility and soil organic partition coefficient (K_{oc}). The application of these indices has contributed monitoring programs for determining compounds with the greatest potential for contamination of water resources.

Due to variety of chemical groups of pesticides, many researches has been carried out involving the optimization of analytical methods (Sabin *et al.*, 2009; Scheyer *et al.*, 2005; Ahumada *et al.*, 2013). The use of SPME has increased in recent years as an alternative to the traditional methods, due simplicity and wide application. The process has higher sensitivity and precision, easy handling, possibility of reuse of fiber, and does not use organic solvents (Milhome *et al.*, 2011). Gas chromatography coupled to mass spectrometry (GC-MS) has shown high efficiency and sensitivity in determining multiresidue (Lanchote *et al.*, 2000). Ion trap analyzer has been applied successfully for screening of contaminants in environmental matrices (Scheyer *et al.*, 2005; Pozzi *et al.*, 2011).

The paper aimed to the application of indices (EPA, GUS and GOSS) to determine the contamination of groundwater and surface water irrigated areas Iguatu in High Jaguaribe, Ceará, Brazil and the screening of pesticides using chromatographic method by SPME/IT-MS-MS. The results can be used for environmental agencies for managing toxic residues on water resources.

Material and Methods

Local of study and sampling

The sub-basin of the High Jaguaribe, located in the southwest of Ceará-Brazil, corresponds to greater sub-basin of state. The main tributaries of the Jaguaribe river, this stretch are the Carrapateiras, Trici, Puiu, Jucás, County, Carius, Trussu rivers and the Conception stream. Twenty-seven municipalities belong to this sub-basin, including Iguatu. The municipality has a tropical savanna climate (Köppen-geiger classification: Aw), average annual temperature of 26-28°C, with average annual rainfall of 806 mm, long periods of drought and high evaporation, with Oxisols, Ultisols and Vertisol soils (IPECE 2015; USDA, 1999).

Surface water samples were collected of the Trussu reservoir at three different sampling points, in 2015 March. Groundwater samples were collected from two representative wells of the region. Sampling sites are described in Figure 1. The samples were collected in a glass container with volume of 1 L, previously washed and then kept placed in a refrigerated environment (5 °C), following the recommendations of the *Standard Methods for the Examination of Water and Wastewater* (APHA *et al.*, 2005).

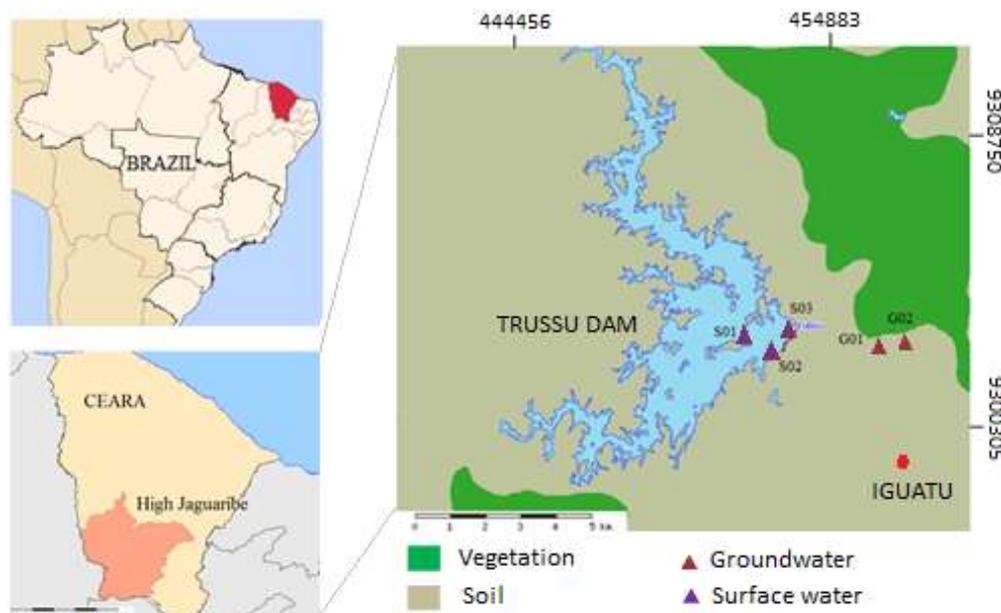


Figure 1. Location of sample points from surface water (S1, S2 and S3) and groundwater (P1 and P2) in the region of Iguatu, Ceará, Brazil.

