Article

Multiresidue Determination of Herbicides in Environmental Waters from Primavera do Leste Region (Middle West of Brazil) by SPE-GC-NPD

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Foi desenvolvido um estudo sobre a presença dos herbicidas simazina, metribuzim, metolacloro, trifluralina, atrazina e seus metabólitos desisopropilatrazina (DIA) e desetilatrazina (DEA) em água superficial e subterrânea da região de Primavera do Leste, Mato Grosso, Brasil. O procedimento analítico baseou-se na extração em fase sólida com cartuchos descartáveis Sep-Pak C_{18} e eluição com acetato de etila. Os níveis de resíduos foram determinados por cromatografia a gás com detector de nitrogênio e fósforo. Para a maior parte dos pesticidas, a recuperação média nos diferentes níveis de fortificação foi >70% com estimativa do desvio padrão relativo <19%. As recuperações observadas para o DIA e a trifluralina foram 25% e 56%, respectivamente. As baixas recuperações foram atribuídas à retenção incompleta do DIA e à forte retenção no sorvente e alta volatilidade da trifluralina. Os limites de detecção variaram de 0,023 a 0,088 µg L^{-1}. Este método foi aplicado na análise de 5 amostras de águas superficiais e 28 de águas subterrâneas, em pontos usados para abastecimento de água para consumo humano, coletadas em Primavera do Leste, Mato Grosso. O nível mais elevado encontrado nas amostras de água foi 1,732 µg L^{-1} de metolacloro enquanto o herbicida encontrado com maior freqüência foi o metribuzim.

A study on the presence of herbicides, namely simazine, metribuzin, metolachlor, trifluralin, atrazine and two metabolites, deisopropylatrazine (DIA) and deethylatrazine (DEA), was performed in ground and surface waters from Primavera do Leste region, Mato Grosso state (Middle West of Brazil). The analytical procedure was based on solid-phase extraction (SPE) with Sep-Pak C_{18} disposable cartridges and ethyl acetate for elution solvent. Residue levels were determined by gas chromatography with nitrogen-phosphorus detection. For most of the pesticides average recoveries at different fortification levels were >70% with relative standard deviation <19%. The recoveries of DIA and trifluralin in water were 25% and 56%, respectively, which were attributed to the incomplete retention of DIA and strong retention on the sorbing material and high volatility of trifluralin. Detection limits ranged from 0.023 to 0.088 µg L^{-1}. This method was applied for the analysis of 5 superficial water samples and 28 groundwater samples, in places used for human consumption without previous treatment, collected in Primavera do Leste, Mato Grosso, Brazil. Results indicated that the highest level of contamination in a water sample was 1.732 µg L^{-1} for metolachlor, while metribuzin was the most frequently detected herbicide with maximum concentration of 0.351 µg L^{-1}.

Keywords: solid-phase extraction, water, herbicides, pesticides, GC-NPD

Introduction

The Primavera do Leste region (Mato Grosso state, Middle West of Brazil) is an area with a high agricultural production, that has expanded greatly since its start 30 years ago. As consequence of the monoculture conditions under which soybean, cotton, rice, maize and bean are grown, they are susceptible to pest attack throughout the year. Therefore, herbicides are extensively used in horticultural crops to control weeds that may produce yield reduction. However,

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after their application, pesticide residues may remain in the crops, soil and natural water and constitute a health risk because of their toxicity. A literature review revealed data on pesticide contamination of aquatic environment in the tropical and subtropical areas.[1-6] In Brazil, although research on pesticide leaching from agricultural areas to groundwater was initiated years ago, the knowledge of the levels of contamination of groundwater is still very scarce in the regions of the Middle West and North of Brazil. Unfortunately, there are few methods for determining pesticide residues in Brazilian environmental compartments. Among them, atrazine, simazine and amethrin were studied in a waterworks of São Paulo state.[7] Trifluralin, endosulfan, λ-cyhalothrin, dicofol, captan, methyl parathion, chloro-thalonil, and chlorpyrifos were determined in groundwater and surface water in Guaíra region, São Paulo state.[8] In another study, 29 pesticides and 3 metabolites were determined in surface water of northeastern area of Pantanal region and glifosate and its main metabolite were studied in water from a rice-growing area.[9-10]

The present work reports the optimization of an SPE method for simultaneous determination of simazine, metribuzin, metolachlor, trifluralin, atrazine and two of its metabolites, deisopropylatrazine (DIA) and deethylatrazine (DEA), in water by means of gas chromatography using nitrogen-phosphorus detection. The pesticides selected are the most frequently used in this agricultural area. The method was successfully applied to determine the levels of these herbicides in water samples taken from different water sources located in Primavera do Leste region.

