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## Occurrence and levels of pesticides in South Lebanon water

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This study reviews the detection of pesticides in different surface and groundwater samples collected from South Litani region in South Lebanon during 2012. These have been analyzed using an optimized and validated solid phase extraction method followed by gas chromatography coupled with mass spectrometry. Organochlorine and organophosphate pesticides were mostly noted at levels below the recommended value for individual pesticide in water except pirimiphos-methyl that was recorded at 300.87 ng L<sup>-1</sup> in groundwater sample, designated for drinking water and collected in February. DDE concentration exceeded 100 ng L<sup>-1</sup> in both surface and groundwater in October. The reported results represent the first Lebanese statistical data illustrating the quantification of pesticides in water over a period of time. More importantly, it draws attention to the need of pesticides' monitoring programs in the Lebanese water resources.

**Keywords:** pesticides; surface and groundwater; South Lebanon; SPE; GC–MS

### 1. Introduction

The increased production and consumption of pesticides were earlier considered as a marked evidence of progress in agriculture responding to the need for increasing the world food production. The World Health Organization reported that the developing countries use about 20% of pesticides in the world and this consumption is getting wider and wider.[1] However, these pesticides were defined as the most dangerous contaminants of the environment. They can move through air, soil, and water as persistent organic pollutants (POP), i.e. they accumulate in the environment longer than the required time for their intended use. Their transport in the different environmental media is controlled by its strength, sorption to soil, half-life in soil, clay content of soil, and duration between pesticide's application and first rainfall.[2] Pesticides' contamination of water has been well documented worldwide to be considered as a potential risk for the ecosystem. These chemicals reach the aquatic environment mainly through surface runoff, leaching from surface pesticides' applications, careless disposal of empty containers, and equipment washings.[3] Moreover, these hazardous chemicals are capable of bioaccumulation, resulting in an impact load on the human health. Increasing cases of cancer, chronic kidney diseases, sterility, neurological and behavioral disorders, suppression of the immune system, and endocrine disorders have been attributed to chronic pesticides poisoning [4] due to different routes of exposure as dermal contact, inhalation, and ingestion.[5] Accordingly, strict regulations to limit these effects have been established over the world, and scientists were activated to develop analytical techniques that can determine pesticides' concentrations at low

levels. In 1982, the Lebanese Government started to address the pesticides' issue by creating a scientific committee to define and study the pesticides' use and set conditions for authorization of their import, sale, preparation, and labeling.[6] As a result, the Ministry of Agriculture under decree 1/94 banned a package of 109 pesticides including aldrin, DDT, and heptachlor. However, the first valuable step to protect the environment and human health against the POP was carried out in the ratification of the Stockholm Convention by Lebanon. Despite the existence of legislations by Ministry of Agriculture and that of Environment, the Lebanon government is still incapable to control the import and usage of pesticides. Trabulsi [7] and Abou Fakhr et al. [8] regarded that banned pesticides are spread over the country by illegal means and being used by untrained public. In addition, the Ministry of Environment reported that the ability to control any problem resulting from pesticides is still low, and sufficient statistical data is unavailable.[9] Traditionally, solid phase extraction (SPE) methods,[10–13] have been applied for the analysis of pesticides in water particularly. These have been considered as efficient techniques for isolation, separation, and concentration of analytes in water samples prior to its identification by chromatographic methods. The importance of sample preparation results from several considerations: (i) too dilute analytes cannot be detected, (ii) sample matrix may contain components that can interfere with analysis, and (iii) sample matrix may be not compatible with chromatographic system. SPE is the most favored technique due to its ability to determine a broad range of pesticides with different physicochemical properties within an accepted time interval and

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solvent consumption. Moreover, it offers the following advantages: low cost, manipulation, high recoveries and pure extracts, simple and easy automated, and compatible with instrumental techniques. GC has been the technique of choice for the analysis of environmental samples containing semi-volatile and volatile organic compounds due to its favorable combination of high selectivity and resolution, good accuracy and precision, wide dynamic concentration range, and high sensitivity.[14] Numerous applications based on gas chromatography coupled with mass spectrometry (GC–MS) have been reported for the determination of pesticides in water samples.[15,16]

Recognizing the negative effects of water contamination by pesticides [17,18,19,20] and the lack of effective analytical projects in Lebanon, this work reports for the

first time, the detection and quantification of pesticides in surface water and groundwater (GW) samples collected from South Litani region in particular during the four seasons of year 2012. An optimized and validated SPE followed by GC–MS [21] was applied for this purpose.

