Determination of 48 pesticides in water by using DI-SPME coupled to GC/MS

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Abstract

This paper discusses the optimization and validation of a complete and simple method for the simultaneous determination of 48 pesticides in water by combining direct immersion solid-phase micro-extraction (DI-SPME) and gas chromatography- ion trap tandem mass spectrometry (GC-ITMS/MS). For the extraction, the different SPME parameters were tested and optimized. As a result, the polyacrilate fiber (PA 85μm) was selected in direct immersion mode; the extraction temperature was set to 60ºC with an extraction time of 45 min and a stirring speed of 250 rpm; the thermal desorption time of the fiber in the injector port was fixed to 10 min, at 275ºC. Concerning the analysis, MS/MS parameters were optimized and figures of merit were compared. Later, the method was validated and showed good linearity in the concentration ranging from 0.05 to 100 ng mL-1. The reproducibility of measurements expressed as relative standard deviation (% RSD) was found to be satisfactory. Furthermore, the detection limits obtained were in the low or sub ppt levels. Finally, the proposed DI-SPME-GC-ITMS/MS method was tested successfully for water samples collected along the watershed of Abou Ali River (North Lebanon).

Keywords: Pesticides, GC-ITMS/MS, DI-SPME, Abou Ali River

Introduction

Pesticides have been intensively used, in the last decades, in the purpose of increasing agricultural production (Costa *et al*. 2008) by preventing yield damage, crop destruction and controlling pests (Jacobson *et al*. 2005). In addition to this, pesticides have been applied also for non-agricultural practices such as disinfection and wood protection (Isabel *et al*. 2010).

These compounds are known to be immensely persistent in the environment and able to bio-accumulate. Therefore, they can be found not only in sediments and atmosphere but also in water including surface and groundwater systems (Komatsu *et al*. 2004). The existence of pesticide residues in water can cause harmful effects on human health, aquatic life and the ecosystem itself (Costa *et al*. 2008; Pablos *et al*. 1999; Pablos *et al*. 2001). For all these reasons, their monitoring has been a major global concern (Costa *et al*. 2008) and strict regulations have been established.

In this context, the European Community (EC), Directive 98/83/EC has defined a maximum permissible concentration of 0.1 μg L^{-1} for each single compound and a maximum allowed concentration of 0.5 μg L^{-1} for the sum of pesticides in environmental and water used for human consumption (EU. 1998). Furthermore, a Water Frame Directive (WFD) has been implemented by the EC (2000/60/EC) for the protection of aquatic environment. This framework has listed in Annex X the priority and hazardous substances and the permissible limits of each one, which ranged from ng L^{-1} to low μg L^{-1} (EU. 2008).

Pesticides exist in trace levels in water samples in the environment and are characterized by their diversity and different physico-chemical characteristics (Frenich *et al*. 2000; Stajnbaher and Zupancic-Kralj, 2003). Accordingly, a highly sensitive and selective analytical method coupled to a fast and reliable pre-concentration technique should be established in order to detect the maximum number of possible pesticides (Barceló and Hennion. 1997; Frenich *et al*. 2000; Pinheiro and Andrade. 2009). The conventional techniques applied for the extraction of pesticide residues from water matrices involved liquid-liquid extraction (LLE) (Wang *et al*. 2009) and Solid-Phase Extraction (SPE) (Jiping ma *et al*. 2009; Kouzayha *et al*.2011). However, these techniques are protracted, costly and require large volume of solvents that can be toxic (Xiaojing *et al*. 2010). Hence, Solid-Phase Micro-Extraction (SPME) was applied, in this study, since it is a single-step, solventless (Vázquez *et al*. 2008), highly selective (Córtes-Aguado *et al*. 2008) and flexible technique (Sakamoto and Tsutsumi. 2004). Recently, SPME was applied to detect pesticides and broad range of organic compounds in water (Goncalves and alpendurada. 2004; Flynt *et al*. 2006; Pedersen-Bjergaard and Rasmussen. 1998; Xiaojing *et al*. 2010).

Gas chromatography- mass spectrometry (GC-MS) is the most commonly implemented methodology for the

analysis and quantification of pesticide deposits in water. This system is distinguished by its high selectivity and capability to achieve low detection limits and mass resolution; thus, making it suitable for the analysis of pesticide residues from various chemical groups (Filho *et al*. 2010). Moreover, the ability of the MS detector to perform tandem mass spectrometry (MS-MS) promotes the analysis of pesticides in the low picogram levels even in the presence of interferences by reducing background noise significantly (Goncalves and alpendurada. 2004; Reyzer and Brodbelt. 2001 ; Sheyer *et al*. 2005).