Experimental

Reagents

Ethyl acetate, acetone and methanol (Mallinckrodt Baker Inc., Paris, KY, USA) of nanograde purity were used. The pesticide standards of deisopropylatrazine (96.5%), deethylatrazine (95.5%), trifluralin (99.2%), atrazine (98.4%), simazine (99.2%), metribuzin (99.5%) and metolachlor (95.0%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The individual stock solutions of the analytes were prepared by diluting 1.0 mg of the standard in 10.0 mL of ethyl acetate to obtain a concentration of 100 µg mL^{-1}. The working standard solutions were prepared by diluting the stock solutions as required. The deionized water was purified with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Hydrochloric acid of analytical grade was from Merck (Darmstadt, Germany). Sodium chloride of residue analysis grade was purchased from

Merck (Darmstadt, Germany). Sep-Pak C$_{18}$-bonded silica commercial cartridges (500 and 1000 mg) were purchased from Waters (Mildford, MA, USA).

Apparatus

A Hewlett-Packard 6890 gas chromatograph equipped with a split/splitless injector and a nitrogen-phosphorus detection system was employed. A DB-5 fused-silica capillary column (30 m × 0.32 mm i.d., 0.25 µm; J & W Scientific, Folsom, CA, USA) was used, with nitrogen (purity 99.999%) as carrier and make up gas at flow-rates of 1 mL min^{-1} and 7 mL min^{-1}, respectively. Detector gases: hydrogen 3 mL min^{-1} and air 60 mL min^{-1}. The injector temperature was set at 240 °C and the detector temperature was 300 °C. The oven temperature was programmed as follows: 70 °C for 1 min, increased to 150 °C at 20 °C min^{-1}, then to 180 °C at 3 °C min^{-1} and followed by final ramp to 240 °C at 10 °C min^{-1} (hold for 1 min). The data were acquired and processed by HP Chemstation software. An aliquot (1 µL) of the water extracts, standards and blanks was injected in the splitless mode into the GC-NPD system.

Sample collection and preparation

In the beginning of the rain season in this tropical area (December 1998), thirty-three water samples were collected from different water sources in agricultural zone located in Primavera do Leste region (Middle West of Brazil between 15 32'S to 15 34'S and 54 17'W to 54 19'W) in 1 L amber glass bottles pretreated with acetone and methanol. After being filled with water, the bottles were sealed with Teflon-lined screw caps and transported on the same day to the laboratory in refrigerated conditions. In the laboratory, before the solid-phase extraction, the water samples were filtered in a 0.45 µm cellulose nitrate membrane filter, the pH was adjusted between 6.5 and 7.5 with 1 mol L^{-1} HCl and the NaCl was added to ionic strength correction (17.5%, m/v). The sampling sites were irrigation and drinking water wells (23), waterholes (5), dam (2) and Cabeceira dos Bois river (3). Numbers between parenthesis represent number of sampling points at each sampling sites.

Extraction procedure

A Sep-Pak Vac C$_{18}$ cartridge was placed on top of a vacuum block and it was conditioned with 10 mL of methanol followed by 10 mL of water, before applying the sample. An analytical aliquot of 500 mL water was transferred to the cartridge at a flow-rate of *ca.* 5 mL min^{-1}. The herbicides were eluted with 2 × 10 mL

of ethyl acetate at a flow-rate of *ca.* 1 mL min⁻¹. The combined fractions were concentrated in a rotary evaporator and the residue was redissolved in 1 mL of ethyl acetate for GC-NPD analysis.