Data collection and analysis of potential of contamination

Informations of active ingredients were obtained through technical visits at (EMATERCE) of Iguatu-CE, which professionals reported pesticides more consumed by fruit producers in the region. Table 1 shows characteristics, physicochemical properties of pesticides studied obtained from database (PPDB(a), 2016; PPDB(b), 2016) and toxicological classification (T) from National Health Surveillance Agency (Anvisa, 2015).

Then EPA (Cohen *et al.*, 1995), GUS index (Gustafson 1989) and GOSS method (Goss, 1992) were applied to evaluate the potential contamination according to the characteristics of substances used in agriculture.

The Groundwater vulnerability index- GUS (Gustafson, 1989) can be calculated based on the half-life values in soil ($DT50_{soil}$) and absorption coefficient of the organic matter in the soil (K_{oc}) of active ingredient, according to the equation 1. Based on GUS value obtained, the active ingredients are classified according to their tendency to leaching (Table 2).

Table 1. Physical and chemical properties of the main pesticides used in agriculture in Ceará, Brazil.

Pesticide	S (mg.L ⁻¹)	Log K _{ow}	pKa	VP (mPa)	H (Pa.m ³ mol ⁻¹)	DT50 _{soil} (d)	DT50 _H (d)	K _{oc} (mL.g ⁻¹)	T**
<i>Nematicide</i>									
Abamectin*	1.21	4.40	-	3.7 x10 ⁻³	2.7 x10 ⁻³	30.0	E	5,638.0	I
<i>Insecticides</i>									
Alpha-cypermethrin	0.004	5.50	5.00	3.4x10 ⁻⁴	6.9 x10 ⁻²	35.0	101.0	57,889.0	II
Beta-cyfluthrin	0.0012	5.90	-	5.6x10 ⁻⁵	8.1 x10 ⁻³	13.0	215.0	64,300.0	II
Chlorpyrifos	1.05	4.70	-	1.4	0.48	50.0	25.5	8,151.0	II
Deltamethrin	0.0002	4.60	-	1.2x10 ⁻⁵	3.1x10 ⁻²	13.0	E	10.24 x10 ⁶	III
Imidacloprid	610.0	0.57	-	4.0x10 ⁻⁷	1.7 x10 ⁻¹⁰	191.0	E	-	III
Lambda-cyhalothrin	0.005	5.50	-	2.0x10 ⁻⁴	2.0 x10 ⁻²	175.0	40	283,707.0	III
Methomyl	55,000.0	0.09	-	7.2x10 ⁻¹	2.1 x10 ⁻⁶	7.0	E	72	I
Monocrotophos	818,000.0	-0.21	-	2.9x10 ⁻¹	-	7.0	134.0	19.0	I
<i>Herbicides</i>									
Atrazine	35.0	2.70	1.70	3.9 x10 ⁻²	1.5 x10 ⁻⁴	75.0	86.0	100.0	III
Clethodim	5,450.0	4.14	4.47	2.1 x10 ⁻³	1.4 x10 ⁻⁷	0.55	E	-	II
2,4-D	24,300.0	-0.83	3.40	0.9 x10 ⁻²	4.0 x10 ⁻⁶	4.4	E	39.3	I
Ethoxysulfuron	5,000.0	1.01	5.28	6.6 x10 ⁻²	1.9 x10 ⁻³	18.0	259.0	134.0	III
Fenoxaprop-p-ethyl	0.70	4.58	0.18	5.3 x10 ⁻⁴	2.7 x10 ⁻⁴	0.4	23.2	11,354.0	II
Paraquat	620,000.0	-4.50	-	1.0 x10 ⁻²	4.0x10 ⁻¹²	3,000.0	E	1.0 x10 ⁶	I
Picloram	560.0	-1.92	2.30	8.0x10 ⁻⁵	3.0x10 ⁻⁷	82.8	E	13.0	I
<i>Fungicides</i>									
Mancozeb	6.20	1.33	10.30	1.3 x10 ⁻²	5.9x10 ⁻⁴	0.1	1.3	998.0	III
Pyrimethanil	121.0	2.84	3.52	1.10	3.6x10 ⁻³	55.0	E	-	III
Tebucunazole	36.0	3.70	5.0	1.3x10 ⁻³	1.0x10 ⁻⁰⁵	63	E	-	IV
Trifloxystrobin	0.61	4.50	-	3.4x10 ⁻³	2.3x10 ⁻³	7.0	40.0	-	II