The objective of this study is to develop a fully automated and simple SPME-GC-MS/MS method for the simultaneous determination of 48 pesticides in water samples. The influence of the different SPME parameters on the extraction proficiency will be studied in details. Likewise, the GC and MS-MS parameters were optimized to obtain the highest sensitivity and selectivity. Finally, the optimized and validated method was used for the analysis of surface water samples collected from the watershed of "Abou Ali" River. The Pesticides designated for this study belong to 12 different chemical groups as shown in Table1.

Materials and Methods

Chemicals and reagents

Three separate certified pesticide mixtures, highly pure (> 98%) and containing 10 mg L^{-1} of each individual pesticides were purchased from LGC Standards (Germany). The composition of each mixture is represented as follow: Mixture1 (Cyprodinil, Myclobutanil, Penconazole, Tebuconazole, Alachlor, Bromopropylate, Buprofezin, Fludioxonil, Kresoxim-methyl, Metalaxyl, Pendimethalin, Procymidone, Propyzamide, Trifluralin, Vinclozolin, Chlorpropham, Propoxur) ; Mixture2 (Aldrin, 4,4'-DDT, 4,4'-DDE, 4,4'DDD, Dieldrin, Endosulfan-alpha, Endosulfan-beta, Endosulfan-total (sulfate), Alpha-HCH, Beta-HCH, Gamma HCH (Lindane), Delta-HCH, Heptachlor-exo-epoxide, Hexachlorobenzene, Methoxychlor, Quintozene, Chlorpyrifos, Chlorpyrifos methyl) and Mixture 3 (Diazinon, Dichlorvos, Ethion, Ethoprophos, Pirimiphos-methyl, Bifenthrin, Lambda-cyhalothrin, Cypermethrin, Amitraz, Pyridaben, Dimethoate, Methomyl and Methamidophos). The deuterated internal standards, Alachlor-d13 and beta-Endosulfan-d4 (purity 98%) were obtained respectively from Sigma Aldrich Chemical Co (Milwaukee, WI) and ChemService (USA).

A 3 mg L^{-1} working standard solution, combining the three pesticides mixtures, was prepared in acetonitrile and stored in the freezer. This working solution was used for both the preparation of acqueous solutions, used for the optimization of extraction parameters, by spiking water to the appropriate concentration (250ng mL^{-1}) and in the validation of the method with concentrations ranging from 0.05 to 100 ng mL^{-1}.

All the solvents used were Chromasolv HPLC-grade (>99.9 % purity) provided by Sigma Aldrich Chemical Co (Milwaukee. WI). Double distilled water, with 18.2 MΩs conductivity, was generated from a Simplicity water purification system (Millipore, Bedford, MA).

The different types of fibers, polyacrylate (PA, 85 μm), polydimethylsiloxane (PDMS, 7 μm) and polydimethylsiloxane (PDMS, 7 μm) were obtained from Supelco (Bellefonte, PA). These fibers were conditioned, as endorsed by the manufacturer, to eliminate potential contaminants before usage. The magnetic stirrer used was the VarioMag stirrer (USA).

SPME extraction procedure

A Combi-PAL auto-sampler (CTC, Sweden) coupled to the GC/MS machine was used for the SPME extraction of the targeted pesticides from water samples. The extraction was performed by direct immersion (DI) of the PA fiber in an 18 mL water sample placed in 20 mL amber glass vial for 40 min under magnetic stirring of 250 rpm agitation speed and at a temperature of 60˚C. Then, the fiber was moved to the GC injector port where desorption took place in the splitless mode for 10 min and at 275˚C.

GC-MS instrumental conditions

GC-MS analysis was carried in a Varian CP3800 Gas Chromatograph (GC) (Walnut Creek, CA, USA) assembled with a split-splitless injector and linked to a Saturn 2200 ion trap Mass Spectrometer (ITMS).the separation was done with a Varian Factor Four VF-5MS capillary column (30 m×0.25 mm id., 0.25 μm film thickness) (Varian Inc, Lake forest, CA). The helium (99.99%) was used as carrier gas at a flow rate of 1 mL min^{-1}. The oven temperature program was as follows: initial temperature of 60ºC (hold 1 min), 30ºC/min to 180 ºC (hold 3 min), and 5ºC/min to 280 ºC (hold 3 min). The complete analysis time was 30 min for each sample.