## 2. Experimental

### 2.1. Chemicals

Acetonitrile (ACN), methanol (MeOH), dichloromethane (DCM), and ethanol (EtOH) (HPLC grade  $\geq 99.9\%$ ) were purchased from Sigma-Aldrich (Sigma-Aldrich, St Louis, MO, USA). Pesticide standards of high purity level (98–99.8%) were purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany) and Chem-Service (West Chester,

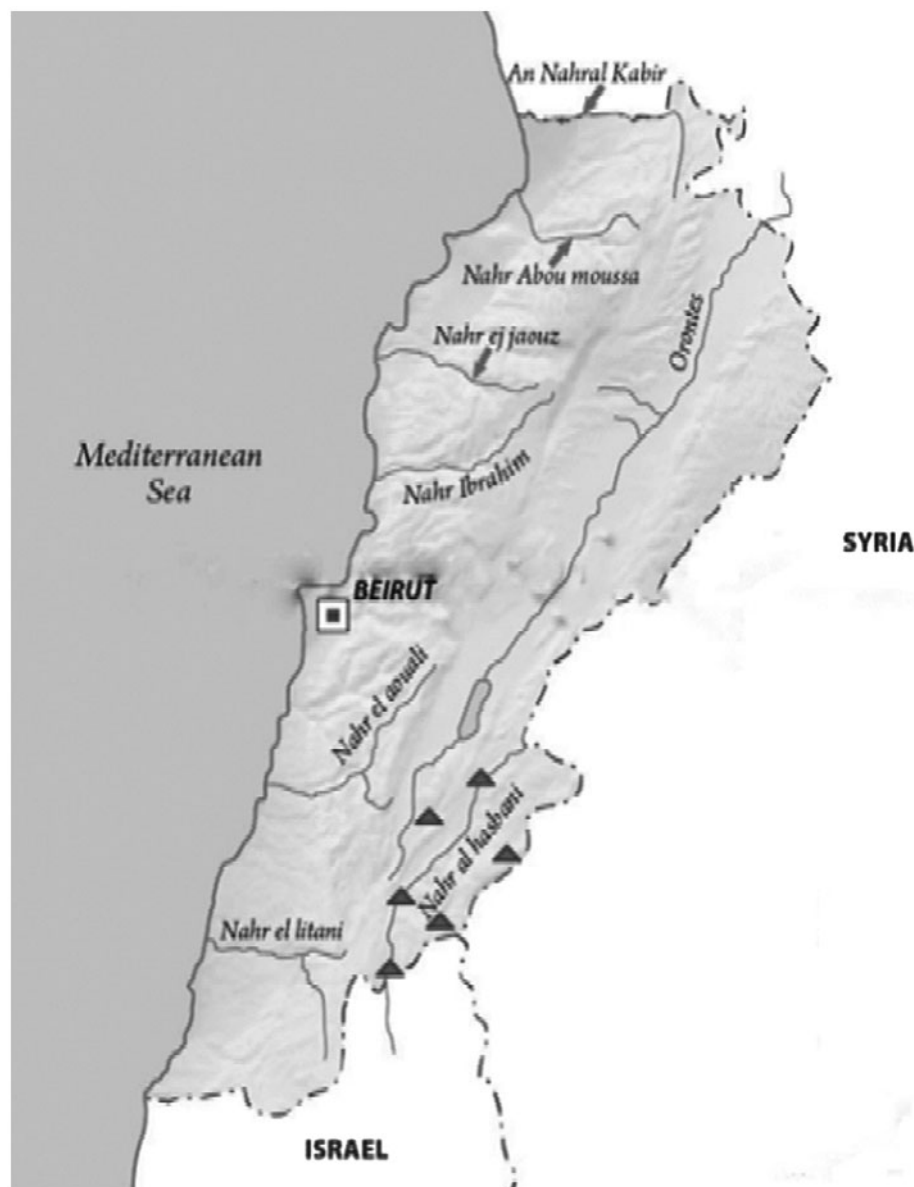


Figure 1. Map illustrating sampling sites.

PA, USA). Individual standard pesticide solutions were prepared in ACN with a concentration of about  $1000 \text{ mg L}^{-1}$ . Three standard mixture pesticide solutions were prepared by diluting each individual standard solution with ACN, in order to get a concentration of about  $35 \text{ mg L}^{-1}$  for each compound. Working standards solutions were prepared by diluting the three standard mixture pesticide solutions with ACN at a concentration of  $1.0 \text{ mg L}^{-1}$ . All standard solutions were stored in dark below  $-20 \text{ }^\circ\text{C}$ .