(PPDB(a), 2016; *PPDB(b), 2016; **Anvisa, 2015). S: solubility in water (20 ° C); Kow: partition coefficient octanol/water, pH 7, 20 ° C; VP: vapor pressure (25 ° C); H: Henry constant; DT50: half-life; Koc: adsorption coefficient on organic carbon; NA: Not applicable (species not suffer ionization); E: stable

$$GUS = \log(DT50_{soil}) \times (4 - \log K_{oc})$$

Equation (1)

Table 2. Pesticides validation parameters investigated using SPME and GC-IT/MS/MS

Nº	Active principle	t _R (min)	Equation	R ²	LOD (µg/L)	LOQ (µg/L)	RSD (%)
1	Chloroneb	8.63	Y = 124.36+903.913X	0.9988	1.00	3.30	9.6
2	Propachlor	9.06	Y = -57593.4+23561.9X	0.9957	0.09	0.29	1.3
3	Molinate	9.08	Y = -17700.4+8355.79X	0.9996	0.25	0.83	7.4
4	Lambda-cyhalothrin	9.49	Y = -17553.3+5283.99X	0.9988	1.00	3.30	5.5
5	Trifluralin	10.80	Y = -1877.75+569.341X	0.9937	3.00	9.00	9.4
6	Simazine	11.73	Y = -636.17+206.889X	0.9988	0.25	0.83	6.7
7	Atrazine	11.88	Y = -10727+2252.6X	0.9992	0.25	0.83	9.8
8	Chlorothalonil	13.05	Y = -80444.5+30122.4X	0.9984	0.07	0.24	6.6
9	Parathion-methyl	14.24	Y = -26427.3+4123.41X	0.9938	0.25	0.83	10.7
10	Alachlor	14.48	Y = -52479.2+19173.1X	0.9982	0.87	2.88	11.6
11	Metalaxyl	14.65	Y = -332.44+104.88X	0.9996	0.17	0.56	10.4
12	Fenitrothion	15.21	Y = -1596040+313287X	0.9937	0.02	0.07	8.6
13	Malathion	15.53	Y = -81008.9+22332.1X	0.9969	0.18	0.59	5.6
14	Aldrin	15.63	Y = 777.585+1164.75X	0.9980	0.21	0.68	10.5
15	Carbofuran	15.70	Y = -38934.1+9376.81X	0.9788	1.07	3.52	8.4
16	Hexachlorobenzene	15.90	Y = -325447+88820.8X	0.9913	0.11	0.36	4.4
17	Metolachlor	15.78	Y = -144151+64085.7X	0.9992	0.09	0.28	11.3
18	Chlorpyrifos	15.90	Y = -443412+92621.9X	0.9951	0.07	0.23	5.6
19	Pendimethalin	17.07	Y = -1264340+160349X	0.9743	0.10	0.32	7.3
20	Chlorobenzilate	17.16	Y = -2761.47+2964.99X	0.9944	2.00	6.60	11.8
21	Triflumizole	17.92	Y = -10536+2005.81X	0.9971	1.00	3.30	7.5
22	Ametryn	19.26	Y=443.593+11.1257X	0.9999	0.25	0.83	9.7
23	Kresoxim-methyl	20.12	Y = -98534.9+24289X	0.9968	0.17	0.56	11.5
24	Triazophos	21.92	Y = -10988.1+4191.13X	0.9971	0.17	0.56	9.4
25	Bromuconazole	24.59	Y = -9299.36+4010.38X	0.9988	0.59	1.95	11.4
26	Carbosulfan	24.74	Y = -17700.4+8355.79X	0.9996	0.28	0.92	11.6
27	Fenpropathrin	25.21	Y = 6667.17+891.734X	0.9747	0.17	0.56	10.3
28	Pyriproxyfen	26.55	Y = -33599.8+13547.9X	0.9995	0.66	2.18	10.7
29	Permethrin (<i>cis</i>)	28.94	Y = 340.396+3134.73X	0.9987	0.50	1.65	9.6
30	Permethrin (<i>trans</i>)	29.25	Y = 695.334+911.3X	0.9951	1.00	3.30	9.1