Recovery studies

Recovery studies were carried out with tap water samples free of residual pesticides, which were spiked with standard mixture at different concentration levels. At each fortification level, six replicates were analyzed. Quantification was performed by external calibration using certified standards. Sample analyses were run in duplicate and most relative standard deviations (RSDs) of less than 19% were achieved. The extraction procedure described above was followed. The limits of detection and quantification were determined based on the criteria established by Thier and Zeumer.[11] The limit of detection (LOD) was calculated using equation 1.

$$LOD = \frac{2 \cdot t_{(f;95)} \cdot s_{comb}}{S} \tag{1}$$

Where s_{comb} is the combined standard deviation; S is the sensitivity; $t_{(f;95)}$ is the unilateral t of Student, with f degrees of freedom and confidence level of 95%; f=d-1 and d is the number of replicates at each fortification level.

The sensitivity was determined as a measure of the proportionality of the instrumental response and the analyte concentration.

The combined standard deviation (s_{comb}) was calculated using equation (2).

$$s_{comb} = \sqrt{\frac{(m-1)s_A^2 + (n-1)s_B^2}{m+n-2}} \tag{2}$$

where s_A is the standard deviation of the measured concentrations at the lowest fortification level used in the recovery experiment; m is the number of replicates at the lowest fortification level; s_B is the standard deviation of the responses of the blank determinations and n is the number of blank determinations.

The limit of quantification (LOQ) was the lowest fortification level where mean recovery between 70 and 120% and relative standard deviation less than 20% were obtained.

Results and Discussion

GC-NPD conditions

In a first approach, the GC-NPD conditions were optimized to separate the herbicides studied. For that,

different temperature programs were tested in order to resolve the pesticides of the standard mixture. The representative chromatograms of the standard mixture, fortified water sample and water control sample are shown in Figure 1. No interfering peaks were present. The total running time was 20 min.

Optimization of solid-phase extraction

The proposed SPE method was based on previous procedures established by Junker-Buchheit and Witzenbacher[12] and Eisert *et al.*[13] for the determination of pesticide residues in water. Different parameters related to the extraction process were evaluated. Table 1 shows the experiments realized to the optimization of the SPE procedure in order to improve the recovery. These experiments were performed in triplicate. The extraction carried out by the method A showed lower recovery for DIA and trifluralin with high relative standard deviation (RSD) values for both pesticides (Table 2). The low recovery for trifluralin was due to the effect of irreversible adsorption taking place on the C_{18} surface and high volatility, while some uncontrollable loss of DIA occurred during the SPE procedure, once it is not well retained by the sorbent. In method B, considering the same amount of C_{18} material, the influence of the sample volume was assayed. The average recoveries for DIA and trifluralin were improved from 19% to 60% and 20% to 59%, respectively. No significant differences in DIA recoveries were noted from water samples analyzed by methods B, C and D. The eluent volume used for subsequent study was set at 20 mL. In method E, the effect of addition of salt was also evaluated with water sample salted with NaCl. Salt increases the ionic strength of the water sample and enhances the extraction from water because it reduces analyte solubility. Greater areas for DIA were registered when 87.5 g of NaCl were added. Further experiments were performed by the addition of NaCl (17.5%, m/v).