## 2.2. Sampling and sample treatment

Water samples from different water bodies in South Litani region are illustrated in Figure 1, and they were taken in 2.5 L dark glass bottles during four seasons of the year 2012. The used bottles were pre-cleaned and dried at  $250 \text{ }^\circ\text{C}$  for 24 h. Surface water samples from Hassbany River at two distinct points, 3 km apart approximately, were collected at 30 cm deep during all seasons. However, surface water samples from Wazzany River were only gathered during spring–summer period. On the other hand, groundwater samples were taken from three wells that are located in urban regions at approximately 100 m depth. Water was pumped directly into the bottles. Moreover, water samples from either Dardara Lake (Khyam) or NebaaJawz (Shebaa) were collected at the nearest point that can be reached from the original source.

All water samples were filtered under vacuum using glass  $\mu$ -fiber filter from Whatman with a porosity of  $0.7 \text{ }\mu\text{m}$  that was pre-dried at  $400 \text{ }^\circ\text{C}$  over night. All water samples were fortified with the surrogate standard (PCB 52) previously prepared in MeOH at a level of  $50 \text{ ng L}^{-1}$ . Then, they were shaken in an ultrasonic bath (Type T 760 DH, Prolabo, VWR International, France) to achieve homogenization and stored at  $4 \text{ }^\circ\text{C}$  before analysis.

## 2.3. Solid phase extraction

Water samples were extracted for pesticides' analysis using a VacElut vacuum manifold from Varian (Santa Clara, CA, USA) with a Visiprep large-volume sampler from Supelco (Sigma-Aldrich, St. Louis, MO, USA). Oasis<sup>®</sup> HLB (hydrophilic–lipophilic balance) 60 mg, 3 mL, and  $50 \text{ }\mu\text{m}$  from Waters (Milford, MA, USA) was used as a SPE cartridge. HLB cartridges were firstly conditioned with 3 mL of MeOH and then 3 mL of water. Each water sample was dripped using vacuum through SPE cartridge with a flow rate of approximately  $10 \text{ mL min}^{-1}$ . SPE cartridges were dried under vacuum, and analytes were eluted with 3 mL DCM followed by 3 mL of MeOH/DCM mixture (1:1) and finally 3 mL of MeOH. The SPE procedure was described by Kouzayha et al. [21] The extracts were concentrated to about 0.1 mL using nitrogen gas stream (Techne, UK) at  $55 \text{ }^\circ\text{C}$ . Then,  $200 \text{ }\mu\text{L}$  of ACN solvent was used to reconstruct the obtained extracts. PCB 153, used as an internal

standard, was added at the end of the extraction procedure ( $50 \text{ }\mu\text{L}$  of 1 ppm standard). Finally, the vials were shaken using the ultrasound shaker and stored in the dark at  $-20 \text{ }^\circ\text{C}$  until GC–MS analysis.

## 2.4. Gas chromatography coupled to mass spectrometer analysis

An Agilent 7890A GC coupled to an Agilent 5975C MS was used to analyze our water extracts. The GC–MS was equipped with 7693A auto-sampler and a multi-mode inlet. The used capillary column was HP-5MS (30 m,  $0.25 \text{ mm i.d.}$ , and  $0.25 \text{ }\mu\text{m}$  thickness). The carrier gas was helium at a flow rate of  $1 \text{ mL min}^{-1}$  and average velocity of  $26.358 \text{ cm sec}^{-1}$ . The oven temperature was programmed as following: initially, the temperature was set at  $70 \text{ }^\circ\text{C}$  and held for 1.57 min. Then, the temperature increased by  $10 \text{ }^\circ\text{C min}^{-1}$  until  $160 \text{ }^\circ\text{C}$  was reached and held for 5 min. Later, the temperature increased to  $240 \text{ }^\circ\text{C}$  by  $3 \text{ }^\circ\text{C min}^{-1}$  and held on this value for 17.9 min. Injector temperature was set up at  $70 \text{ }^\circ\text{C}$ . A sample of  $5 \text{ }\mu\text{L}$  volume was injected in programmed temperature vaporization mode at injection speed of  $35 \text{ }\mu\text{L min}^{-1}$ .

MS system was operated in electron ionization mode with ionization energy of 70 eV using selected ion monitoring mode.[21] MS ion source temperature was held on  $230 \text{ }^\circ\text{C}$ , whereas MS quadruple temperature was  $150 \text{ }^\circ\text{C}$  and solvent delay was 5.5 min.