Análisis multiresiduo

Certified standards for pesticides (purities exceeding 97.0%) were purchased from Sigma-Aldrich (Brazil) and Dr. Ehrenstorfer (Brazil). Chromatographic grade solvents (methanol, ethyl acetate, acetone) were acquired from Merck (Brazil).

Methods using solid-phase microextraction (SPME) and gas chromatograph coupled to ion trap mass spectrometers (GC-IT/MS-MS) were used for screening of pesticides in water samples. Table 2 shows the screening method validation parameters used for investigation of pesticides in water samples. The method has 30 pesticides that are widely applied in the predominant culture of Ceara (Guedes *et al.*, 2016; Sousa *et al.*, 2013) and some are required to monitor by water quality control legislation (Brasil, 2011)

The pesticide preconcentration was performed with polydimethylsiloxane fiber (100 μm). The conditioned fiber (1 h, at 250-300 $^{\circ}\text{C}$) was immersed into 20 mL of the aqueous solution and maintained at the equilibrium time (15min) under stirring (150 rpm) at ambient temperature ($28 \pm 2^{\circ}\text{C}$). After extraction of analyte, the fiber was thermally desorbed during 15 min into system injection of the GC-IT/MS-MS (ITQ 1100, Thermo, USA).

Pesticides separations were accomplished on RTX-5ms column (30 m x 0.25 mm x 0.25 μm). The temperature program was the following: initial temperature 100 $^{\circ}\text{C}$ held for 1 min, and 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ rate to 180 $^{\circ}\text{C}$, then 4 $^{\circ}\text{C}\cdot\text{min}^{-1}$ rate to 270 $^{\circ}\text{C}$, held for 2 min (total 33.5 min). The injection temperature was 250 $^{\circ}\text{C}$, mass ion source temperature 200 $^{\circ}\text{C}$ and MS Transfer Line 270 $^{\circ}\text{C}$. Helium was used as the carrier gas at a flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$.

Results and Discussion

Analysis of risk of groundwater contamination

Corn and bean crops predominate in rural Ceará, but banana, cotton and rice are also produced (Gama *et al.*, 2013; Milhome *et al.*, 2009). The pesticides used in agriculture of Iguatu (Table 1) belonging to a variety of chemical groups, such as pyrethroids, organophosphate, carbamate, triazine, triazole, sulfonylurea, among others. The most are applied as insecticides and herbicides, but fungicides and nematicides are also used (Figure 2a). Among the marketed products in rural zone of Ceará, a significant percentage (30% Class I and 30 % Class II) was considered of high toxicity, as shown in Figure 2b. These data indicate the need for research about the pesticides used in the region and the potential of contamination of residues in the aquifers.