Table 1. Analytical parameters assayed for the optimization of the SPE method

Method	Sample volume / (mL)	Sorbent amount / (mg)	Cartridge conditioning	NaCl addition	Eluent volume / (mL)
A	500	500	5 mL H₂O + 5 mL MeOH	no	2×5
B	250	500	5 mL H₂O + 5 mL MeOH	no	2×5
C	200	500	5 mL H₂O + 5 mL MeOH	no	2×8
D	500	1000	10 mL MeOH 10 mL H₂O+ 10 mL MeOH	no	2×10
E	500	1000	10 mL H₂O+ 10 mL MeOH	yes	2×10
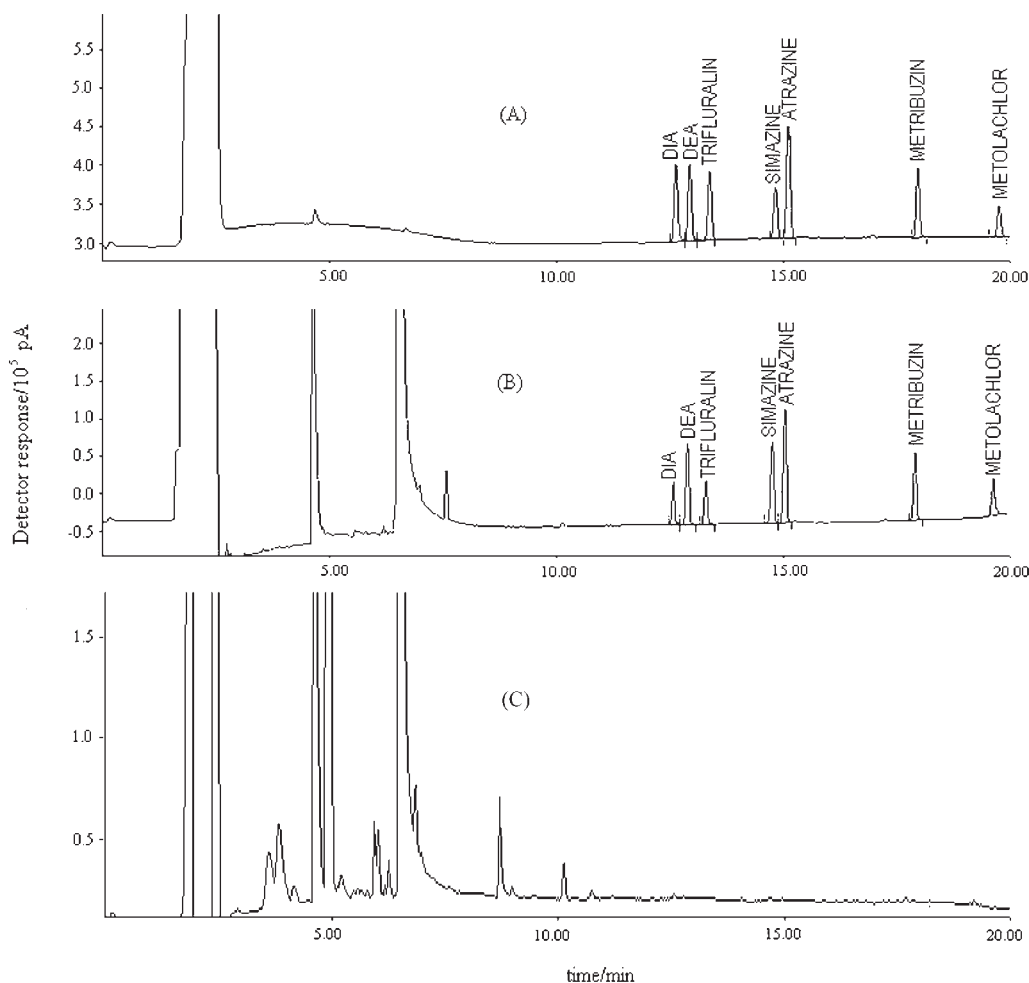
Figure 1. GC-NPD chromatograms of (A) standard mixture containing atrazine (0.314 µg mL^{-1}), DIA (0.208 µg mL^{-1}), DEA (0.188 µg mL^{-1}), simazine (0.200 µg mL^{-1}), metribuzin (0.424 µg mL^{-1}), metolachlor (0.824 µg mL^{-1}), trifluralin (0.408 µg mL^{-1}); (B) water sample fortified with atrazine (0.107 µg L^{-1}), DIA (0.104 µg L^{-1}), DEA (0.094 µg L^{-1}), simazine (0.100 µg L^{-1}), metribuzin (0.212 µg L^{-1}), metolachlor (0.412 µg L^{-1}) and trifluralin (0.204 µg L^{-1}); (C) water control sample. For chromatographic conditions, see text.

Table 2. Effect on the herbicide recovery of different methods

Herbicide	A Rec[a]	RSD / (%)	B Rec	RSD / (%)	C Rec	RSD / (%)	D Rec	RSD / (%)	E Rec	RSD / (%)
DIA	19	79	60	30	57	27	54	14	83	14
DEA	82	5.7	108	6.6	106	7	104	10	87	19
Atrazine	97	5.9	101	7.9	91	3.5	100	5.3	94	14
Simazine	93	9.9	91	4.7	86	5.4	93	6.2	92	11
Metribuzin	87	8.3	82	6.6	96	16	94	19	75	10
Trifluralin	20	63	59	4.8	45	19	82	11	67	14
Metolachlor	98	5.9	102	1.7	92	9.2	109	5.5	91	3.0