## 2.5. Analytical quality control

All data were subjected to strict quality control procedures, including the analysis of procedural and instrumental blanks in addition to spiked samples with each set of samples analyzed. Blanks were used to avoid laboratory contamination and analytical interferences, and none of the target compounds were detected in a quantifiable value. Method performance was assessed using spiked water samples (spiking level at  $50 \text{ ng L}^{-1}$ ), and the method was shown to have good precision and high recoveries. Average recovery, relative standard deviation, and limit of detection of the analytical method applied were % of spiked amount, %, and  $\mu\text{g L}^{-1}$ , respectively. The target pesticide quantification was based on peak area ratio of the target ion divided by the internal standard (PCB 153). Surrogate standard (PCB 52) recoveries were calculated to monitor the performance of the analytical process, and obtained values were better than 60%. Further details of the method have been previously published.[21]

## 3. Results and discussion

The investigated pesticides include 67 compounds from various chemical classes (organochlorines, organophosphates, carbamates, pyrethroids, triazines, pyrimidines, azoles, and triazoles) used as insecticides, herbicides,

Table 1. The concentration range in ng L<sup>-1</sup> of detected pesticides in 15 surface water samples.

Chemical class	Pesticide	Limit of quantification (ng L <sup>-1</sup> )	Frequency of detection (%)	February n = 3	April n = 5	July n = 5	October n = 2	
Organochlorine	Aldrin	2.0	13.3	N.D.	N.D.	N.D.	N.Q.	
	p,p'-DDT	5.0	60.0	N.Q.	N.Q.	N.D.	N.Q.	
	p,p'-DDE	1.0	93.3	28.7–31.4	4.1–7.4	N.Q.	92.3–135.6	
	p,p'-DDD	1.0	86.6	1.1–1.7	N.Q.	N.Q.	4.5–5.6	
	m,p'-DDD	2.0	66.6	2.3–3.1	N.Q.	N.Q.	2.9–5.6	
	Heptachlor epoxide	0.5	20.0	N.D.	N.D.	N.Q.	N.Q.	
	HCB	0.5	93.3	0.5–0.7	N.Q.	0.5–0.7	0.7–0.7	
	Methoxychlor	1.0	40.0	2.9–3.6	N.D.	N.Q.	1.1–2.1	
	Organophosphorus	Bromophosethyl	0.5	66.6	0.5–0.7	N.Q.	N.Q.	1.1–2.2
		Cadusafos	4.0	6.6	N.Q.	N.D.	N.D.	N.D.
Diazinon		5.0	73.3	5.6–8.7	5.2–15.7	N.Q.	N.Q.	
Ethion		1.0	6.6	N.D.	N.D.	N.Q.	N.D.	
Methidathion		1.0	6.6	N.D.	N.D.	1.2–46.3	N.D.	
Pirimiphosmethyl		1.0	6.6	1.2–28.9	N.D.	N.D.	N.D.	
Others		Chlorpyrifos	10.0	6.6	N.D.	N.D.	N.Q.	N.D.
		Tolclofos-methyl	0.5	6.6	N.D.	N.D.	N.D.	N.Q.
		Bifenthrin	0.5	20.0	N.D.	N.D.	N.Q.	2.9–4.8
		Fenprothrin	5.0	20.0	N.D.	N.D.	N.Q.	6.1–9.5
	Bromopropylate	0.5	93.3	1.9–5.4	N.Q.	N.Q.	0.5–0.6	
	Tetradifon	1.0	13.3	N.D.	N.D.	N.D.	1.0–2.0	
	Chlorfenapyr	4.0	13.3	N.D.	N.D.	N.D.	6.6–7.1	
	Fipronil	0.3	33.3	0.4–1.6	N.D.	N.D.	N.Q.	
	Myclobutanil	1.0	6.6	N.D.	N.D.	N.D.	N.Q.	
	Procymidone	0.5	13.3	1.1–1.6	N.D.	N.D.	N.D.	
Trifluralin	0.5	13.3	N.D.	N.D.	N.D.	N.Q.		

Note: Not Detected; N.D., Not Quantified; N.Q.

Table 2. The concentration range in ng L<sup>-1</sup> of detected pesticides in 11 groundwater samples.