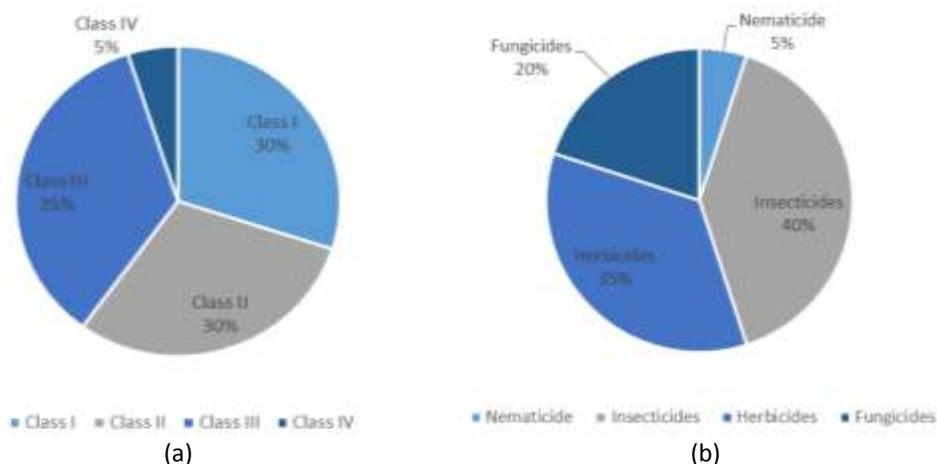


Figure 2- Distribution (%) of class(a) and toxicity (b) of pesticides applied in Iguatu-CE agriculture.

EPA and GUS index were used for the assessment of pesticide contamination potential in groundwater. According to the EPA, it is considered a pesticide with high potential for contamination is attend the following criteria:

- Solubility in water (20 ° C) > 30 mg.L⁻¹
- $K_{oc} < 300-500 \text{ mL.g}^{-1}$
- $K_H < 10^{-2} \text{ Pa.m}^3.\text{mol}^{-1}$
- Especiation (Esp): negatively charged at ambient pH (5-8)
- $DT_{50 \text{ soil}} > 14 -21 \text{ days}$
- $DT_{50 \text{ water}} > 175 \text{ days}$

GUS index values based on the parameters $DT_{50 \text{ soil}}$ and K_{oc} (characteristic each compound) are classified according to the ranges: $GUS < 1.8$: not leaching (NL); $1.8 < GUS < 2.8$: intermediate leaching (IL); $GUS > 2.8$: potential leaching (PL). The results of the analysis of the potential contamination of groundwater by using EPA and GUS indices are shown in table 3.

According to Table 3 about 60% (12) of substances are classified as high potential contaminant, based on EPA method. However, analysis of GUS index showed that only 20% (4) were considered high potential contaminant. This discrepancy occurs because the EPA method consider more parameters that GUS Index, such as solubility, especiation, K_H and $DT_{50 \text{ water}}$. Paraquat pesticide, for example, has high solubility and agree to 4 criteria of the EPA, being considered as a potential contaminant. In relation to the GUS index is shown as non-leaching ($GUS = -7.4$). So it is important to associate the two indices to assess the global risk of contamination in groundwater.

Table 3. Comparison of the method of the EPA and the GUS index for assessing the potential for groundwater contamination

Pesticide	S	K _{oc}	K _H	Esp	DT ₅₀ Soil	DT ₅₀ water	Results of EPA	GUS index	Results of GUS	Global Risk in groundwater
Nematicide										
Abamectin*	□	□	■		■	■	PC	0.37	NL	IN
Insecticides										
Alpha-cypermethrin	□	□	□	■	■	■	IN	-1.53	NL	NC
Beta-cyfluthrin	□	□	■		□	■	NC	-1.17	NL	NC
<u>Chlorpyrifos</u>	□	□	□		■	□	NC	0.17	NL	NC
<u>Deltamethrin</u>	□	□	□		□	■	NC	-4.26	NL	NC
<u>Imidacloprid</u>	■		■		■	■	PC	3.74	PL	PC
<u>Lambda-cyhalothrin</u>	□	□	□		■	□	NC	-3.28	NL	NC
<u>Methomyl</u>	■	■	■		□	■	PC	2.19	TZ	PC
<u>Monocrotophos</u>	■	■			□	■	PC	2.30	TZ	PC
Herbicides										
Atrazine	■	■	■	■	■	□	PC	3.20	PL	PC
<u>Clethodim</u>	■		■	■	□	■	PC	-0.69	NL	IN
2,4-D	■	■	■	■	□	■	PC	1.69	NL	IN
<u>Ethoxysulfuron</u>	■	■	■	■	■	■	PC	2.02	TZ	PC
<u>Fenoxaprop-p-ethyl</u>	□	□	■	■	□	□	NC	0.02	NL	NC
<u>Paraquat</u>	■	□	■		■	■	PC	-7.4	NL	IN
<u>Picloram</u>	■	■	■	■	■	■	PC	6.03	PL	PC
Fungicides										
<u>Mancozeb</u>	□	□	■	□	□	□	NC	-1.00	NL	NC
Pyrimethanil	■		■	■	■	■	PC	2.65	TZ	PC
Tebucunazole	■		■	■	■	■	PC	2.85	PL	PC
Trifloxystrobin	□		■		□	□	NC	0.19	NL	NC