[a]Rec = Recovery (n=3); RSD = Relative Standard Deviation

Based on these results, the method E was selected to determine the herbicides studied in spiking samples of tap water at different levels for each pesticide. Each recovery analysis was repeated 6 times. The results of the average recoveries ranged from 72% to 110%, with RSD values of 2% to 19%, as can be seen in Table 3, except for DIA and trifluralin, which gave lower recoveries 25% and 56%, respectively. Lower recoveries of DIA and trifluralin have been reported in the literature.[9,14-16]

Table 3. Recovery efficiency of herbicides from fortified water by GC-NPD analysis (*n=6)

Herbicide	Fortification level / (μg L^{-1})	Recovery / (%)			RSD / (%)
		Range	Average*	SD	
DIA					
	0.104	66-104	83	11.6	14
	0.402	34-141	84	43.7	52
	2.08	18-28	25	4.3	17
DEA					
	0.094	56-104	87	16.5	19
	0.376	97-119	109	8.7	8
	1.88	76-90	85	6.4	8
Atrazine	0.054	83-140	110	19.8	18
	0.107	74-110	92	10	11
	0.428	98-112	104	4.4	4
	2.14	94-103	98	3.7	4
Simazine	0.050	82-118	104	11.4	11
	0.100	71-108	94	13.1	14
	0.400	97-123	110	10.2	9
	2.00	96-101	99	2.4	2
Metribuzin	0.106	70-115	92	13.8	15
	0.212	61-103	75	14.5	19
	0.848	81-104	91	9.1	10
	4.24	61-79	72	7.9	11
Trifluralin	0.102	54-96	75	12.8	17
	0.204	54-82	67	9.4	14
	0.816	48-63	56	5.5	10
	4.08	46-69	57	9.1	16
Metolachlor	0.206	73-106	95	11.4	12
	0.412	87-96	91	2.7	3
	1.648	90-103	98	4.1	4
	8.24	102-107	105	2.1	2

Many authors have described methods for the determination of these herbicides in water using gas chromatography with nitrogen phosphorus detection or mass spectrometric detector or ultraviolet or mass selective detector through different interfaces for HPLC technique, Table 4. In terms of recovery the effectiveness of the C$_{18}$ cartridge extraction procedure was compared with those obtained using SDVB resins and GCB sorbent. Therefore, the overall results are in good agreement with the one previously published by Laabs *et al.*[9] who reported recoveries of these pesticides of 77-116% using SPE involving much larger sample volume (1000 mL) than in the present work.

Linearity

Under the chromatographic conditions described, good linearity and correlation coefficient were achieved for the compounds studied. Replicates (n=3) of the standard pesticide mixture of different concentrations were analyzed and the detector response (peak area) was plotted against analyte concentrations. The correlations were found to be linear in the range from 0.009 to 2.060 μg mL^{-1}.

The correlation coefficients obtained for the pesticides were higher than 0.997 as shown in Table 5.

Limits of detection (LOD) and quantification (LOQ)

The criteria established by Thier and Zeumer to find LOD and LOQ was used in this study.[11] The LOD for herbicides studied ranged from 0.023 to 0.088 μg L^{-1}, which was calculated considering the sensitivity of the method and the standard deviation values obtained from recovery experiments at the lowest fortification level and the blank analysis. The LOQ were determined as the lowest concentration of the compounds that gave a response that could be quantified with a RSD of less than 20% and a recovery of at least 70%. Consequently, the LOQ values for these compounds were between 0.050 and 0.206 μg L^{-1} as shown in Table 5. The detection limits obtained were in good agreement with those previously published by Panshin *et al.*[17] and Pinto and Jardim,[18] but higher than the one obtained by Laabs *et al.*[9] and Quintana *et al.*[16] However, the last method used other sorbent material and GC-MS technique, Table 4. On the other hand, the LOD values were lower than or equal to the maximum admissible concentration established by the European Union for the sum of all pesticides (0.5 μg L^{-1}) or for an individual compound in drinking water (0.1 μg L^{-1}).