Chemical class	Pesticide	Limit of quantification (ng L <sup>-1</sup> )	Frequency of detection (%)	February GW (n = 3)	April GW (n = 3)	July GW (n = 3)	October GW (n = 2)	
Organochlorine	Aldrin	2.0	18.1	N.D.	N.D.	N.D.	N.Q.	
	p,p'-DDT	5.0	54.5	N.Q.	N.D.	N.D.	N.Q.	
	p,p'-DDE	1.0	100.0	21.8–28.6	4.6–9.0	N.Q.	70.4–144.8	
	p,p'-DDD	1.0	100.0	1.0–1.1	N.Q.	N.Q.	3.0–4.5	
	m,p'-DDD	2.0	81.8	N.Q.	N.Q.	N.Q.	3.1–5.1	
	Heptachlor epoxide	0.5	18.1	N.D.	N.D.	N.Q.	N.Q.	
	HCB	0.5	100.0	0.6–1.1	N.Q.	0.5–0.8	N.Q.	
	Methoxychlor	1.0	36.3	2.4–3.4	N.D.	N.D.	N.Q.	
	Organophosphorus	Bromophosethyl	0.5	81.8	N.Q.	N.Q.	N.Q.	1.1–1.9
		Cadusafos	4.0	0.0	N.D.	N.D.	N.D.	N.D.
Diazinon		5.0	90.9	4.1–6.5	3.0–14.3	N.Q.	N.Q.	
Ethion		1.0	0.0	N.D.	N.D.	N.D.	N.D.	
Methidathion		1.0	0.0	N.D.	N.D.	N.D.	N.D.	
Pirimiphosmethyl		1.0	18.1	73.3–300.8	N.D.	N.D.	N.D.	
Others		Chlorpyrifos	10.0	0.0	N.D.	N.D.	N.D.	N.D.
		Tolclofos-methyl	0.5	9.0	N.D.	N.D.	N.D.	N.Q.
		Bifenthrin	0.5	27.2	N.D.	N.D.	N.Q.	2.6–3.5
		Fenprothrin	5.0	18.1	N.D.	N.D.	N.D.	N.Q.
	Bromopropylate	0.5	90.9	0.8–1.3	N.Q.	N.Q.	N.Q.	
	Tetradifon	1.0	18.1	N.D.	N.D.	N.D.	N.Q.	
	Chlorfenapyr	4.0	18.1	N.D.	N.D.	N.D.	4.4–4.9	
	Fipronil	0.3	18.1	N.D.	N.D.	N.D.	N.Q.	
	Myclobutanil	1.0	9.0	N.D.	N.D.	N.D.	N.Q.	
	Procymidone	0.5	9.0	N.Q.	N.D.	N.D.	N.D.	
Trifluralin	0.5	18.1	N.D.	N.D.	N.D.	N.Q.		

Table 3. Agriculture use, chemical class, and physicochemical properties of detected pesticides.[60]

Pesticide (Use/chemical class)	Water solubility (mg L <sup>-1</sup> at 20–25 °C)	Vapor pressure (Pa at 25 °C)	K <sub>H</sub> (Pa m <sup>3</sup> mol <sup>-1</sup> at 25 °C)	Log K <sub>oc</sub>	Log K <sub>ow</sub>	GUS index	DT <sub>50s</sub> (years)
Aldrin (I/OC)	0.027	0.00308	50.8	4.69	6.50	-0.35	5–10
p,p'-DDT (I/OC)	0.0055	2.50 × 10 <sup>-5</sup>	5.30	5.38	6.36	-4.47	10.5–11.8
p,p'-DDE (I/OC)	0.0013	8.27 × 10 <sup>-4</sup>	27.4	4.85	5.69	22.19	2.73
p,p'-DDD (I/OC)	0.002	1.33 × 10 <sup>-4</sup>	2.18	4.91	5.99	–	2–15.6
Heptaaxoepoxide (*OC)	0.275	0.00256	3.25	4.32	3.65	–	3
Hexachlorobenzene (F/OC)	0.0051	0.00028	139	3.59	6.18	-2.31	2.65–5.72
Methoxychlor (I/OC)	0.1–0.25	1.910 × 10 <sup>-4</sup>	1.6	4.95	4.20	-1.88	0.49–1
Bromophosethyl (I-A/OP)	2	6.1 × 10 <sup>-3</sup>	1.66	4.73	6.15	–	0.17
Cadusafos (I-A-N/OP)	248	1.2 × 10 <sup>2</sup>	0.758	2.16–2.55	3.9	2.60	0.03–0.17
Diazinon (I-A/OP)	60	0.0187	0.074	2.76	3.02	1.14	0.05–0.27
Ethion (I-A/OP)	1.1	0.0002	0.0699	4.19	5.07	0	0.24
Methidathion(I-A/OP)	220	25 × 10 <sup>-5</sup>	1.97 × 10 <sup>-4</sup>	0.84–1.75	2.2	1.40	0.02
Pirimiphosmethyl (I-A/OP)	11	0.0023	6.08 × 10 <sup>-5</sup>	3.04	3.9	2.82	0.106
Chlorpyrifos (I/COP)	0.47	0.0025	1	4.13	5.11	0.15	0.08
Tolclofos-methyl (F/PT)	0.30	0.0573	57.5	3.39	4.56	0.25	0.08
Bifenthrin (I/P)	<1	178 × 10 <sup>-5</sup>	7.74 × 10 <sup>-5</sup>	5.11–5.48	6	-1.94	0.33–0.94
Fenprothrin (I-A/P)	0.0141	7.33 × 10 <sup>-4</sup>	1.82	3.70	6	-0.85	0.01
Bromopropylate (A/BDPh)	0.1	11 × 10 <sup>-6</sup>	0.004	4.32	5.4	0.35	0.16
Tetradifon (A/BDPh)	0.078	3.2 × 10 <sup>-8</sup>	1.46 × 10 <sup>-4</sup>	3.89	4.61	4.10	0.33
Chlorfenapyr (I-A/Py)	0.112	9.81 × 10 <sup>-6</sup>	5.81 × 10 <sup>-4</sup>	4.07	4.83	-0.01	0.0038
Fipronil (I/PhP)	3.78	0.02 × 10 <sup>-3</sup>	3.74	2.91–3.84	4	2.45	0.3
Myclobutanil (F/Ta)	132	198 × 10 <sup>-6</sup>	4.33 × 10 <sup>-4</sup>	2.97	2.89	3.54	1.53
Procymidone (F/DC)	4.50	0.023 × 10 <sup>-3</sup>	1.181	3.18	3	1.20	0.02
Trifluralin (H/Dn)	8.11	0.0029	10.2	4.19	5.27	0.13	0.49