The ITMS functioned in the electron impact mode (EI) at 70 eV. Full scan, Automated Method Development (AMD) and MS-MS experiments were developed throughout this study. The temperatures of the manifold, ion source and transfer line were set to 150, 250 and 280ºC, respectively. The analysis was executed with a filament-multiplier delay of 3 min and acquisition was performed with a mass/charge (m/z) ratio ranging from m/z 45-550. Furthermore, to enhance the sensitivity and linearity of the MS detector, the electron multiplier voltage and the total target ion counts (TIC) should be adjusted. Hence, the voltage of the electron multiplier was set to 2000 V throughout an auto tuning procedure and the TIC values were set to: 65 000 in full scan MS, 25 000 in AMD and 5000 in MS-MS. The MS data analysis and the control of the system were done by using the Varian MS Workstation software (Version 6).

Results and discussion

Development of the GC-MS/MS method

The development of a GC-MS/MS requires three steps: (1) Determination of the retention times and parent ions, (2) realization of efficient isolation and storage of the parent ion, (3) optimization of collision induced dissociation (CID).

The selection of the retention times and parent ions were done by injection of the working standard solution

containing 10 µg ml-1 of each individual pesticide using FULL SCAN mode. Then, analytes were identified by comparing the single-MS spectra obtained with EI-MS libraries (NIST). The selected parent ion should have the highest m/z value to reduce background noise and the highest intensity to increase sensitivity. The retention time and parent ion chosen for each pesticide are represented in Table 1.

The realization of efficient isolation and storage of the parent ion relies on the excitation radiofrequency storage level applied (ESL). ESL was calculated by the MS tool kit software taking into account the mass of the chosen parent ion of each pesticide under study and the "q" value which was set to 0.3 for all the compounds except for methomyl and methamidophos for which the value was set to 0.4 as the ESL obtained with a value of 0.3 was below the acceptable limit.

For the collision induced dissociation (CID) there is two excitation modes: non- resonant and resonant. For each compound we had to choose the excitation mode which gave enough energy to cleave the bonds into the molecule and give good quality spectra. The optimization of CID, in resonant or non-resonant excitation mode, corresponds to the optimization of excitation amplitude (EA) for each compound. This latter was executed by using the automated method development (AMD) integrated in the MS tool kit software. The secondary spectra obtained for each pesticides were studied and analyzed and the one presenting numerous and intense daughter ions with a parent ion abundance of 10% was selected. The selected CID parameters for each individual pesticide are summarized in Table 1. After the optimization of CID conditions, the MS/MS was performed through a multiple reaction monitoring (MRM) mass spectrometry procedure. The latter enables the identification and quantification of the large number of the targeted pesticides in one selective chromatogram.

Optimization of SPME parameters

The optimization of SPME parameters is essential in order to obtain efficient extraction. For this aim, the fiber type, extraction mode, temperature and time, in addition to the stirring speed and desorption time were investigated throughout this study.

The selection of the proper fiber characteristics and coating is critical for the SPME technique. Three commercial SPME fibers (7 µm PDMS, 100 µm PDMS and 85 µm PA) were compared for the extraction of the studied 48 pesticides. Fig. 1 clearly shows that the 85 µm PA had the greatest extraction efficiency for the majority of the selected pesticides followed by the 100 µm PDMS and lastly the 7 µm PDMS fiber. Accordingly, the 85 µm PA fiber was implemented for further investigations. In addition to this and since the SPME involves two extraction modes: the direct immersion mode (DI-SPME) in which the fiber is totally immersed in the aqueous phase of the sample and the headspace mode (HS-SPME) where the fiber is positioned in the headspace over the liquid; both modes were evaluated in this paper. The results obtained and illustrated in Fig.2 showed that DI-SPME

mode had better sensitivity then HS-SPME and was capable to extract all the targeted compounds. Hence, this mode was used for the development of the method.