Application of the method

The proposed method was applied to the determination of herbicides in water samples of different water sources located in Primavera do Leste region, Middle West of Brazil. These analyses are part of a project that aimed to study the contamination by herbicides of water used for human consumption. The results showed that out of 33 water samples, 73% had detectable herbicide residues. Figure 2 shows the chromatogram of a drinking water sample where DEA, metribuzin and metolachlor were detected. Metribuzin (16 cases) was the most frequently found pesticide in water samples, followed by simazine and DEA (6 cases each), metolachlor and atrazine (4 cases each) and trifluralin (2 cases). DEA was detected at high concentrations (0.206 μg L^{-1}), but DIA was not found in water samples. This behaviour can be explained by considering that the removal of an ethyl chain is preferential over an isopropyl chain. Therefore DEA is more stable. Moreover, the herbicide found in most cases at concentration over the EU limits was metolachlor (1.732 μg L^{-1}), which has high water

Table 4. Comparison among different SPE methods for the determination of herbicides in water

Method	Sorbent[a] / (mg)	Water / Volume (mL)	pH salt addition	Elution[b]	Technique	Recovery / (%)[c]	LOD / (µg L^{-1})	LOQ / (µg L^{-1})
Laabs et al.[9]	C$_{18}$(1250)	≤1000	pH 3 20 g L^{-1} KCl	8 mL Hex + 12 mL ethyl acetate	GC/MS	AT-103 SM-108 MTL-108 MTR-116 TRF-77		0.002 0.002 0.002 0.002 0.002
Lacorte et al.[14]	Oasis [SDVB N-pyrrolidine] (60)	200	pH 7-pH 2	2.5 mL ACN: DCM (1:1) + 3.2 mL DCM	GC/MS	AT-120 (pH 7) AT-143 (pH 2) SM-147 (pH 7) SM-149 (pH 2) TRF-53 (pH 7) TRF-56 (pH 2)		
Azevedo et al.[15]	Oasis (60)	200	pH 4	2.5 mL ACN: DCM(1:1) + 3.2 mL DCM	GC/MS	AT-95 SM-92 MTL-81 TRF-56	0.009 0.02 0.01 0.005	
Quintana et al.[16]	SDVB(200)	500		2 × 2.5 mL ethyl acetate	GC/MS	DIA-96 DEA-95 AT-86 SM-98 MTR-80 MTL-102 TRF-73	0.008 0.009 0.008 0.008 0.035 0.012 0.013	
Panshin et al.[17]	GCB(250)	100-175		3 mL ethyl acetate+ 8 mL DCM: MeOH (70:30)	GC/MS	AT-90-110 DEA-90-107 DIA-94-103	0.07 0.04 0.03	
Pinto and Jardim[18]	C$_{18}$(250)	250	pH<2 5 g NaCl	1 mL MeOH	HPLC/UV	AT-76 SM-77.8	0.018 0.012	0.055 0.037
Carabias-Martínez et al.[19]	SDVB [Lichrolut EN](200)	100		5 mL MeOH +5 mL ethyl acetate	HPLC/DAD	AT-95 DEA-99	0.02 0.02	
Gferer et al.[20]	C$_{18}$(1000)		pH>7	Hex:DCM: ethyl acetate	GC/MS	AT-86.9 DIA-20.1 DEA-56.4 SM-90.3		0.001 0.004 0.004 0.005
DiCorcia et al.[21]	GCB(500)	1000-4000		1.5 mL MeOH +8 mL MeOH: DCM (20:80) +50 mmol L^{-1} formic acid	HPLC/ES/MS	AT-91-99 SM-89-95 MTL-98-105	0.0001 0.0001 0.0001	
Carabias-Martínez et al.[22]	Oasis HLB	500		10 mL ethyl acetate	HPLC/DAD	AT-76 MTR-77.8	0.004 0.010	
Jeannot et al.[23]	C$_{18}$(1000)	500-1000		2 × 2 mL MeOH	HPLC/DAD HPLC/MS HPLC/MS/MS	AT SM DIA DEA	0.02 0.02 0.02 0.02	
Belden et al.[24]	C$_{18}$(1000)	1000		3 × 3 mL Acet:Hex (1:1)	GC/NPD	AT-80-90 SM-65-74 MTL-79-91	0.081 0.049 0.066	
Loos and Niessner[25]	LiChrolut EN(200)	200		4 mL MeOH:ethyl acetate (3:2)	GC/MS	AT-124.8 DIA-99.8 DEA-102.5		0.005
Tolosa et al.[26]	GCB(500)	1000	pH 7 60 g NaCl	2 × 6 mL DCM	GC/NPD	AT-89-112 DIA-90-104 DEA-92-103 SM-93-112	0.0013 0.0023 0.002 0.0013	
	SDVB(200)	1000	pH 7 60 g NaCl	2 × 3 mL ethyl acetate	GC/NPD	AT-80-103 DIA-84-106 DEA-89-100 SM-83-98	0.0014 0.0025 0.0021 0.0014	