Notes: F, Fungicide; I, Insecticide; A, Acaricide; N, Nematicide; OP, Organo Phosphorus; OC, Organo Chlorine; PhP, Phenyl Pyrazole; DC, DiCarboximide; BDPh, Bridged DiPhenyl; P, Pyrethroid; COP, Chlorinated Organo Phosphate; PT, Phosphorothioates; Ta, Triazole; Py, Pyrrole; Dn, Dinitroaniline.

\*Oxidation product of heptachlor.

and fungicides. The pesticides chosen for this study were selected based on their widespread current or past use, toxicity, transport potential, and persistence in the environment. Among 67 compounds that have been investigated, only 25 pesticides were detected in one or more surface and groundwater sites in at least one of the seasons. The detected pesticides, limit of quantification (LOQ), frequency of detection, and their concentration range in all surface and groundwater samples collected in four seasons of 2012 are given in Tables 1 and 2. Table 3 represents the agriculture use, chemical class, and physicochemical properties of the detected pesticides.

Organochlorine pesticides (OCP) were the most frequently detected in our samples, whereas the average frequency of detection was 59.16% in surface water samples and 63.63% in groundwater samples. OCP are well known for their hydrophobicity and lipophilicity.[22] Thus, their presence can carry serious human health effects even at nanolevels and environmental impacts due to their long-range transportable nature [23] and ability to enter water bodies by runoff and atmospheric deposition.[24]

Aldrin was detected at trace levels and below LOQ in all water samples during October. This observation is due to its ban in Lebanon, thus its low concentration contributes to historic activities that were masked by dilution factor in previous samplings (February–July).

Kouzayha et al. [21] reported in their study the existence of aldrin at low concentrations in one or more groundwater samples taken from three different wells in Lebanon during November 2010. However, it was observed at higher concentrations (50–1550 ng L<sup>-1</sup>) in water samples collected from Black Sea Rivers of Turkey [25] and at concentration range of 10–20 ng L<sup>-1</sup> in samples collected from Weiga stations in Ghana.[26] Similarly, heptachlor epoxide was recorded at levels below the LOQ in both surface and groundwater samples during July and October. Heptachlor epoxide is an

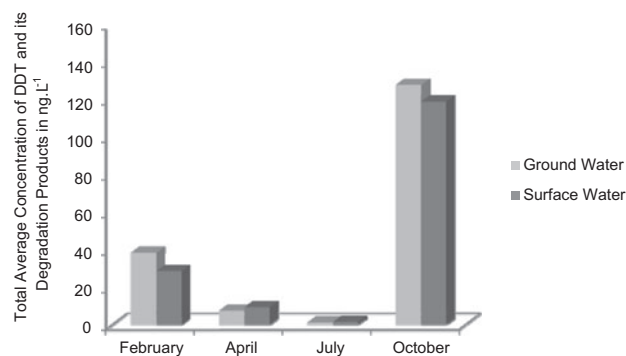


Figure 2. The variation of total average concentration of DDT and its degradation products in ng L<sup>-1</sup> with sampling period.