The extraction temperature affects the extraction kinetically and thermodynamically: the rise in temperature leads to a reduction in the extraction time, conversely it decreases the sum of analytes adsorbed on the fiber (Xiaojing et al. 2010). In the present study, the influence of the extraction temperature was evaluated in the range between 30 and 70 ºC. Fig. 3 shows that the peak area of almost all the compounds was enhanced at a temperature up to 60 ºC; while after this temperature we noticed a drop in the extraction efficiency. Consequently, the optimum extraction temperature was 60 ºC.

SPME is a partition process of compounds between the sample and the fiber, thus it is an equilibrium procedure and the determination of the optimum extraction time (equilibrium time) for which the maximum amount of analytes are extracted by the fiber is required (Chen. 2004). The extraction time was carried out between 15 and 75 min and graphs showing the peak area of analytes versus the extraction time were plotted. An example of the graphs for 8 different pesticides is represented in Fig.4 and showed that the response of analytes increased when the extraction time reached 45 min, and accordingly this extraction time was selected.

For SPME, a constant agitation of the sample should be applied during fiber exposure in order to improve extraction efficiency and minimize extraction time (Dugay et al. 1998). The effect of stirring speed was evaluated at 250, 500 and 750 rpm. The results obtained are shown in Fig.5. it was concluded that the best extraction yield was achieved at a stirring rate of 500 rpm. This can be explained by the fact that the increase in stirring speed lead to the movement of the compounds to the headspace above the sample thus causing a wash of the fiber and reducing extraction efficiency. This was also witnessed by Filho et al (2010). A stirring speed of 500 rpm was then chosen.
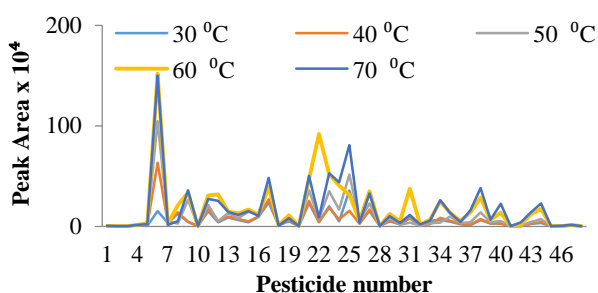
The desorption time of analytes into the injector port was investigated from 5 to 15 minutes, and a desorption time of 10 min was selected.
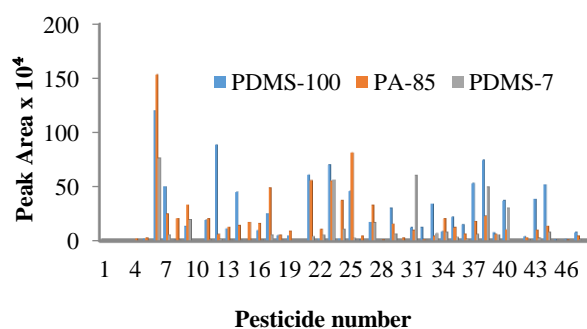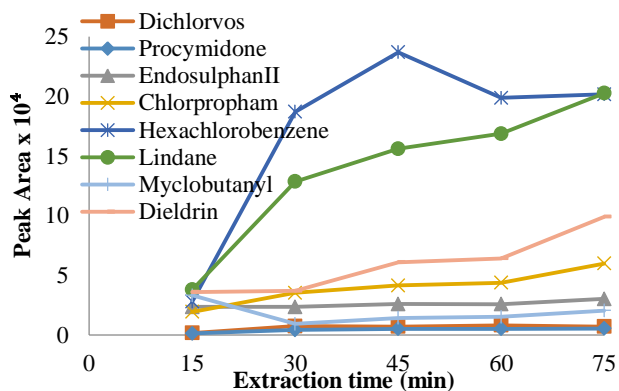

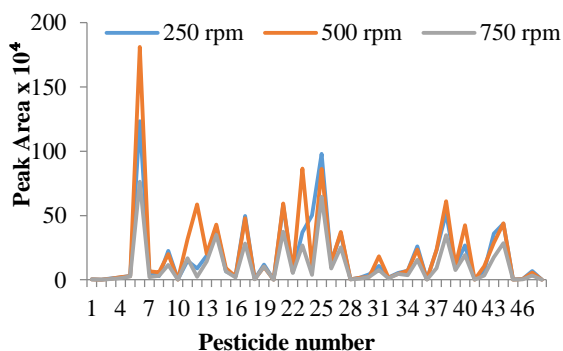**Figure 1.** Effect of three SPME fibers on extraction efficiency
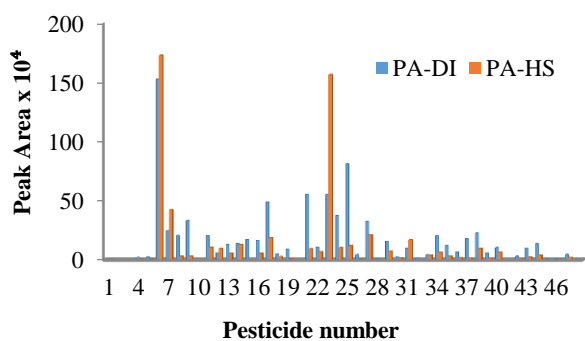
Figure 2. Effect of extraction mode (DI-SPME and HS-SPME) on extraction efficiency