■ agrees with the EPA criteria; □: disagrees with the EPA criteria; PC: potential contaminant; IN: intermediate potential contamination; NC: not contaminant ; |: Inconclusive (not available data)); PL: potential leaching; TZ: transition zone; LN: no leaching. * Result of the risk of contamination in groundwater considering the two indices (EPA and GUS)

The method of Goss (1992), proposes criteria that classify each active ingredient in high, medium or low potential contamination of surface water, through transport associated with the sediment or dissolved in water. The parameters of classification are summarized in Table 4. Compounds that do not belong to any criterion (high or low) are considered as moderate potential of transport (Andrade *et al.*, 2011).

The results of risk of contamination in groundwater and surface water can be summarized according to figure 3(a) and 3(b), respectively. Among the active principles studied, only three (15%) showed high TAS: clethodim, lambda-cyhalothrin and paraquat. According to Figure 3(b) the most (35%) had low TAS. For TDW, about 45% (9 pesticides) showed moderate potential contamination. Atrazine, clethodim, paraquat and picloram had high TDW. Due to the absence of some Koc values, inconclusive analysis (I) were obtained for three pesticides (15%)

Table 4. GOSS method for assessing the potential for contamination of surface water.

GOSS Method			
Transport associated with the sediment (TAS)		Transport dissolved in water (TDW)	
Criteria	Classification	Criteria	Classification
$DT50_{soil} \geq 40$; $K_{oc} \geq 1000$	High potential	$DT50_{soil} > 35$; $K_{oc} < 100000$; $S \geq 1$	High potential
$DT50_{soil} \geq 40$; $K_{oc} \geq 500$; $S \leq 0.5$		$DT50_{soil} < 35$; $K_{oc} \leq 700$; $10 \leq S \leq 100$	
$DT50_{soil} < 1$		$K_{oc} \geq 100000$	
$DT50_{soil} \leq 2$; $K_{oc} \leq 500$	Low potential	$DT50_{soil} \leq 1$; $K_{oc} \geq 1000$	Low potential
$DT50_{soil} \leq 4$; $K_{oc} \leq 900$; $S \geq 0.5$		$DT50_{soil} < 35$; $S < 0.5$	
$DT50_{soil} \leq 40$; $K_{oc} \leq 500$; $S \geq 0.5$			
$DT50_{soil} \leq 40$; $K_{oc} \leq 900$; $S \geq 2$			