oxidative product of the banned heptachlor insecticide dissolves more easily in water than its parent compound and is more likely to be found in the environment.[27] It was found in drinking water, groundwater, river, and land runoff at seven locations in the USA and Europe at nanolevels.[28] Recently, this compound was detected in Chinese surface water samples [29] and rivers in Vietnam.[30]

DDT has been always defined as the most abundant group among OCP due to its long-time usage and high persistency. In Lebanon, DDT was not used as insecticide but as malaria control agent permitted by the Ministry of Public Health during 1970–1980. However, records about distributing quantities are unavailable. When DDT is released to the environment, it is either evaporated and transported away from application sites or attached strongly to soil particles. In soil, DDT is slowly biodegraded into DDD and DDE [31] with soil half-life ranges from 2 to 15 years. These metabolites are more stable than their mother is and as toxic as it is. DDT and its degradation products reach surface water by eroded sediments. However, its detection in our aquifers with shallow groundwater tables is due to intensive rainfall.[32] In addition, our examined wells are more vulnerable to contamination because they are close to surface water.[33] The frequency of detection of DDT and its degradation products was 76.66% in surface samples and 84.09% in groundwater. The variation of its total average concentrations by sampling period is represented graphically in Figure 2. DDE has been significantly noticed in all samples during 2012, because neither it is biodegraded nor hydrolyzed. Its level variation is logic due to dilution factor; however, its high detectable value in both waters in October is unacceptable, thus raising a question about possible current uses of DDT. DDD is always recorded at lower levels, which is in agreement with [34,35] and can be justified that DDD degrades faster than DDE does. In Lebanon, studies about examination of DDT and its metabolites in water sources are unavailable except that reported by Kouzayha et al. [21] In their study, only DDD and DDE were detected in groundwater samples at trace levels. On the other hand, research conducted by the American University of Beirut (2004) and the International Development Research Center – Canada (2003) revealed that DDT was recorded at low levels in two areas in Saida, and DDT with its metabolite DDE were observed at measurable amounts in sediments of El-Kabir watershed. Moreover, the Lebanese National Council for Marine Science (1993) reported that levels of DDT, DDD, and DDE in fish species found on the coast exceeded regulatory standard for daily intake of DDT. In Egypt, DDTs were observed at highest levels in groundwater, followed by Nile River, and then in tap water.[36] A Syrian study tested six soil samples and groundwater samples in an agricultural land over a period of 11 months, indicated that DDT was only observed in soil.[37] DDT was recorded in Saudi Arabic groundwater at

$1.07 \times 10^5 \text{ ng L}^{-1}$  in Gazan, while DDE at  $5.6 \times 10^3 \text{ ng L}^{-1}$  in Wadi Al-Dawaser and  $9 \times 10^4 \text{ ng L}^{-1}$  in Gazan.[38] Our results were also compared to those reported by Zhou et al. [39] and DDE was found to dominate DDT family in surface water of Qiantang River. The observed concentrations of DDTs were the highest in summer–autumn period similar to ours; however, our concentrations are much higher.

On the other hand, methoxychlor was detected during February and October in 40% of surface water samples and 36.36% in groundwater samples. The observed concentrations ranged from 2.9 to  $3.6 \text{ ng L}^{-1}$  in surface samples and  $2.4\text{--}3.4 \text{ ng L}^{-1}$  in groundwater during February. These concentrations decreased in samples collected during October indicating that this pesticide is no longer used nowadays. Our results were compared to others reported in different studies all over the world. Methoxychlor was recorded at higher concentrations ( $88 \times 10^2\text{--}249 \times 10^2 \text{ ng L}^{-1}$ ) in samples from Hindon River.[40]

Hexachlorobenzene (HCB) was frequently detected over 2012 at trace levels, and frequency of its detection was 93.33% in surface water and 100% in groundwater. HCB is extremely stable, globally distributed, and to be a most persistent POP.[41] However, records about its agricultural applications are unavailable in Lebanon indicating that the detected HCB is a possible result of unintended byproduct in chemical processes, incomplete combustion or an impurity in pesticides.[42] Higher concentrations of HCB were observed in different Chinese rivers, shallow groundwater, and reservoirs.[43] Similar results in groundwater samples were reported by Kouzayha et al. [21] On the other hand, organophosphate pesticides are less persistent and toxic than OCP because they degrade rapidly depending on its formulations, application method, and climate changes.[44] Bromophosethyl was detected in our tested samples all over 2012 at low concentrations with a high frequency of detection. In agreement with other monitoring programs,[45] the low obtained concentrations revealed that this pesticide is no longer used. It is considered as persistent contaminant because of its slow degradation process in all media. Similar observation for bromopropylate (bridged diphenyl) was also detected at trace levels during our analyses and other studies.[46,47] Diazinon with its moderate solubility in water, moderate mobility in soil, and slow degradations illustrates its presence in water systems. However, it was detected at low levels over 2012 indicating that it was mainly used in the past. Its concentration decreased in warm season due to its high volatility. These characteristics also explain why frequency of detection in groundwater (90.9%) is higher than that in surface water (73.33%). Diazinon was observed in 25.9% of stream water samples collected in 30 US states [48] and 63.33% of lake water samples in Canada and Northeastern US.[49] High leachability of pirimiphos-methyl illustrated its presence in high concentration in groundwater samples during February. Although records about possible agricultural