Figure 3. Evaluation of five extraction temperature (30, 40, 50, 60 and 70 ºC)

Figure 4. Effect of extraction time on the effectiveness of extraction

Figure 5. Effect of stirring speed on extraction efficiency

Method Performance and Validation

The validation of the developed SPME-GC-MS/MS method was performed by assessing the linearity range (LR), limit of detection (LOD), limit of quantification (LOQ), precision (% RSD) and average recovery at different fortification levels.To study the linearity of the proposed method, calibration curves were constructed with 6 standard solutions, analyzed in triplicate, with concentrations ranging from 0.05 to 100 ng mL^{-1}. Subsequently, graphs showing the ratio of the area of the studied pesticide to the area of the internal standard versus the ratio of the concentration of the studied pesticide to the concentration of the internal standard were plotted. The calculated correlation coefficient (r^2) ranged between 0.994 and 1 as reported in Table 2. These results were similar and even better than those reported in the literature (Filho *et al*. 2010; Goncalves and alpendurada. 2004; Kouzayha *et al*. 2011).The limit of detection (LOD) and limit of quantification (LOQ) for each analyte were calculated based on statistical analysis of the calibration curves using equations (1) and (2), where a is the slope, b is the intercept at the origin and s(b) the standard deviation of b (according to ISO 5725 requirement).

(1) LOD$=\frac{b+3s(b)}{a}$ (2) LOD$=\frac{b+10s(b)}{a}$

The calculated LOD and LOQ varied, correspondingly from 0.001 to 0.458 ng mL^{-1} and from 0.039 to 0.732 ng mL^{-1} for all the analyzed compounds except for methomyl, and, hexachlorobenzene, for which values obtained were in the range of 0.991 to 1.09 ng mL^{-1} for LOD and 1.361 to 1.432 ng mL^{-1} for LOQ as shown in Table 2. These values are in the same order of those obtained by other researchers such as Filho *et al*. 2010 and Passeport *et al*. 2010. The relative recoveries were evaluated by comparing the average response of the detector (n=3) obtained with real water samples spiked with known concentration of the studied pesticides, to the average response of the detector (n=3) obtained with ultra-pure water spiked at the same concentration. The recovery varied between 75.6 to 137.31 % at 0.5 ng ml^{-1}, 78.68 to 122.16 % at 5ng ml^{-1} which proved the accuracy of the developed method (Codex Alimentarus. 2000)The intra and inter-day precision of the optimized method were calculated as relative standard deviation (%RSD) and their values were below 20% for almost all the compound, these results are comparable to those obtained by other researchers (Sakamoto and Tsutsumi. 2004; Filho *et al*. 2010; Xiaojing *et al*. 2010).

Application to real water samples

To evaluate the performance of the optimized SPME-GC-MS/MS method, the later was applied for the analysis of 5 surface water samples taken from different locations from the watershed of Abou Ali **Table 1.** Chemical group (CG) and optimized operating conditions for MS/MS analysis