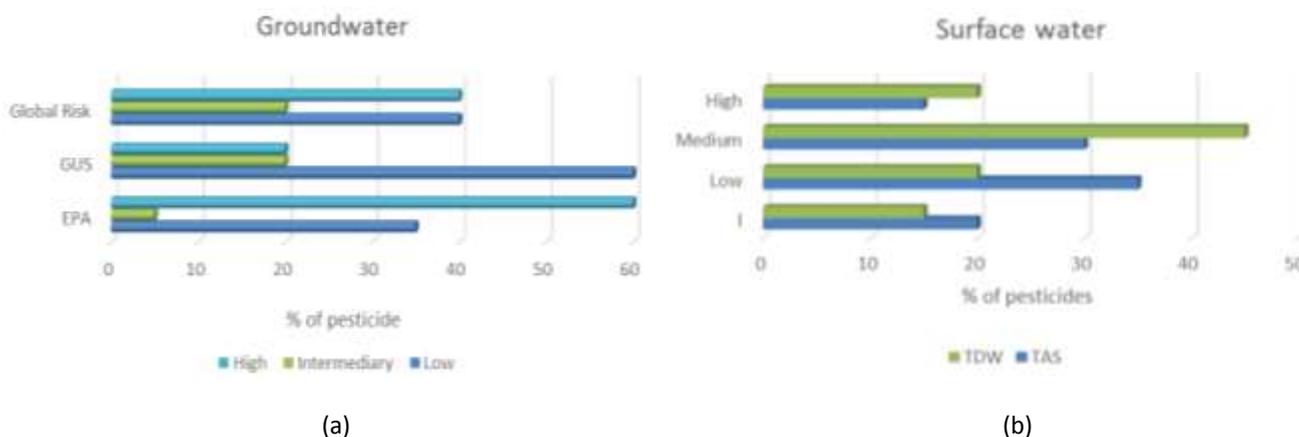


Figure 3. Assessment of contamination potential (a) groundwater (EPA and GUS) (b) surface water (Goss method)

Multiresidue analysis

Method for multiresidue analysis by SPME and GC-IT-MS-MS detection has been validated for pesticides of different classes used in the Ceará (Milhome *et al.*, 2009). Validation of the method was carried out following the criteria established by ABNT, 2000. Screening of pesticides was performed in full scan mode with ion trap analyzer, which has high efficiency for qualitative analyzes. Screening method was fast, simple and reduces the risk of false positive results in determination of traces. The MS/MS mode increased selectivity and sensitivity being more suitable for quantitative purposes (Cortes-Aguado *et al.*, 2008). Peaks with considerable area (signal: noise ratio > 3) were analyzed qualitatively. According to the Chromatograms (Figure 4) was not detected no presence of the pesticide in the surface and groundwater samples. However due to use of active ingredients of high toxicity in the region it is important to encourage the implementation of monitoring programs in rural Ceará, Brazil to ensure the quality of water supplied to the population.

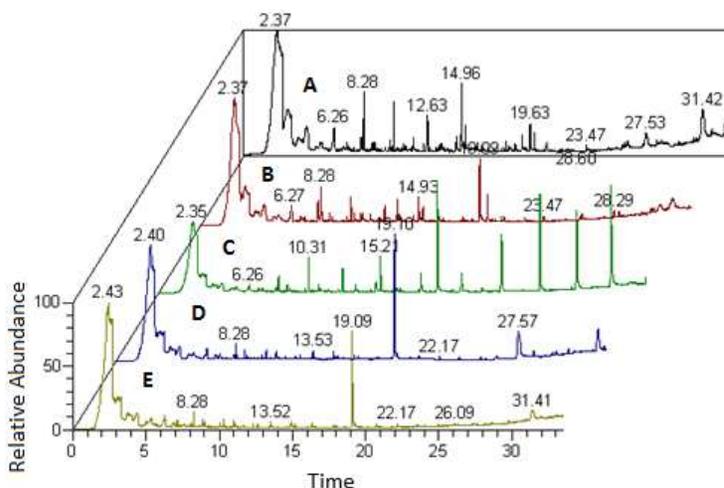


Figure 4. Chromatograms overlaid multiresidue analysis by GC-IT-MS/MS of groundwater (A, B) and surface water (C, D, E) samples.

Conclusion

The results indicate that several pesticides used in agricultural of Iguatu-CE region are of high toxicity (I and II). Application of EPA and GUS index showed that imidacloprid, methomyl, monocrotophos, atrazine, ethoxysulfuron, picloram, pyrimethanil and tebuconazole pesticides are potentials contaminants (PC) in groundwater. Among the active principles studied, only three (15%) showed high TAS and four (20%) high TWS. Analysis of water samples using SPME and GC-IT-MS/MS was satisfactory, but was not detected the presence of pesticides. The results can assist governmental agencies in the pesticide residue management on the environment.

Acknowledgements

The authors gratefully the CNPQ and IFCE for financial support of this search and the NUTEC and UFC for providing the infrastructure of laboratories for chromatographic analysis.

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