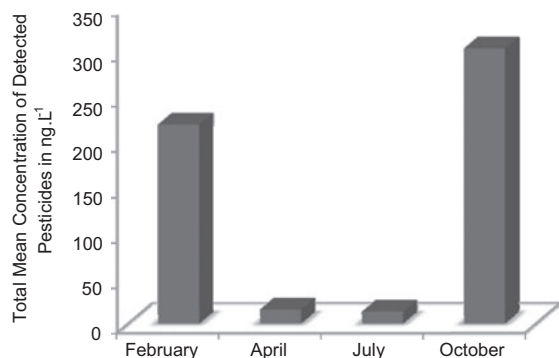


Figure 3. The variation of total mean concentration of detected pesticides in  $\text{ng L}^{-1}$  with sampling period.

uses are unavailable, yet its disappearance may be attributed to possible hydrolysis [50] cooperated with dilution. This compound was detected in surface samples collected in Egypt.[51]

Cadusafos, ethion, methidathion, chlorpyrifos, bifenthrin, fenprothrin, fipronil, myclobutanil, and procymidone are recently used in South Litani as pesticides to protect citrus fruits, apple trees, peach and vine fields, pome fruits, and vegetables. As a result, their detection in our aquatic environment is verified and the low concentrations are due to their solubility in water and soil mobility. These pesticides were mainly detected in surface samples rather than groundwater samples due to their non-leacher identity. All these pesticides were observed at similar levels in studies conducted all over the world.[52–57] Finally, tolclofos-methyl, tetradifon, chlorfenapyr, and trifluralin were detected in all examined water samples in October. These compounds are not used in our region and highly adsorbed to soil particles indicating that their detection resulted from persistent contamination that was previously masked by dilution.

The variation of total mean concentration of detected pesticides with the sampling period is represented in Figure 3. Most pesticides are sprayed into fields during spring periods and reach soils as intercepted by the crop or lost as spray drift.[58] In warmer and drier summer, soils are cracked and pesticides residues will persist in soil through summer until autumn. These residues are later transported by heavy rain into water bodies during winter. This agrees with the high total level of pesticides that were observed in February samples (wet season). During February–April, the flow rate of rivers and groundwater levels increases, as a result, the concentration of existed pesticides in both waters is diluted. On the contrary, the obtained total mean concentration of pesticides in July water samples is approximately equal to those of April. This observation could be attributed to the absence of intensive rainfall events that can carry more pesticide residues. The level of water can still limit the detected amount of pesticides, and sample preservation sounds difficult due to high temperature.

Nevertheless, the great elevation in October samples is highly attributed to a significant reduction in potential dilution. With respect to diazinon, ethion, methidathion, and chlorpyrifos, their concentrations have decreased in October. Higher temperatures will accelerate the volatilization and degradation reactions of such pesticides' residues in surface water.[59]

#### 4. Conclusion

This work represents a success but requires more advanced applications of the proposed SPE-GC–MS method for routine pesticides' analysis. This method was capable to detect various pesticides belonging to different chemical families at trace levels. Banned pesticides, mainly organochlorines, such as aldrin, heptachlor epoxide, and DDT, persist in the aquatic environment of South Litani. DDE and HCB were the most frequently detected pesticides in both surface (93.3%) and groundwater (100%). DDE concentration exceeded  $100 \text{ ng L}^{-1}$  in both surface and groundwater in October. Moreover, pesticides' contamination in water is highly affected by seasons' variation, where the highest concentrations are recorded during autumn season ( $303.76 \text{ ng L}^{-1}$ ). As a result, regular monitoring of pesticides should be performed over a wide period of time and with high frequency to account all seasonal variations in order to set regulations to reduce pesticides' impact on environment and human health.

#### Disclosure statement

No potential conflict of interest was reported by the authors.

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