PN	Pesticide	CG	PC	RT (min)	MW	PI	ESL (V)	EM	EA	DI
1	Methomyl	C	I	4.092	162	105	46	NR	17	102.9
2	Methamidophos	OP	I	5.025	141	94	41.2	NR	41	63.9
3	Dichlorvos	OP	I	5.065	220	185	61	NR	50	92.8
4	Propoxur	C	I	7.856	209	110	36.1	NR	34	82/81.1
5	Ethoprophos	OP	I	8.176	242	158	52	NR	25	93.8/113.8/130
6	Trifluralin		H	8.345	335	306	101.1	NR	50	264.2
7	Chlorpropham		H	8.428	213	213	70.3	NR	25	171/212.3
8	*alpha-hexachlorocyclohexane* (Alpha-HCH)	OC	I	9.16	288	219	72.3	NR	40	181/183/216.9
9	Hexachlorobenzene	OC	F	9.26	282	282	93.2	R	0.7	247.2
10	Dimethoate	OP	A	9.416	229	125	41.1	R	0.25	78.9
11	Beta- *hexachlorocyclohexane* (Beta-HCH)	OC	I	9.824	288	219	72.3	NR	41	181/183/216.9
12	Pentachloronitrobenzene (Quintozene)	OC	F	9.88	293	249	82.2	NR	73	214/212/177/179/246.9
13	Gamma-hexachlorocyclohexane (Lindane)	OC	I	10.029	288	219	72.3	NR	43	181/183/217
14	Diazinon	OP	I	10.079	304	179	59	NR	49	177/149/137/115/110.9
15	Propizamide	Benz	H	10.101	256	173	57	NR	48	145/109
16	Delta-hexachlorocyclohexane (Delta-HCH)	OC	I	10.84	288	219	72.3	NR	42	181/183/217
17	Chlorpyriphos-methyl	OP	I	11.589	321	286	94.5	NR	77	208/241.1/144.1/271.1 /180
18	Vinclozolin	Dicarb	F	11.679	285	212	69.9	R	0.38	172.1/177.1
19	Alachlor	CA	H	11.784	269	188	62	NR	41	160/186.1
20	Metalaxyl	AA	F	12.038	279	206	67.9	NR	45	162.1/132.1
21	Pirimiphos-methyl	OP	I	12.408	305	290	95.8	NR	65	150.9/262
22	Chlorpyriphos	OP	I	13.029	349	314	103.8	NR	44	258.1/286
23	Aldrin	OC	I	13.22	362	263	86.9	R	0.44	261.2/228.2
24	Pendimethalin	DA	H	14.137	281	252	83.2	NR	41	208.2/191.2/162.1
25	Cyprodinil	P	F	14.204	225	224	73.9	R	0.55	208.4/222.3
26	Penconazole	TA	F	14.377	283	248	81.9	NR	60	192/206.1
27	Heptachlor epoxide	OC	I	14.502	386	353	116.7	R	0.3	351.1
28	Procymidone	Dicarb	F	14.829	283	283	93.5	NR	53	255.2
29	EndosulfanII	OC	I	15.732	404	241	79.6	NR	66	239/204.2/206.1/170.2 /205.2
30	Fludioxonil	PP	F	16.257	248	248	81.9	NR	65	182/154.2

31	4,4-Dichlorodiphenyldichloroethylene (4,4-DDE)	OC	I	16.47	318	318	105.1	NR	73	246.6/316.3/248.3
32	Myclobutanil	TA	F	16.632	288	179	59	R	0.28	151.7/125
33	Dieldrin	OC	I	16.683	378	175	57.7	NR	46	132.1/173.1
34	Buprofezin		I	16.704	305	175	57.7	R	0.27	132
35	Kresoxym-methyl		F	16.749	313	116	38.1	NR	35	89.1
36	EndosulfanI	OC	I	17.806	404	241	79.6	R	0.31	239/205.1
37	Ethion	OP	I	17.885	384	231	76.2	R	0.21	202.9/174.9
38	4,4- dichlorodiphényldichloroéthane (4,4-DDD)	OC	I	17.954	318	235	77.6	NR	58	165.2/199.2
39	Endosulfansulphate	OC	I	19.135	420	272	89.8	R	0.27	270/237
40	4,4-Dichlorodiphenyltrichloroethane (4,4-DDT)	OC	I	19.254	352	235	77.6	R	0.36	200.1/165.2/199.2
41	Tebuconazole	TA	F	19.763	308	250	82.5	R	0.34	249.1/125
42	Bifemthrin	Pyr	I	20.913	422	181	59.6	R	0.33	166.1/165.2
43	Bromopropylate		A	21.028	426	341	112.7	R	0.23	339.2/183/185.9
44	Metoxychlor	OC	I	21.252	344	227	74.9	R	0.39	212.2/225.2/196.2/195.3
45	Amitraz		A/I/S	22.805	162	162	53.3	NR	28	161.1/147/141
46	Lambda-cyhalothrin	Pyr	I	22.839	449	181	59.6	NR	58	152
47	Pyridaben		I/M	24.701	364	147	48.4	NR	33	119.1/105
48	Cypermethrin	Pyr	I	26.424	415	163	53.7	NR	34	126.9