[a]C$_{18}$ = octadedecylsilica, SDVB = styrenedivinylbenzene, GCB = grafitized carbon black; [b]DCM = dichloromethane, MeOH = methanol, ACN = acetonitrile, Hex = hexane; [c]AT = atrazine, SM = simazine, MTL = metolachlor, MTR = metribuzin, TFR = trifluralin.

Table 5. Calibration data, detection limit and quantification limit of the herbicides analyzed by GC-NPD

Pesticide	Linear range / (μg mL^{-1})	Equation	Correlation coefficient (r^2)	LOD / (μg L^{-1})	LOQ / (μg L^{-1})
DIA	0.010-0.416	y = -178 + 9468 x	0.9971	0.041	0.104
DEA	0.009-0.376	y = -143 + 13146 x	0.9990	0.041	0.094
Trifluralin	0.020-1.020	y = -2.19 + 5084 x	0.9997	0.078	0.102
Simazine	0.010-0.400	y = -44 + 14056 x	0.9996	0.023	0.050
Atrazine	0.011-0.428	y = -17 + 13727 x	0.9993	0.036	0.054
Metribuzin	0.021-1.060	y = -88 + 6204 x	0.9991	0.069	0.106
Metolachlor	0.103-2.060	y = -55 + 3338 x	0.9990	0.088	0.206
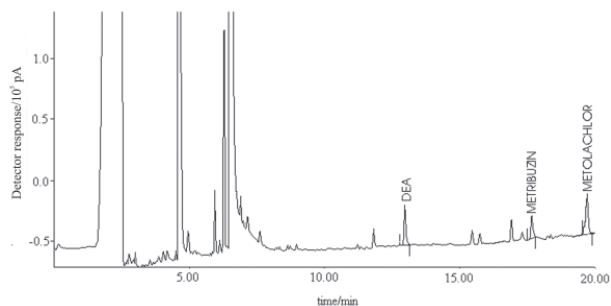
Figure 2. GC-NPD chromatogram of a drinking water well sample. For chromatographic conditions, see text.

Table 6. Occurrence of herbicides in water samples collected in the Primavera do Leste region (Middle West of Brazil) during December 1998

Sampling site	n	Compound	freq.	Concentration / (μg L^{-1}) min.	max.
drinking water well	20	DEA	14	< 0.041	0.078
		atrazine		< 0.036	0.063
		simazine		< 0.023	0.061
		metribuzin		< 0.069	0.351
		metolachlor		< 0.088	0.091
waterhole	5	metribuzin	4	< 0.069	0.090
		metolaclor		< 0.088	1.732
dam	2	metribuzin	1	< 0.069	0.138
Cabeceira dos Bois river	3	simazine	2	< 0.023	0.047
irrigation well	3	DEA	3	< 0.041	0.206
		atrazine		0.078	0.156
		simazine		< 0.023	0.085
		metribuzin		< 0.069	0.129
		trifluralin		< 0.078	0.102

n: number of water samples; min. - max.: minimum and maximum concentrations; freq.: number of positive samples.

solubility, followed by metribuzin (0.351 μg L^{-1}). Table 6 contains a summary of the occurrence and concentrations of herbicides detected in samples collected during December 1998.

Conclusions

A rapid and simple SPE method for determining herbicide residues in water by GC-NPD was described. The method was adapted and validated aiming water monitoring in a region with intense agriculture activities. The low detection and quantification limits achieved with this method allow its application in the determination of herbicide levels below the MRL established by EU directive for drinking water. The SPE method was applied to determine herbicides selected in superficial and groundwater samples collected in Primavera do Leste region (Mato Grosso state, Brazil) and metribuzin was detected in many of the samples analyzed, whereas DIA was not found.

Acknowledgments

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