Abbreviations:

PN: pesticide number, PC: pesticide class; I: Insecticide; A: Acaricide, F: Fungicide, H: Herbicide, M: Miticide; S: Scabicide

CG: Chemical group; C: Carbamate, OP: organophosphate; OC:Organochloride;Benz:Benzamide; DCB:dicarboxymide; CA: chloroactanilide; AA: acylalanine; DA: dinitroaniline; P: Pyrimidine; TA: Triazole; PP: Phenylpyrrole; Pyr: pyrethroid

RT: retention time; MW: Molecular weight; PI:Parent ion; ESL: Excitation storage level; EM: Excitation mode; EA: Excitation amplitude; DI: Daughter ions

Table 2. Analytical parameters of the optimized SPME-GC-MS/MS method

Pesticide	Linearity Range (LR) (ng ml^{-1})	Correlation Coefficient (r^2)	Limit of detection (LOD) (ng ml^{-1})	Limit of quantification (LOQ) (ng ml^{-1})	Average recovery % (n=3)	
					0.5 ng ml^{-1}	5 ng ml^{-1}
Methomyl	0.5-50	0.9989	1.09	1.432	105.37	100.48
Methamidophos	0.05-50	0.9991	0.458	0.732	99.77	80.34
Dichlorvos	0.5-75	0.9997	0.328	0.585	91.12	93.37
Propoxur	0.05-50	0.9992	0.3	0.557	129.26	118.88
Ethoprophos	0.05-75	0.9995	0.117	0.366	115.68	122.16
Trifluralin	0.05-5	0.9957	0.008	0.076	80.21	101.69
Chlorpropham	0.05-75	1	0.024	0.06	95.28	98.86
Alpha-HCH	0.05-10	0.9992	0.04	0.091	84.68	88.44
Hexachlorobenzene	0.5-100	0.9997	0.991	1.361	99.79	88.54
Domethoate	0.05-5	0.9962	0.034	0.098	89.17	98.17
beta-HCH	0.05-100	0.9995	0.028	0.158	108.08	111.81
Quintozene	0.05-50	0.9996	0.003	0.154	137.31	87.3
Lindane	0.05-5	0.9955	0.029	0.099	93.29	98.34
Diazinon	0.05-50	0.9998	0.001	0.098	105.31	92.34
Propizamide	0.05-75	0.9999	0.011	0.096	136.76	91.99
Delta-HCH	0.05-5	0.9968	0.041	0.1	98.95	98.22
Chlorpriphos-methyl	0.05-50	0.9994	0.012*	0.041*	109.08	86.69
Vinclozolin	0.05-75	0.9998	0.054	0.235	104.19	99.03
Alachlor	0.05-75	0.9984	0.08*	0.26	95.09	98.42
Metalaxyl	0.05-25	0.9997	0.051	0.131	77.71	89.47
Pirimiphos methyl	0.05-5	0.9989	0.01	0.043	79.81	99.41
Chlorpyriphos	0.05-5	0.9957	0.03	0.097	85.66	100.73
Aldrin	0.05-5	0.994	0.019	0.099	114.43	102.35
Pendimethalin	0.05-100	0.9995	0.248	0.652	91.4	83.41
Cyprodinil	0.05-75	0.9997	0.041	0.288	110.42	100.27
Penconazole	0.05-10	0.9999	0.02	0.039	88.78	99.98
heptachlor-epoxide	0.05-75	0.9996	0.128	0.4	90.92	99.97
Procymidone	0.05-75	0.9987	0.126	0.362	119.13	104.28
EndosulphanII	0.05-5	0.9979	0.015	0.062	119.43	100.31
Fludioxonil	0.05-75	0.999	0.126	0.554	105.93	83.56
4,4-DDE	0.05-25	0.9953	0.019*	0.064*	128.68	98.17
Myclobutanil	0.05-100	0.9999	0.024	0.181	124.13	100.51
Dieldrin	0.05-75	0.9996	0.255	0.54	116.69	100.27

Buprofezin	0.05-25	0.9997	0.012	0.091	90.62	100.06
Kresoxim methyl	0.05-25	0.9998	0.028	0.099	100.12	100.07
EndosulphanI	0.05-50	0.9992	0.069*	0.229*	136.79	78.68
Ethion	0.05-50	0.9996	0.083*	0.276	121.34	96.04
4,4-DDD	0.05-5	0.9961	0.034	0.098	108.4	101.01
Endosulphan-sulphate	0.05-100	1	0.053	0.099	82.58	97.37
4.4-DDT	0.05-100	1	0.022	0.091	108.21	107.9
tebuconazole	0.05-5	0.9946	0.019	0.095	112.26	102.42
Bifenthrin	0.05-100	1	0.03	0.087	113.06	97.32
bromopropylate	0.05-100	0.9994	0.072	0.427	119.9	81.21
metoxychlor	0.05-5	0.9979	0.017	0.064	87.46	100.71
Amitraz	0.05-100	0.9992	0.205	0.615	122.56	80.73
lambda-cyhalothrin	0.05-5	0.9963	0.019	0.081	104.63	100.8
Pyridaben	0.05-50	0.9998	0.162	0.285	110.41	118.64
Cypermethrin	0.05-5	0.9975	0.042	0.093	75.64	100.72

*Calculated by Signal to noise ratio (S/N) of 3 for LOD and 10 for LOQ

River in North Lebanon. Samples were collected in pre-cleaned amber glass bottles, stored at 4°C and then transported to the environmental engineering laboratory (EEL) at the University of Balamand for analysis. The preliminary results obtained showed that all the collected samples were contaminated with methomyl, methamidophos, trifluralin, alachlor, endosulphanI, ethion and 4,4-DDD with average concentrations of 11.69, 27.33, 0.022, 0.178, 0.017, 0.072 and 0.182 ng mL-1, respectively . Besides it, fludioxonil was found in four samples out of five with an average value of 2.64 ng mL-1. In addition to this, dichlorvos, chlorpropham, beta-HCH, diazinon, delta-HCH, vinclozolin, 4,4-DDE, myclobutanil, tebuconazole, metoxychlor, pyridaben and cypermethrin were also present in different concentrations in three, two or one of the analyzed samples as shown in Table 3. These results were different from those reported by Massoud et al, 2005 which confirmed the absence of pesticide in the surface water samples collected along the watershed of Abou Ali River. Concerning the surface water of Abou Ali river, it is predictable that it will face a serious damage in the future, not only because of the results obtained in this study but also because of the intense, uncontrolled and incorrect use of pesticides carried out in the agricultural areas located in this region.

Conclusions

A highly satisfactory DI-SPME-GC-MS/MS method was optimized and validated for multi-residue analysis of pesticides in water. The developed method showed good linearity, precision and sensitivity to pesticide residues analysis in the sub and low ppt levels. The results obtained in 5 samples collected from 5 locations along the watershed of Abou Ali River indicate potential risk of environmental contamination in the area and explain the need to do a seasonal monitoring for these pesticides, covering all the watershed of Abou Ali River from the source to the mouth.

Table 3: Concentration range and average concentrations of pesticides detected in 5 surface water samples

Pesticides	Number of samples containing pesticides	CR (ng ml^{-1})	AC (ng ml^{-1})
Methomyl	5	7.26-17.38	11.69
Methamidophos	5	11.22-42-6	27.33
Dichlorvos	1	0.77	0.77
Trifluralin	5	0.021-0.022	0.022
Chlorpropham	5	<LOQ	<LOQ
Beta-HCH	2	0.029-0.03	0.029
Lindane	1	0.016	0.016
Diazinon	1	0.043	0.043
Delta-HCH	2	0.027	0.027
Vinclozolin	1	0.23	0.23
Alachlor	5	0.117-0.35	0.178
Pendimethalin	1	<LOQ	<LOQ
Procymidone	2	0.053-0.116	0.084
Fludioxonil	4	0.065-10.14	2.64
4,4-DDE	1	0.016	0.016
Myclobutanil	2	0.092-0.719	0.405
EndosulfanI	5	<LOQ-0.017	0.017
Ethion	5	0.053-0.097	0.072
4,4-DDD	5	0.172-0.190	0.182
Tebuconazole	1	0.22	0.22
Metoxychlor	1	0.229	0.229
Pyridaben	1	2.42	2.42
Cypermethrin	3	0.103-0.496	0.364

AC: Average concentration; CR: Concentration range

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